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Nanotubes

Evidence of an Equimolar C_2H_2–CO_2 Reaction in the Synthesis of Carbon Nanotubes**

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Chemical vapor deposition (CVD) is considered to be the most viable process for the in situ production of nanotubes integrated into a device. Researchers have successfully attempted to control accurately the physical form of the carbon nanotubes produced.[1,2] However, the method still suffers from low yields with respect to the carbon source and from high temperatures required for this conversion. A huge effort has been devoted to enhance the production efficiency at lower temperatures by modifying the catalyst (pregrowth chemical activation)[3,4] or by avoiding catalyst poisoning (e.g., by introducing an etching agent that prevents encapsulation by the precipitated amorphous carbon).[5,6]

The influence of numerous growth parameters on nanotube characteristics, such as diameter, length, number of graphene layers, and defect density, has been studied and reviewed.[7–9] Hence, a basic understanding of the growth mechanism has been established: the catalytic decomposition of the carbon precursor molecules on the surface of the supported metal catalyst is followed by diffusion of the carbon atoms produced, either on the surface or in the metal particles. The solubility of the metal particle in carbon is controlled by particle size and growth temperature. Supersaturation of the metal results in the precipitation of solid carbon, which subsequently builds the nanotube structure. Two different growth mechanisms can occur depending on the catalyst–support interaction. Tip growth takes place when the catalyst is lifted from the support while the carbon nanotube is growing. In contrast, root growth occurs when the carbon nanotube is growing while the metal–support contact is preserved.

Regardless of the carbon source, carbon synthesis is limited to classical decomposition reactions, for example, $C_xH_y \leftrightarrow x\,C + y/2\,H_2$ and $2\,CO \leftrightarrow C + CO_2$. Recent outstanding results have shown that the presence of a small amount of a species that contains oxygen atoms in addition to the carbon source dramatically improves the yield of the reaction: Hata et al. demonstrated the high efficiency of a water-assisted CVD process.[5] Amorphous carbon is effectively etched by H_2O, which preserves and stimulates catalyst activity. Zhang et al. observed a similar effect when O_2 was used.[6] In addition to the cleansing role, oxygen acts as scavenger of H radicals and provides conditions rich in carbon radicals under which nanotube growth is promoted. Nasibulin and coworkers showed that the role of the gaseous product from CO disproportionation in the presence of hydrogen is essential for nanotube synthesis in a high-pressure CO conversion process (HiPCO).[10] Hence, H_2O and CO_2 produced during the growth, act as etching agents to prevent encapsulation of catalyst particles by amorphous carbon.

Herein, we report a reaction between acetylene (C_2H_2) and CO_2, mixed in an equimolar ratio, to produce carbon nanotubes (CNTs). A dramatic enhancement of the CNT yield compared with those of previous syntheses has been observed. Furthermore, the lifetime of the catalyst is considerably extended and the initial growth rate is enhanced compared with those of classical acetylene decomposition reactions. Our results indicate that the production of CNTs is much more favored when this C_2H_2–CO_2 reaction is confined to the "triple-point junction", where acetylene, CO_2, and metal catalyst are close to each other.

For the synthesis of carbon nanotubes, $CaCO_3$ is one of the most efficient supports.[11–13] We demonstrated in a previous report that the yield of multiwalled CNTs (MWCNTs) strongly correlates with the growth temperature (700 °C) and the decomposition temperature range of the carbonate support.[14] $CaCO_3$ stability is ruled by a dynamic equilibrium of the decomposition reaction $CaCO_3 \leftrightarrow CaO + CO_2$ that proceeds at temperatures ranging from 600 °C to 820 °C. Consequently, CO_2 is present as a gas and in the support (as $CaCO_3$) in a ratio that depends on the temperature applied. The $CO_2(g)/C_2H_2$ ratio is constant for a given temperature as long as the carbonate supplies CO_2 by decomposition. In a first approximation, the partial pressure of CO_2 and the average decomposition rate of the carbonate can be deduced from thermogravimetric analysis (TGA) of $CaCO_3$.[13]

Figure 1 a shows a significant and complex dependence of the quantity of produced MWCNTs on $CaCO_3$ decomposition. In the temperature range between 640 and 680 °C—at which about 5 % of $CaCO_3$ decomposes—about 350 mg of

