Carbon nanotube formation from milled iron-phthalocyanine

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Abstract. Organometallics supply carbon and metal catalyst needed for carbon nanotube synthesis. It is shown that experiments involving prior milling of iron-phthalocyanine (FePc, FeC₃₂H₁₆N₈) before pyrolysis at 800 °C in argon produces carbon nanotubes with diameters ranging from 5 to 15 nm. Under the same conditions, the diameters of nanotubes produced from non-milled FePc range from 20 to more than 50 nm. Milling decreases the onset of sublimation of FePc from about 450 to 200 °C and also reduces the activation energy barrier of sublimation at 360 °C from 287 to 193 kJ/mol. This appears to be due to changes in molecular packing of the phthalocyanine precursor. It is suggested that the decrease in nanotube diameter is due to greater homogeneity in the gas phase on pyrolysis after milling, which leads to more systematic capture of carbon species during the catalytic growth of the carbon nanotubes.

1. Introduction
Carbon nanotubes (CNT) can be useful for a number of nanotechnology applications. Several production methods such as arc discharge, laser ablation, and chemical vapour deposition have been employed for the synthesis of CNTs. Recently, organometallics such as iron phthalocyanine (FeC₃₂H₁₆N₈, FePc) have been successfully converted to CNTs by pyrolysis at 800 – 1000 °C. By employing ball milling treatment of the FePc precursor prior to pyrolysis, Chen et al.,¹ have achieved a significant improvement of the structural quality and yield of the CNT product. They have also shown that ball milling reduces the onset of sublimation of the FePc precursor from 600 to 200 °C, however there is no detail of mechanism.

Here, we examine the effect of the ball milling on FePc lattice, molecular structure and activation energy of sublimation during heating prior to pyrolysis and CNT formation.

2. Experimental
Iron-phthalocyanine (FePc) powder (Sigma-Aldrich, >90% purity) was ball milled using a Pulverizette 6 (Fritsch) planetary mill. Five-gram sample was loaded in 80 ml container together with 300 balls with diameter of 5 mm. The milling was carried out for 100 h at 400 r.p.m in argon (>99,999 purity) under atmospheric pressure. Mid infrared spectra in the 4000 – 400 cm⁻¹ wavenumber region were recorded on a Bruker Vertex 70 spectrometer (≈ 0.5 mg sample in 200 mg KBr, 128 scans, 2 cm⁻¹ resolution). Carbon K-edge X-ray Absorption Fine structure (NEXAFS) spectra were acquired with fluorescence yield detection (FY). The spectra were normalized by dividing by the current measured from a gold mesh placed before the sample. The NEXAFS spectra showed a structure near 300 eV, which was due to carbon contamination on the monochromator optics. The exact position of this structure was at 299.2 eV after referencing to the π*-transition at 285.4 eV of a graphite sample. The
spectra were referenced to 299.2 eV peak in their spectra, which acted as an internal energy standard. The spectra were background and baseline corrected in the pre-edge and post-edge regions by using an algorithm developed by Newville et al. and implemented in software IFEFFIT. Activation energies \(E_a\) in the temperature range of 40 - 550 °C were determined by NETZSCH Phoenix 204 F1 differential scanning calorimeter (DSC). The DSC data were collected at scanning rates of 1, 5, 10, 25 and 50 deg/ min in argon (>99.999 % purity) flowing at 25 ml/min. The \(E_a\) values were determined according to \(\ln(q) = -E_a/(RT_p) + \text{const.}\) where, \(q\) (K.s\(^{-1}\)) is the heating rate, \(T_p\) (K) shifts with the heating rate, \(E_a\) is activation energy, \(R\) (8.3 J/molK) is the gas constant. The logarithm of the heating rate \(\ln(q)\) was plotted over the reciprocal temperature of the maximum temperatures of DSC curves (1/Tp). The slope of the yielded straight line is proportional to the activation energy \(E_a\).

3. Results
For clarity, the Transmission Electron Micrographs of CNT produced by pyrolysis at 800 °C from non-milled and milled FePc are shown in Figure 1 A and B. It is seen that the CNTs produced from non-milled FePc have irregular shape of the walls and a diameter of about 40 nm (Figure 1 A). The CNTs produced from milled FePc however, show straighter walls and some of the examined CNT samples have diameter down to about 10 nm (Figure 1 B).

Figure 1. TEM micrographs of CNTs produced from (A) non milled and (B) milled FePc

Figure 2 compares normalized fluorescence yield (FY) carbon K-edge NEXAFS spectra for non-milled and milled FePc. The existence of several peaks and shoulders at the carbon K-edge NEXAFS spectrum of non-milled FePc can be explained by the presence of two distinct chemical environments for carbon atoms in the phenyl (C=C) and the pyrrole (C=N) subunits.

