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INFLUENCE OF THE CATALYST SUPPORTERS UPON THE CATALYST NANO PARTICLE FOR SYNTHESIZING SINGLE-WALLED CARBON NANOTUBES

Shuhei Inoue, Kazuya Nomura, and Yukihiro Matsumura

Department of Mechanical System Engineering, Hiroshima University
1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

ABSTRACT

Controlling diameter and chirality of single-walled carbon nanotubes are most interesting aspects on synthesis, and these kinds of controls are desired to be done during the synthetic processes. In fact combination of catalysts, modifying their species, and adjusting the size of catalyst can roughly control the diameter distribution. However, since catalysts including cobalt atoms work much better for synthesizing SWNTs in alcohol catalytic chemical vapor deposition process, which is considered one of the best processes to synthesize, this fact restricts the flexibility of catalyst combination. Usually, supporters are used for avoiding the condensation of catalysts, but it turns out that sometimes these supporters give bad effects on catalysts of losing their catalytic activities.

In this paper we synthesized SWNTs by using catalysts on different supporters and considered the influence of supporters by calculating their electronic structures.

1. INTRODUCTION

Single-walled carbon nanotubes (SWNTs) [1] have been considered ideal materials for many kinds of application owing to their outstanding properties, and various techniques [2-8] have been developed for the high-quality macroscopic production. Among these processes, the alcohol catalytic CVD (ACCVD) process [9] can produce pure SWNTs without any purification. Recently, Hata *et al.* developed super growth process [10] to realize the macroscopic production using water molecule to maintain the activity of catalyst nano-particles on silicon substrate. This process may grow millimeter order SWNT, but accurate control of water molecules are needed.

On the other hand, controlling the diameter of SWNTs is another important aspect. At present, synthesis temperature and catalyst size are considered to be main factors of determining the diameter. Referring to our previous work [11], catalyst species can be another factor, since they have different interaction with carbon atoms when the catalysts support the core of SWNTs at the

beginning of nucleation stage. Here, one problem comes out that catalysts with cobalt atoms seem to work well on decomposing ethanol in ACCVD, so that catalysts had better include cobalt; however this restricts the combination of catalysts such as iron – cobalt (typically used), molybdenum – cobalt. At the previous conference we reported the relationship among catalysts combinations and their electronic density of states (DOS) around Fermi level. [12] As a result it turned out that the number of DOS was quite important for their activities; however, this result was assumed isolated catalysts. Generally, catalysts are supported by a certain supporters such as zeolite, magnesium oxide, and aluminum oxide. If the catalysts are large enough, the effect of supporters is negligible, but in case of SWNTs synthesis each catalyst is desired to be small enough.

In this paper we synthesized SWNTs with different catalysts supporters and calculated their effect on catalytic activities.

2. METHODS

The following is a brief introduction of ACCVD process employed in this study. As shown Fig. 1 a vessel containing ethanol is bathed in a water tank to maintain its temperature at 10 °C. This ethanol is used as a carbon source, and it is led to the catalysts prepared on a certain supporter. The catalyst is set in the middle of the electric

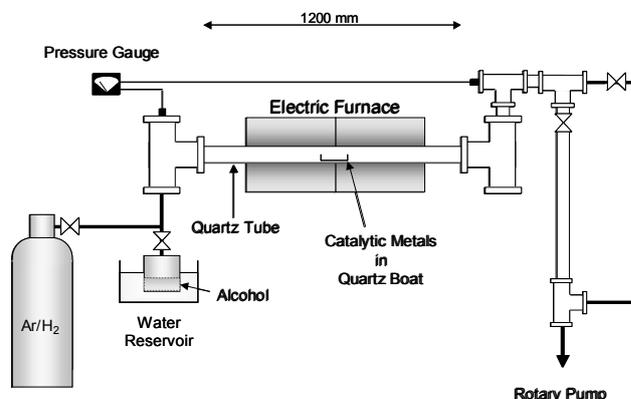


Fig. 1. A schematic view of the experimental setup.

furnace, and the ethanol is decomposed on the catalyst at 700-1000 °C. In this work, we have prepared two types of catalysts (Fe/Co and Ni/Co), and three types of supporters (zeolite, magnesium oxide (MgO) and aluminum oxide (Al₂O₃)). The samples are measured in Raman spectrometer to identify their purities by comparing G/D ratio, which is usually used for expressing the purity.

Generally, the number of electrical states around the Fermi level is critical for the reaction, because it means the activities of catalysts. In this paper we also calculated the electrical density of states around the Fermi level of cobalt particles supported with zeolite and MgO by using density functional theory (DFT). Our calculated system is that some cobalt atoms are placed above zeolite or MgO crystal with the distance of 1Å-2Å, which was roughly estimated shown in Fig. 2 by density functional theory. Gaussian03 [13] was used to determine the minimum energy distance between supporters and the cobalt cluster with their own structure were fixed. Becke's three-parameter exchange functional with Lee-Yang-Parr correlation functional (B3LYP) [14, 15] was also applied. The Los Alamos effective core potential plus DZ (LANL2DZ) [16] was used as the basis set. To simplify the system, we assumed the local structure of zeolite was comparable to the SiO₂ crystal, because our zeolite almost consisted of SiO₂ (more than 99%).

