Formation of Carbon Nanotubes through Ethylene Decomposition over Supported Platinum Catalysts: Effects of Silica Coating on Catalytic Performance of Platinum

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Pt metal particles supported on carriers such as MgO and SiO_2 showed high activity for the formation of carbon nanotubes (CNTs) through ethylene decomposition at 973 K. However, these CNTs were not uniform in diameter because of the sintering of Pt metal particles during the reaction. Covering Pt catalysts with silica prevented the sintering of Pt metal particles during ethylene decomposition, resulting in the formation of CNTs with a uniform diameter.

Carbon nanotubes (CNTs) have attracted a great deal of interest because they have remarkable and unique magnetic, electronic, chemical, and mechanical properties. Catalytic decomposition of hydrocarbons (CCVD; catalytic chemical vapor deposition) is a promising technique for the production of carbon nanotubes. Supported transition-metal catalysts such as Fe, Co, and Ni are frequently utilized for the production of CNTs through the decomposition of hydrocarbons.[1,2] During the hydrocarbon decomposition over these transition-metal catalysts, carbon atoms are deposited on the metal surface. These carbon atoms diffuse throughout the surface and the body of the metal particles while forming CNTs.[3] Transition metals such as Fe, Co, and Ni are responsible for the growth of CNTs because they can exist as metal carbides during hydrocarbon decomposition at high temperatures.[4] In contrast, carbon atoms cannot dissolve into precious metals such as Pt and Au. Few reports thus describe the formation of CNTs by hydrocarbon decomposition over precious metals.[5]

To use CNTs in some applications, it is necessary to modify their surface with another phase to form a highly functionalized composite. The composites are frequently prepared by coating the outer surface of CNTs with highly functional metal particles.[6] The CNTs, which are formed during the hydrocarbon decomposition over metal catalysts, intrinsically contain metal particles. The CNTs are thus highly functionalized composites and may be used without further modification.[7] Precious metals have excellent chemical performance in catalytic and electrochemical reactions. The formation of CNTs by hydrocarbon decomposition over precious metal catalysts is of interest for the preparation of CNT–precious metal composites.

In this study, ethylene was decomposed over Pt metal catalysts supported on different carriers. The supported Pt metal catalysts were also covered with silica layers in order to grow CNTs with a uniform diameter.

Supported Pt metal catalysts (Pt loading = 10 wt %) were prepared by a conventional impregnation method. Carbon black (denoted as CB, Vulcan XC-72 supplied from Cabot Co.), MgO (JRC-MGO4-500A supplied from Catalysis Society of Japan), Al_2O_3 (JRC-ALO8 supplied from Catalysis Society of Japan), and SiO_2 (Cab–O–Sil supplied from Cabot. Co.) were utilized as supports for Pt. The coverage of Pt/CB with silica was done using successive hydrolysis of 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS).[8] Pt/CB was dispersed into a solution of ethanol and distilled water after which aqueous NH_3 and APTES were added. This procedure results in the hydrolysis of APTES on Pt/CB. TEOS was also added to the solution so that Pt/CB would be covered with a thick silica layer. All the Pt catalysts were reduced with hydrogen at 673 K prior to the reactions. Ethylene (20 kPa) diluted with hydrogen was contacted with the reduced catalysts at 973 K for 90 min, resulting in the formation of CNTs. The carbon yield from the ethylene decomposition over each catalyst was evaluated from the change in catalyst weight before and after the ethylene decomposition. TEM images of the catalysts before and after the ethylene decomposition were measured with a JEOL JEM-3000F.

Figure 1 shows TEM images of Pt metal catalysts on different supports after the ethylene decomposition at 973 K. CNTs were observed in the TEM images of all the Pt catalysts after ethylene decomposition, indicating that the Pt metal catalyzed the decomposition of ethylene to form CNTs. The diameters of CNT, formed on these Pt catalysts, ranged from 5 to 30 nm

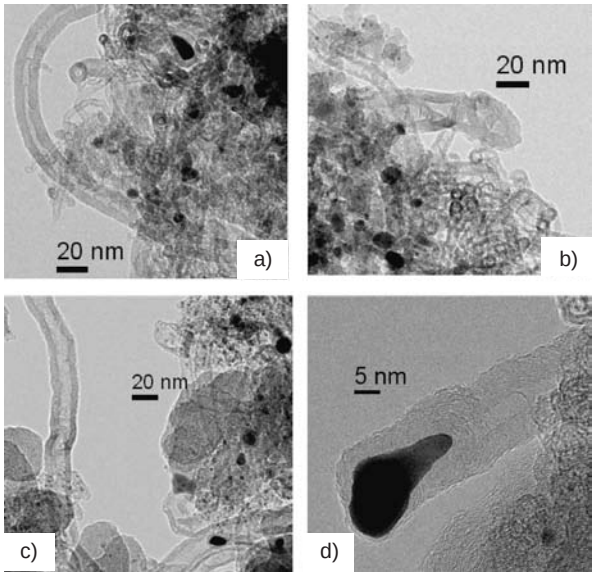

Figure 1. TEM images of supported Pt metal catalysts after the ethylene decomposition at 973 K. a) Pt/MgO; b) Pt/SiO_2; c) and d) Pt/CB.

