Rapid Synthesis of Carbon Nanotubes by Solid-State Metathesis Reactions

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Solid-state exchange reactions between carbon halides and lithium acetylide catalyzed by cobalt dichloride enable the rapid synthesis of carbon nanotubes as observed by TEM. Without the catalyst, only graphite and amorphous carbon form. These reactions are self-propagating and can be initiated with a heated filament. Regulating the reaction temperature provides a method for controlling these reactions. The theoretical temperature for a reaction between hexachloroethane and lithium acetylide is 2302 K assuming adiabatic conditions. Calculations indicate that increasing the length of the carbon chain can lower the reaction temperature by up to 61 K. Replacing chlorine with fluorine can further reduce the temperature by up to 384 K. Replacing chlorine with hydrogen can, in principle, lower the reaction temperature by up to 925 K. These calculations suggest that polymers such as poly(vinyl chloride), poly(vinylidene chloride), and poly(tetrafluoroethylene) can be used as precursors to carbon nanotubes. This is confirmed experimentally using a copolymer of poly(vinyl chloride) and poly(vinylidene chloride) with a 5 mol % (based on carbon) iron trichloride catalyst to produce multi-walled carbon nanotubes.

The discovery of multi-walled[1] and single-walled[2,3] carbon nanotubes has generated great interest due to their remarkable mechanical, thermal, and electrical properties.[4−7] Carbon nanotubes have already been used as scanning tunneling microscopy tips[8,9] and could potentially lead to nanometer-scale electronic devices,[10,11] hydrogen storage media,[12−14] and carbon−carbon composites for strong lightweight structures.[4−7,15] These future applications are highly dependent on the development of a low-cost, rapid, and readily scalable route to carbon nanotubes. Single- and multi-walled nanotubes are typically synthesized by time-, energy-, and/or cost-intensive processes including arc evaporation,[3,16,17] laser vaporization,[18−20] and chemical vapor deposition.[21,22] Recent reports indicate that multi-walled nanotubes can also be synthesized from decomposition reactions[23−25] or by heating a polymer resin.[26] Here we report the rapid synthesis of carbon nanotubes using solid-state metathesis (exchange) reactions.

Solid-state metathesis reactions have been developed over the past few years into a simple and effective route to materials that are difficult to synthesize by conventional methods.[27−29] These highly exothermic reactions often use molecular precursors to produce crystalline products. A heated filament can be used to initiate these self-propagating reactions. Solid-state metathesis reactions are driven by the formation of stable salt byproducts. The salt can subsequently be washed away with water and/or alcohol enabling the desired product to be isolated. For example, when a reaction between hexachloroethane and lithium acetylide (eq 1) is ignited with a heated filament, crystalline graphite is produced along with the byproduct salt, lithium chloride:

$$C_2Cl_6 + 3Li_2C_2 \rightarrow 8C + 6LiCl \qquad (1)$$

This reaction has an enthalpy of −2057 kJ/mol (−257 kJ/mol of carbon) with a theoretical maximum reaction temperature of 2302 K. This maximum temperature assumes complete reaction and adiabatic conditions. A powder X-ray diffraction pattern of the washed products of the reaction described in eq 1 is presented in Figure 1 (top). The marked peaks correspond to the 002, 100, and 101 diffraction lines of graphite.

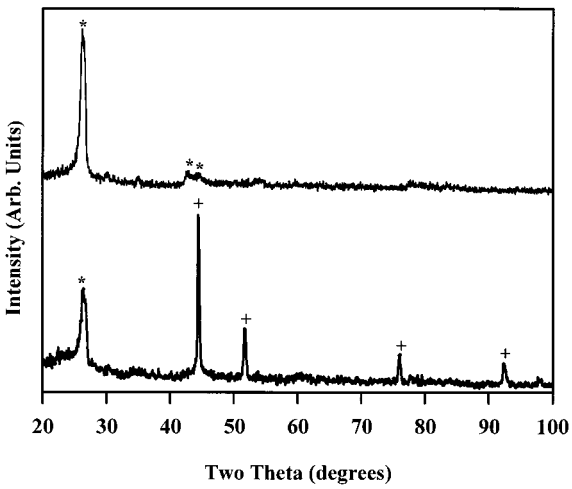

Figure 1. Powder X-ray diffraction (top) of the products from the solid-state metathesis reaction between C_2Cl_6 and Li_2C_2 without and with (bottom) the addition of a 5 mol % (based on carbon) $CoCl_2$ catalyst. The peaks corresponding to graphite are marked with an asterisk (*), and the peaks corresponding to face-centered cubic cobalt metal are marked with a plus (+).