Figure 2. Normalized C K-edge NEXAFS fluorescence yield spectra of non-milled and milled FePc.
The peak labelled with (*) symbol at 299.2 eV due to surface contamination of the synchrotron optics and was used as an internal standard. The NEXAFS spectra of the two samples are essentially identical, which suggests that the milling does not modify the phthalocyanine bond structure. Figure 3 compares the mid infrared spectrum in the region of 800 – 675 cm\(^{-1}\), where the most significant spectral differences between the two samples are observed. The resonances in this spectral region are due to the out-of-plane C-H deformations of the phenyl rings (732 and 781 cm\(^{-1}\)), and from the C=C in-plane ring deformations (755 cm\(^{-1}\)).

Upon milling, the latter shifts to 753 cm\(^{-1}\) while the resonances 732 cm\(^{-1}\) and 781 cm\(^{-1}\) shift by 7 cm\(^{-1}\) to 725 and 774 cm\(^{-1}\), respectively. These differences could be attributed to different molecular assembling in the non-milled and milled FePc. Stymne et al.,\(^6,7\) reported that the vibrations in the region below 800 cm\(^{-1}\) are sensitive to the Pc molecular packing and can be used to differentiate between various polymorphs of various metal phthalocyanines. It has been reported that the stable \(\beta\)-polymorph gives rise to the vibrations at 732 cm\(^{-1}\), while the metastable \(\alpha\)-polymorph produces a resonance at 725 cm\(^{-1}\).\(^6,7\) Therefore, the IR data indicate the milling causes structural modifications that resemble polymorphic transformation of phthalocyanine.

The heat flow effects were studied by a differential scanning calorimeter (DSC) from ambient temperature to 550 °C at a heating rate of 10 deg/min. The DSC trace of the milled sample revealed endothermic effects at 220, 364 and 434 °C, while the non-milled demonstrated broad and faint endothermic effects at 220, 364, and a stronger peak at 439 °C. The endothermic effects of non-milled and milled FePc shifted to higher temperatures when the heating rate (q) was increased from 1 to 50 deg/min. From the three endothermic effects below 550 °C, however, only those at 364 °C and at about 434 °C were suitable for the activation energy analysis (Figure 4).

**Figure 3.** Infrared spectra of non-milled and milled FePc in the range of 800 - 675 cm\(^{-1}\).

**Figure 4.** Activation energy plots for the transformations at 364 and 434 °C.
The activation energy of sublimation related to the endothermic effect at 364 °C for non-milled sample is 287 ± 10 kJ/mol while for milled sample it is 193 ± 15 kJ/mol. The activation energies of transformation related to the peak at 434 °C are closer; 228 ± 4 kJ/mol and 208 ± 10 kJ/mol, for non-milled and milled FePc, respectively.

The spectroscopic data show that the peripheral phenyl subunits are more influenced by the milling and perhaps there is a weakening of the lateral interactions between neighbour molecules. This may well be because the π-π intermolecular force is stronger in the direction perpendicular to the molecular plane than in the direction parallel to the plane of the molecule. The milling therefore primarily changes the angle between each molecule and the column axis. Since different stacking angles may be correlated to differences in the orbital overlap, this should lead to differences in the sublimation activation energy between the non-milled and milled FePc. The relatively loose structure of milled FePc should require less thermal energy to sublimate than the densely packed non-milled β-FePc precursor.

5. Summary

The milling of iron-phthalocyanines at 400 r.p.m. for 100 h in zirconia ceramic container modifies the three-dimensional packing order. The activation energy calculations show that the increased sublimation rate is related to increased energy potential due to loose packing, weaker interlayer bond strength, and random mutual orientation of the Pc layers of milled sample. All of these structural changes assist sublimation and formation of homogeneous phthalocyanine vapour during sublimation, pyrolysis and formation of CNTs.

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References
[1] Chen, Y.; Chadderton, L. T. *Journal of Materials Research* 2004, 19, 2791.
[2] Newville, M.; Livins, P.; Yacoby, Y.; Rehr, J. J.; Stern, E. A. *Physical Review B: Condensed Matter and Materials Physics* 1993, 47, 14126.
[3] Elder, J. P. *Journal of Thermal Analysis* 1985, 30, 657.
[4] Koch, E. E.; Jugnet, Y.; Himpsel, F. J. *Chemical Physics Letters* 1985, 116, 7.
[5] Kera, S.; Casu, M. B.; Schoell, A.; Schmidt, T.; Batchelor, D.; Ruehl, E.; Umbach, E. *Journal of Chemical Physics* 2006, 125, 014705/1.
[6] Stymne, B.; Sauvage, F. X.; Wettermark, G. *Spectrochimica Acta Part A: Molecular Spectroscopy* 1980, 36, 397.
[7] Kobayashi, T.; Kurokawa, F.; Uyeda, N.; Suito, E. *Spectrochimica Acta Part A: Molecular Spectroscopy* 1970, 26, 1305.