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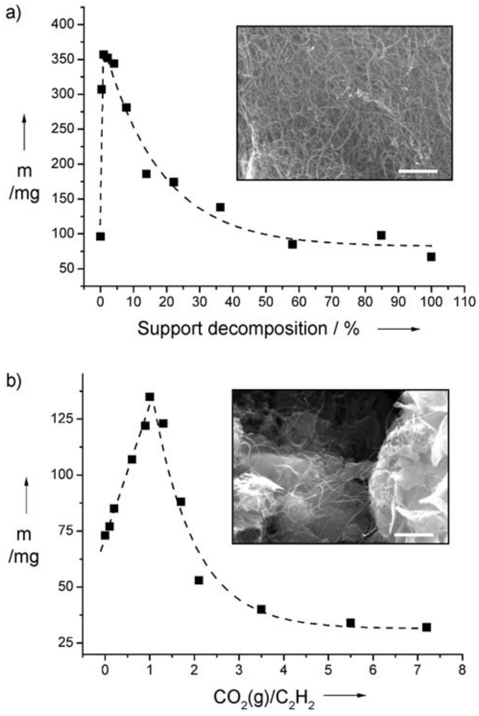


Figure 1. a) Mass of carbon nanotubes (*m*; after purification) versus the percentage of $CaCO_3$ decomposition, which depends on the temperature. Nanotubes are grown from 100 mg of $Fe_2Co/CaCO_3$ supported catalyst. The dashed line is a guide for the eyes. Inset: SEM image of purified MWCNTs produced at 680 °C (scale bar 1 µm). b) Evolution of carbon mass, produced at 680 °C from 200 mg of Fe_2Co catalyst supported on MgO, as a function of $CO_2(g)/C_2H_2$ ratio. At this temperature, the formation of magnesium carbonate from the reaction of CO_2 with MgO is suppressed. Thus, CO_2 is present only as a gas and not as carbonate. The maximum yield is obtained for an equimolar mixture of carbon dioxide and acetylene. Inset: For $CO_2(g)/C_2H_2 \neq 1$, amorphous carbon is produced together with MWCNTs as observed by SEM (scale bar 1 µm).

MWCNTs are produced from 100 mg of $Fe_2Co/CaCO_3$ catalyst in 30 minutes. This mass corresponds to a conversion of about 54 % of acetylene into MWCNTs. A small variation in the decomposition rate of $CaCO_3$, which is controlled by lowering or raising the growth temperature, decreases the yield dramatically. The $CO_2(g)/C_2H_2$ ratio, obtained over $Fe_2Co/CaCO_3$ under the optimum conditions at 660 °C, was measured by quadrupolar mass spectrometry to be 1:100 and was stable over the entire period of growth. $CO_2(g)$ is assumed to act as an etching agent that prevents catalyst poisoning as proposed previously.[14] Presumably, $CO_2(g)$ also limits acetylene polymerization, which occurs by a homogeneous radical chain reaction to produce more-stable oligomers along with heavy oils.[13] As observed with nitric oxides,[15] the polymerization process could be inhibited by the presence of gaseous CO_2.

As with $Fe_2Co/CaCO_3$, the $CO_2(g)/C_2H_2$ ratio cannot be estimated precisely, so additional experiments with an Fe_2Co/MgO catalyst were undertaken, which involved the supply of additional CO_2 (Figure 1 b). At 660 °C, $MgCO_3$ formation is suppressed, therefore, CO_2 is only present as a gas and not as carbonate. The maximum yield is obtained for $CO_2(g)/C_2H_2 = 1$, from which the produced carbon phase is composed of pure MWCNTs. This ratio corresponds to an equimolar reaction between CO_2 and acetylene for the highest efficiency in the synthesis of MWCNTs. Any deviation from the gas-phase composition ($CO_2(g)/C_2H_2 \neq 1$) not only decreases the carbon yield but also leads to the production of amorphous carbon. It must be emphasized that typically no MWCNTs are produced under these growth conditions by acetylene decomposition in the absence of CO_2. Consequently, we assume that the C_2H_2–CO_2 reaction allows the synthesis of MWCNTs in thermodynamically and/or kinetically unfavorable conditions.

