

# Early Stages in the Nucleation Process of Carbon Nanotubes: Density-Functional Tight-Binding Molecular Dynamics Simulations of Acetylene Oligomerization and Cross-Linking on an Fe<sub>38</sub> Particle

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Catalytic chemical vapor deposition (CCVD) is typically used to synthesize carbon nanotubes (CNTs), but the exact role of metal catalysts is still unknown. Since Fe substrate is known to be highly effective for the CNT growth in the CCVD process and C<sub>2</sub>H<sub>2</sub> is an excellent carbon source for high yield [1-5], we performed quantum chemical molecular dynamics (QM/MD) simulations based on the density-functional tight-binding (DFTB) method [6] to investigate the self-assembly process of carbon nanotubes from acetylene molecules on an Fe<sub>38</sub> particle. We found that oligomerization and cross-linking reactions between carbon chains with high H:C ratio were observed as initial steps, preceding any future cap nucleation.

During 30 ps Carbon supply simulation, some of C<sub>2</sub>H<sub>2</sub> loose H or some H transfer to C to form C<sub>2</sub>H<sub>x</sub> and oligomerization occurs, especially the connection between C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H (8/10 ratio), which has a lower barrier of 23.39 kcal/mol and it is an exothermic reaction (15.13 kcal/mol). During 80 ps carbon diffusion simulation, some five or six-membered rings formed from long chain C<sub>6</sub>H<sub>x</sub> or C<sub>8</sub>H<sub>x</sub>, and by cross-linking. We found pentagon-first mechanism. H<sub>2</sub> abstraction possesses a very high barrier and is an endothermic process, then it was consequently never observed in our 110 ps MD simulations. We hope our results can serve as a basis for future study of growth mechanism of CNT as well as catalytic decomposition of hydrocarbon on metal surface.

## References

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