3. RESULTS AND DISCUSSION

Figure 3 shows G/D ratios of SWNTs with Fe/Co catalyst on each supporter, which usually expresses the purity. Referring to Fig. 2, zeolite-supporting catalyst can synthesize well, so that zeolite may be the best supporters among these three supporters; however, MgO can work at specific temperature, this give a very narrow diameter distribution. Saito et al. [17] mentioned the promising technique of baking MgO supporting catalyst for nano particlezation in methane CVD process, but this technique

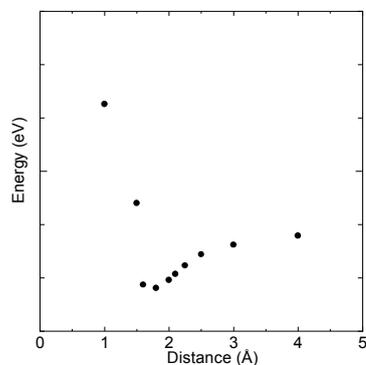


Fig. 2. Distance of the cluster from MgO crystal derived by Gaussian03 calculation.

did not work efficiently for us.

Calculated cluster models are shown in Fig. 4. According to some literatures the catalysts used for SWNTs synthesis should be small enough not to grow as a multi-walled carbon nanotubes. In fact almost all of reports concerning to SWNTs CVD synthesis described the catalysts particle was from 0.5 nm to several nm in diameter. Even if assuming the crystal structure, 1 nm in diameter is comparable to 50 atoms for iron or cobalt. Normally, clusters with up to 100 atoms have singular properties, which are called atomic cluster, and their

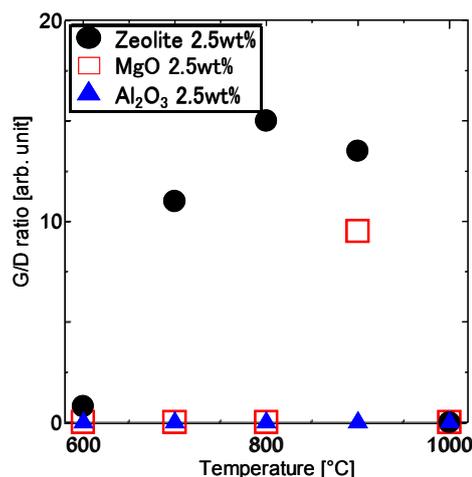


Fig. 3. G/D ratios with excitation wavelength of 514.5 nm.

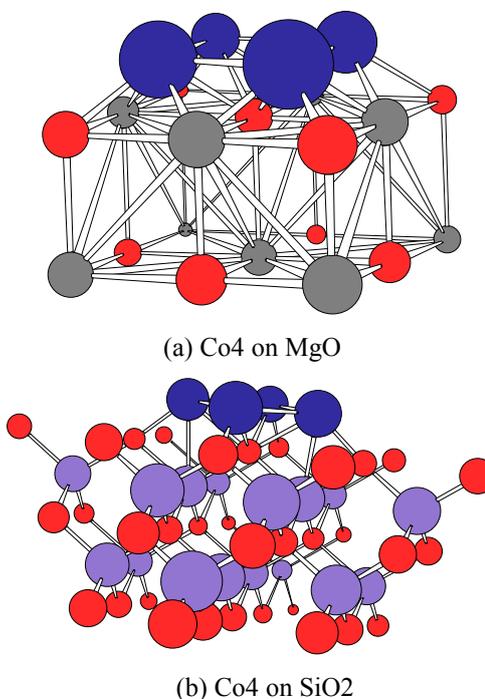


Fig. 4. Calculated cluster models.

structure are different from crystal structure. Because atoms consisting atomic cluster are apt to be on the surface, practical number of atoms are less than 50 in 1 nm atomic cluster. Thus, each catalyst particle is affected by catalysts supporters. To reduce the calculation load in this paper we assumed 4 cobalt atoms on (MgO)₉ and (SiO₂)₁₆ crystals, but it might be desirable to employ more MgO when we consider the previous reason.

Figure 5 shows electronic states of cobalt clusters on zeolite and MgO. USY-zeolite consists of almost of SiO₂ (more than 99%), so we have calculated the hypothetical effect of SiO₂ and MgO to cobalt cluster. Because SiO₂ is a covalent and MgO is an ionic crystal, we have predicted that an electronic orbital around cobalt particles must be attracted to MgO by its coulomb potential, and SiO₂ does not attract electrons; consequently, in MgO system, the number of electronic states is restricted and this makes the reactivity lower.

Referring to the overlap population, which expresses the proportion of covalent bonding, there very small amount of shared orbital between silicon and cobalt atoms; on the other hand, magnesium atoms make strong covalent bonding with cobalt atoms. As a result, the number of states is restricted in the Co-MgO system that makes the catalyst activity lower. Regarding to the proportion of ionic bonding, in both models there looks only small amount of bonding.