By adding 5 mol % (based on carbon) of cobalt dichloride as a catalyst to hexachloroethane and lithium acetylide (eq 1), powder X-ray diffraction suggests the formation of graphite and face-centered cubic cobalt metal (Figure 1, bottom). Transmission electron microscopy (TEM) images of the washed products from the reaction given in eq 1 with the catalyst added indicate that actually single- and multi-walled nanotubes along with graphite-encapsulated cobalt nanoparticles are formed. Some of the multi-walled nanotubes extend up to 50 nm or more in length and possess a bamboo-like structure, as can be seen in

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Figure 2. TEM image of a multi-walled carbon nanotube synthesized by the solid-state metathesis reaction between C_2Cl_6, Li_2C_2, and 5 mol % $CoCl_2$.

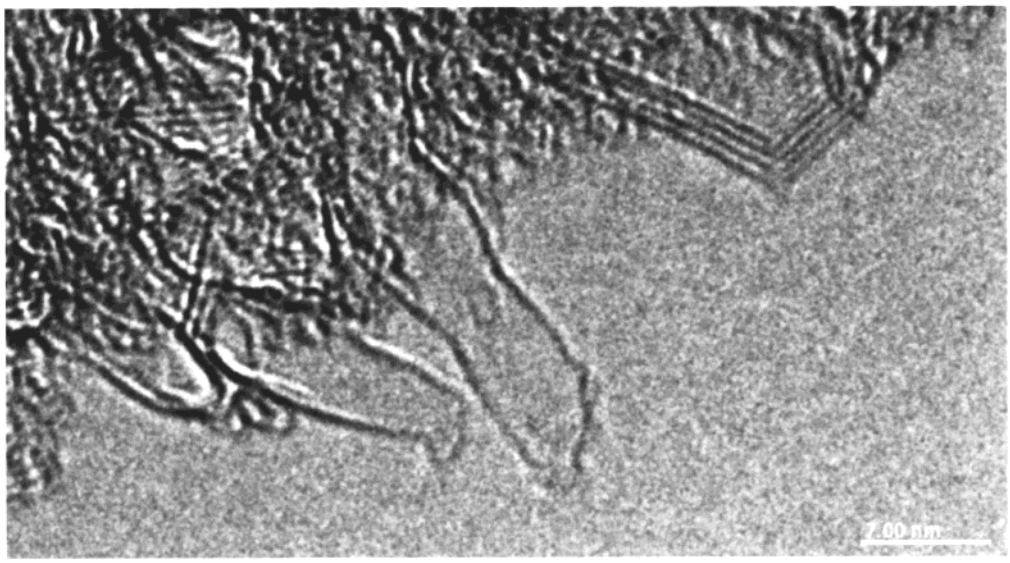

Figure 3. TEM image of some single- and multi-walled carbon nanotubes synthesized by the solid-state metathesis reaction between C_2Cl_6, Li_2C_2, and 5 mol % $CoCl_2$.

the TEM image in Figure 2. The distance between the planes is 0.34 nm (3.4 Å), as expected for carbon−carbon layers and consistent with the 002 X-ray diffraction peak at 26° 2θ. Some irregularly shaped single-walled nanotubes also form, as shown in Figure 3, and are approximately 2.9 nm in diameter and rather short in length.

Along with multi- and single-walled nanotubes, graphite-encapsulated cobalt nanoparticles, free carbon (amorphous and graphitic), and unencapsulated cobalt metal are found. The latter two byproducts can easily be removed by washing in concentrated nitric acid. The graphite-encapsulated cobalt nanoparticles, however, are unaffected by the acidic solution.

To see how the product distribution depends on the catalyst concentration and reaction scale, the amount of catalyst was varied from 2 to 10 mol % (based on carbon) and the reaction scale varied by a factor of 10 (from 1.53 to 0.153 g). At lower catalyst concentrations (<5%), the yield of single-walled nanotubes significantly decreases. Multi-walled nanotubes and graphite-encapsulated cobalt nanoparticles are the main products. At higher concentrations (>5%), the yield of graphite-encapsulated nanoparticles increases significantly with no evidence for the formation of single-walled nanotubes. Thus, the 5 mol % $CoCl_2$ appears to yield the highest percentage of nanotubes. To see the effects of reaction scale on the product

distribution, the catalyst concentration was held relatively constant at 4% and the reaction size was decreased to 1/10 its original size (0.153 g). The smaller reactant size resulted in a precipitous decrease in the yield of carbon nanotubes. Thus, it appears that larger reaction sizes (at least $\geq$1.5 g) lead to higher yields of carbon nanotubes.