Two chemical processes are possible for the reaction of acetylene with CO_2 for the synthesis of carbon nanotubes [Reactions (1) and (2)]. These reactions may occur for both catalyst/support combinations. However, as can be seen in Figure 1, the yield of MWCNTs is significantly higher with $CaCO_3$ than with MgO.

$$C_2H_2 + CO_2 \leftrightarrow 2\,C + H_2O + CO \tag{1}$$

$$C_2H_2 + CO_2 \leftrightarrow C + 2\,CO + H_2 \tag{2}$$

When MgO is the support, the growth proceeds as long as the supplied mixture of acetylene and CO_2 can reach the catalyst particles. This becomes more and more difficult as a dense mat of CNTs is produced. In contrast, when $CaCO_3$ is the support, CO_2 is continuously provided during the growth by diffusion from the bulk towards the surface. The flux is controlled by the decomposition kinetics of $CaCO_3$. Consequently, the synthesis of carbon atoms occurs at the area where acetylene, $CaCO_3$, and the Fe_2Co catalyst meet. This triple-point junction is illustrated in Figure 2. Once generated, carbon can diffuse either on the surface or in the bulk of the metallic particles, which catalyze the growth of the CNTs. Our results suggest that the chemical reactions taking place at the triple-point junction strongly enhance the growth efficiency of the MWCNTs.

Nevertheless, the CO_2 content derived from $CaCO_3$ is substantially below the stoichiometry required in Reactions (1) and (2) to produce 350 mg of MWCNTs. Thus, while CO_2 is available from the bulk carbonate, it must also be generated from the products arising from Reactions (1) and (2). CO_2 regeneration is possible by the water gas shift reaction:[16] $H_2O + CO \leftrightarrow CO_2 + H_2$, or by CO disproportionation:[17] $2\,CO \leftrightarrow C + CO_2$. Indeed, the yield of CO_2 regeneration, calculated from thermochemical data,[18] in both reactions is higher than 90 % at 660 °C (see Supporting Information). We believe that CO_2 regeneration takes place while H_2O and/or CO are adsorbed at the triple-point junction. CO_2 thus formed could be trapped by the support to form carbonate, which would further react with acetylene molecules. These chemical mechanisms are summarized in Scheme 1. It should be noted that in the reaction cycle comprising Reaction (2) and CO disproportionation, C atoms are produced in both parts of the cycle. In addition, the stoichiometric ratio of CO_2 and $CaCO_3$ required for the production of 350 mg of MWCNTs is 30. Therefore, it can be concluded that an average of 30 chemical cycles, described in Scheme 1, is performed by the CO_2 species. In other words,

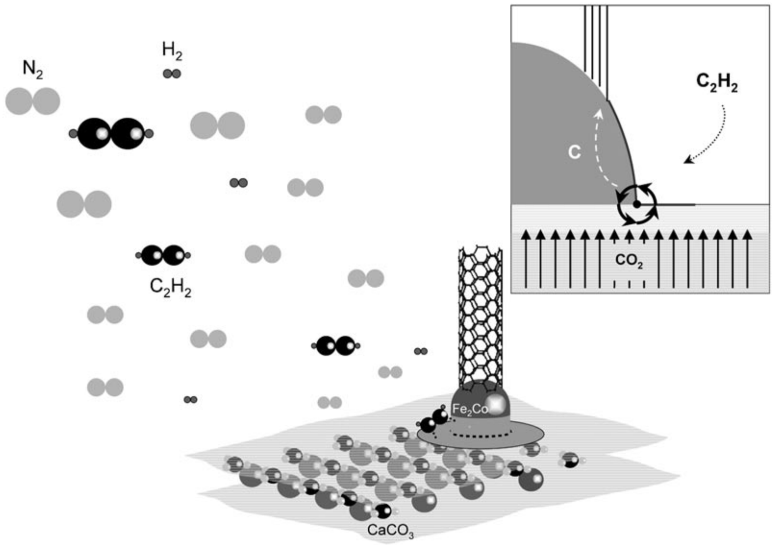
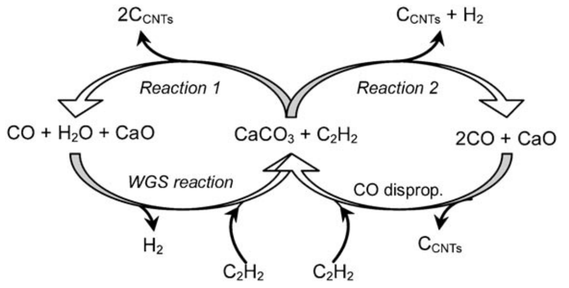


Figure 2. The triple-point junction (gray area) where the reaction described by Scheme 1 takes place corresponds to the area around the metal–support interface (dashed line). The border of this area on the metallic side is considered to be the root of the CNTs and on the support side it is the carbon diffusion length. Inset: the diffusion of the carbon-containing species. In particular, carbon atoms can diffuse on the surface or in the bulk of the metallic particles from the triple-point junction towards the CNTs.