4. CONCLUSION

In this paper, we investigated the influence of catalyst supporters. Though our calculation system was so small, the result was quite consistent with experimental results. As we expected, the number of the electrical states directly affects the catalyst activity; consequently, to use

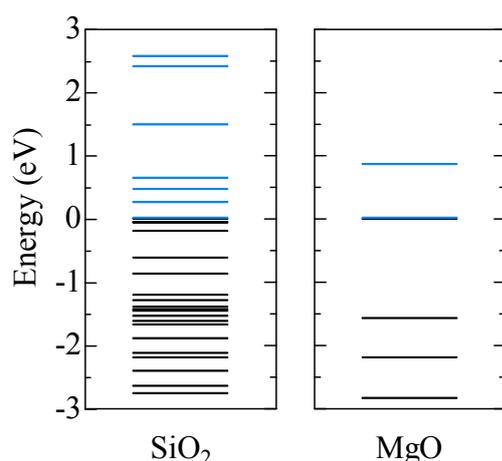


Fig. 5. The number of electrical states of cobalt cluster supported by zeolite (assumed by SiO₂) and MgO around Fermi level. HOMO is set to 0 eV.

zeolite as catalyst supporters is efficient for synthesizing SWNTs. The temperature of 700-800 °C is the best reaction temperature for zeolite supporting system, and that of 900-1000 °C is good for MgO system, but a further experiment should be necessary to solve this difference. We have the possibility of synthesizing SWNTs, which have a narrow diameter distribution with MgO. We can obtain the semi-conductor nanotubes in the special condition.

5. ACKNOWLEDMENT

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6. REFERENCES

- [1] S. Iijima and T. Ichihashi, "Single-shell carbon nanotubes of 1-nm diameter", *Nature*, 363, pp. 603-605, 1993.
- [2] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. Hee Lee, S.G. Kim, A.G. Rinzler, T. Colbert Daniel, G.E. Scuseria, D. Tomanek, J.E. Fischer, and R.E. Smalley, "Crystalline ropes of metallic carbon nanotubes", *Science*, 273, pp. 483-487, 1996.
- [3] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M.L. Chapelle, S. Lefrant, et al. "Large-scale production of single-walled carbon nanotubes by the electric-arc technique." *Nature*, 388, pp.756-758, 1997.
- [4] H.J. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, "Single-wall nanotubes produced by metal-catalyzed disproportionation of carbon monoxide." *Chem. Phys. Lett.*, 260, pp. 471-475, 1996.
- [5] H.M. Cheng, F. Li, X. Sun, S.D.M. Brown, M.A. Pimenta, A. Marucci, et al. "Bulk morphology and diameter distribution of single-walled carbon nanotubes synthesized by catalytic decomposition of hydrocarbons." *Chem. Phys. Lett.*, 289, pp. 602-610, 1998.
- [6] J. Kong, A.M. Cassell, H.J. Dai, "Synthesis of individual single-walled carbon nanotubes on patterned silicon wafers." *Nature*, 395, pp. 878-881, 1998.
- [7] J.H. Hafner, C.L. Cheung, T.H. Oosterkamp, C.M. Lieber, "High-yield assembly of individual single-walled carbon nanotube tips for scanning probe microscopies." *J. Phys. Chem. B*, 105, pp.743-746, 2001.
- [8] Y.G. Zhang, A.L. Chang, J. Cao, Q. Wang, W. Kim, Y.M. Li, et al., "Electric-field-directed growth of aligned single-walled carbon nanotubes." *Appl. Phys. Lett.*, 79, pp. 3155-3157, 2001.

- [9] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, "Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol." *Chem. Phys. Lett.*, 360, 229-234, 2002.
- [10] K. Hata, D.N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, "Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes." *Science*, 306, pp. 1362-1364, 2004.
- [11] S. Inoue, T. Nakajima, Y. Kikuchi, "Trial for diameter-selective synthesis of single-walled carbon nanotubes", *Carbon*, 44, pp. 1287-1291, 2006.
- [12] S. Inoue, T. Nakajima, K. Nomura, Y. Kikuchi, "Growth Mechanism and Selective Synthesis of SWNTs.", *Proc. of ENS06*, pp. 19-24, 2006.
- [13] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [14] A.D. Becke, "Density-Functional Thermochemistry .3. The Role Of Exact Exchange" *J. Chem. Phys.*, 98, pp. 5648-5652, 1993.
- [15] C. Lee, W. Yang, R.G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density", *Phys. Rev. B*, 37, pp. 785-789, 1988.
- [16] P. J. Hay, W. R. Wadt, "Abinitio Effective Core Potentials For Molecular Calculations - Potentials for the Transition-Metal Atoms Sc to Hg", *J. Chem. Phys.*, 82, pp. 270-283, 1985.
- [17] T. Saito, S. Ohshima, W.C. Xu, H. Ago, M. Yumura, S. Iijima, "Size control of metal nanoparticle catalysts for the gas-phase synthesis of single-walled carbon nanotubes", *J. Phys. Chem. B*, 109, pp. 10647-10652, 2005.