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and had a very broad distribution. Figure 1d shows the TEM image of the tip of a CNT formed on the Pt/CB catalyst. A Pt metal particle was observed at the tip of this CNT, and its diameter was similar to that of the CNT. Pt metal particles at the tip of CNTs, therefore, decompose ethylene and allow the growth of the CNT. It should be noted that the Pt metal particle at the tip of CNT was elongated in length, fitting into the cavity of the CNT. This result strongly suggests that Pt metal particles exist in a liquid state during ethylene decomposition.[9] The dissolution of carbon atoms in the Pt metal particles likely lowers the melting point of Pt metal (melting point of Pt metal = 2041 K). Carbon yields in the ethylene decomposition were higher according to the following order: Pt/MgO (160 mol-C mol-Pt^{-1}) > Pt/SiO_2 (57 mol-C mol-Pt^{-1}) > Pt/Al_2O_3 (38 mol-C mol-Pt^{-1}) > Pt/CB (32 mol-C mol-Pt^{-1}) (TEM image for Pt/Al_2O_3 is not shown). The carbon yields for these Pt catalysts seemed to be higher as the average diameter of CNTs was smaller. Small Pt metal particles must, therefore, be effective for the formation of CNTs as Pt metal particles larger than ca. 30 nm rarely form CNTs. These larger metal particles have surfaces that are covered with thick layers of carbon.

As previously described, supported Pt metal catalysts form CNTs through ethylene decomposition at 973 K, but the diameters of these CNTs are not uniform. Pt metal particles with diameters larger than 10 nm are frequently observed in the TEM images of the Pt catalysts after ethylene decomposition. In contrast, the diameter of Pt metal particles in fresh Pt/CB and Pt/MgO ranged from 2 to 5 nm, and the diameter distribution was very narrow (results are not shown). These results strongly suggest that the Pt metal particles on the supports were severely aggregated during the ethylene decomposition at 973 K. These aggregated particles result in the formation of CNTs with various diameters. Supported Pt metal catalysts were thus covered with silica layers using the successive hydrolysis of APTES and TEOS. This was done as the expectation that the coverage of supported Pt catalysts with silica would inhibit the aggregation of the Pt metal particles.[10,11] Figures 2a and 2b show TEM images of silica-coated Pt/CB catalysts before ethylene decomposition. The content of SiO_2, Pt, and CB in silica-coated Pt/CB was estimated with X-ray fluorescence (XRF) spectra and thermogravimetric analysis under an air stream to be 22.5, 9.1, and 68.4 wt %, respectively. From these TEM images, Pt metal particles with a diameter of 1 to 3 nm were observed on the surface of CB supports. The outer surface of CB is uniformly covered with silica layers as seen in Figure 2b. This silica-coated Pt/CB was used as a catalyst for ethylene decomposition. Figures 2c and 2d show the TEM images of silica-coated Pt/CB after ethylene decomposition. Figure 2c shows that CNTs are preferentially formed by ethylene decomposition over silica-coated Pt/CB despite uniform coverage of the Pt metal particles with silica. In general, silica has a porous structure. Ethylene would be supplied to Pt metal surfaces in silica-coated Pt/CB through porous silica layers. The diameter of CNTs formed from silica-coated Pt/CB is also more uniform and smaller (5–7 nm) compared to that formed on Pt/CB without a silica coating. The carbon yield for silica-coated Pt/CB was, however, estimated to be 97 mol-C mol-Pt^{-1} whereas the carbon yield for Pt/CB without silica-coating was 32 mol-C mol-Pt^{-1}. These results suggest that the coverage of Pt metal particles with silica prevents aggregation of the Pt metal particles on the supports during ethylene decomposition. This behavior also results in the formation of CNTs with a uniform diameter as well as an improvement in carbon yield.[12] The tip of a CNT formed from the silica-coated Pt/CB is shown in Figure 2d. It should be noted that a Pt metal particle was not present at the tip of CNTs formed from silica-coated Pt/CB but could be observed at the tip or in the cavity of CNTs formed from Pt/CB without a silica-coating. CNTs are, therefore, formed via the base-growth model in ethylene decomposition over silica-coated Pt/CB,[9] i.e., Pt metal particles are always present on the supports.

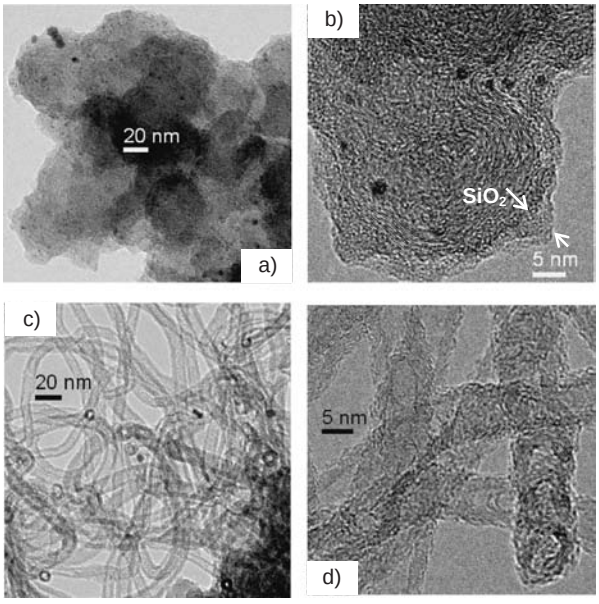

Figure 2. TEM images of silica-coated Pt/CB before and after the ethylene decomposition. a) and b) fresh catalysts; c) and d) used catalysts.

This research was supported by a Grant-in-Aid for Scientific Research (B) (No. 19360361) under the Ministry of Education, Culture, Sports, Science and Technology in Japan.

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Published on the web (Advance View) August 2, 2008; doi:10.1246/cl.2008.944