Other transition metal halides can also be used as catalysts. When either a 5 mol % iron chloride ($FeCl_3$) or a 5 mol % nickel chloride ($NiCl_2$) catalyst is added to the reaction of hexachloroethane and lithium acetylide (eq 1), multi-walled nanotubes and graphite-encapsulated iron or nickel nanoparticles, respectively, are produced.

The temperature of these solid-state metathesis reactions may play an important role in determining the products synthesized. The reaction between hexachloroethane and lithium acetylide has a calculated adiabatic temperature of 2302 K. This temperature approaches the reported graphitization temperature for carbon (2573 K)[7] and helps explain why crystalline graphite can be made in seconds from this chemical reaction. The formation of carbon nanotubes clearly requires a catalyst such as cobalt dichloride. Although the role of the catalyst is not fully understood, it may help to lower the reaction temperature, as salts have been shown to do in other solid-state metathesis reactions.[27−30] Since cobalt dichloride has a boiling point of 1322 K, it will be vaporized in the reaction, suggesting that nanotubes are catalyzed in the vapor phase.

Reaction temperatures in solid-state metathesis reactions can be controlled by changing reactants and/or adding inert salts. Here we consider the effects of increasing the length of the carbon halide chain, substituting hydrogen for chlorine and substituting fluorine for chlorine. Increasing the chain length, i.e., the number of carbons (n) from 1 to 100 as given in eq 2,

$$C_nCl_{2n+2} + (n+1)Li_2C_2 \rightarrow (3n+2)C + 2(n+1)LiCl \quad (2)$$

decreases the calculated maximum reaction temperature by 60 K. By further increasing n to 1000, the maximum reaction temperature is only lowered by an additional 1 K. Thus, an increase in chain length from a monomer such as carbon tetrabromide to a high polymer only decreases the reaction temperature by 61 K.

A more dramatic effect on reaction temperature can be achieved by replacing chlorine with hydrogen in the carbon chain, as given in eq 3:

$$(C_2Cl_{4-x}H_x)_nCl_2 + ((4n-xn)/2+1)Li_2C_2 \rightarrow (6n-xn+2)C + (4n-xn+2)LiCl + ((xn)/2)H_2 \quad (3)$$

If the carbon chain length is held constant at 1000 and the number of hydrogens per monomer unit (x) is increased from 0 to 4 with a corresponding decrease in chlorine content ($4-x$), the maximum reaction temperature is predicted to drop by an additional 925 K. These reaction temperatures are well within the range that single-walled nanotubes have been synthesized.[20] Note also that eq 3 suggests that common polymers such as poly(vinyl chloride) ($[CH_2CHCl]_n$) and poly(vinylidene chloride) ($[CH_2CCl_2]_n$) could be precursors to carbon nanotubes. In fact, a reaction between Li_2C_2 and a copolymer of poly(vinyl chloride) and poly(vinylidene chloride) with a 5 mol % $FeCl_3$ catalyst does produce multi-walled carbon nanotubes.

Analogous effects are seen when fluorine, $(C_2F_{4-x}H_x)_nF_2$, is substituted for chlorine in eq 3. If the carbon chain length is held constant at 1000 and the fluorine content ($4-x$) is increased from 0 to 4, the reaction temperature drops by 384 K. This implies that a reaction between poly(tetrafluoroethylene) ($[C_2F_4]_n$), commonly known as Teflon, and lithium acetylide should reach a reaction temperature of near 1900 K and could potentially form carbon nanotubes. A preliminary test of this reaction indicates that some carbon nanotubes are formed. An extensive search of the literature indicates that a related single-displacement reaction between $[C_2F_4]_n$ and Mg is known by the U.S. military and used in submarines for propulsion of torpedoes and to produce chaff to deflect heat seeking missiles in aircraft.[31] It appears that although the thermodynamics of this reaction have been studied,[32] the carbon byproducts have not been investigated by TEM, nor has a catalyst been added.

In summary, solid-state metathesis reactions are an effective method for synthesizing carbon nanotubes. Using a catalyst, such as $CoCl_2$, is a definite requirement for the synthesis of both single- and multi-walled nanotubes. Without a catalyst, only graphitic and amorphous carbon form. These reactions, once optimized, will likely use cheaper precursors, require less preparation, and need less expensive equipment than existing methods. A potential route to optimization is to lower the reaction temperature. This can be achieved by utilizing longer chain carbon halides, substituting fluorine for chlorine, and/or by increasing the hydrogen to halide content in the precursors.

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