Scheme 1. Chemical cycles involved in the growth of carbon nanotubes from an equimolar mixture of C_2H_2 and CO_2. WGS = water gas shift, CO disprop. = CO disproportionation.

one molecule of CO_2 reacts successively with an average of 30 molecules of acetylene, which shows how fast acetylene is consumed and explains the enhanced reaction rates observed in this study.

In Figure 3, we have plotted the mass of MWCNTs versus the reaction time and have fitted the curve with the model $m(t) = \beta\tau_o\ (1-e^{-t/\tau_o})$ suggested for the water-assisted growth.[19] It is assumed that the number of catalyst particles, whose activity is taken to be homogeneous, is proportional to the yield of carbon nanotubes. The fitting parameters, β and τ_o, are the initial growth rate and the characteristic lifetime, respectively. The product of these two parameters gives the maximum mass of carbon nanotubes that can be produced under the growth conditions applied. The β and τ_o characteristics of the water-assisted growth are 3 mg min^{-1} and 4.7 min, respectively.[19,20]

We performed experiments at 660 °C and 820 °C to compare the kinetics of the C_2H_2–CO_2 reaction and that of acetylene decomposition. At 820 °C, the carbonate is fully decomposed, the reactor is CO_2-free, and MWCNTs are entirely produced by acetylene decomposition ($C_2H_2 \rightarrow 2\,C + H_2$). As can be seen in Figure 3, a drastic enhancement of the catalyst activity occurs when carbon is produced by the C_2H_2–CO_2 reaction. At 820 °C a MWCNTs growth rate of 0.7 mg min^{-1} is measured whereas at 660 °C it reaches 14.6(8) mg min^{-1} from the C_2H_2–CO_2 reaction. Furthermore, the lifetime of the Fe_2Co catalyst is 13.9(5) min and is limited by $CaCO_3$ depletion or by the density of the mat of MWCNTs produced, which hinders the acetylene reaching the triple-point junction.

In conclusion, we have demonstrated that the synthesis of MWCNTs is strongly affected by an equimolar reaction between acetylene and CO_2. When $CaCO_3$ is employed as the support, a two-step cyclic mechanism starts with the reaction of acetylene and $CaCO_3$ (CO_2) then CO_2 regeneration. The reaction takes place at the triple-point junction ($Fe_2Co/CaCO_3/C_2H_2$) around the catalyst–support interface, which strongly enhances the conversion of acetylene. According to this concept, we speculate a base-growth mode for MWCNTs in which the support and metal contact is preserved. When Fe_2Co is supported by MgO, the form of carbon deposited strongly depends on the CO_2/C_2H_2 ratio. For an equimolar mixture of acetylene and CO_2, MWCNTs are grown, whereas amorphous carbon is produced in the absence of CO_2. Analysis of the kinetics of the growth mechanism shows an enhancement of the catalyst characteristics: catalyst lifetime and initial growth rate are drastically enhanced when carbon is produced by the C_2H_2–CO_2 reaction compared with those of the synthesis of MWCNTs by classical acetylene decomposition. Up to now, highly efficient and low-temperature CVD growth of carbon nanotubes has been addressed by enhancing the catalyst activity in the decomposition of the carbon source. Our results demonstrate that new chemical

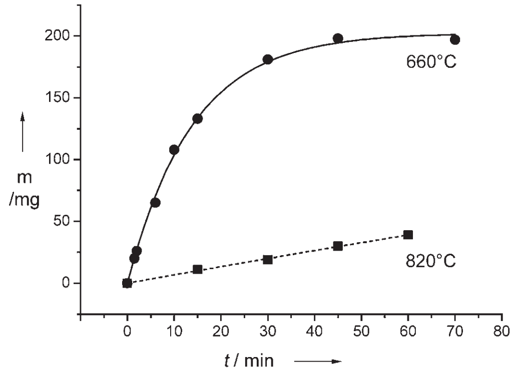


Figure 3. Mass of MWCNTs produced from 50 mg of supported catalyst after different reaction times at 660 °C and 820 °C.

reactions that involve unexplored mechanisms could also be a way to improve nanotube growth.

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