

ARTICLES

Synthesis of Carbon Tubule Nanocoils Using Fe–In–Sn–O Fine Particles as Catalysts

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We have developed Fe–In–Sn–O fine particle or powder catalysts for synthesizing carbon nanocoils by catalytic thermal chemical vapor deposition. The coprecipitation technique was used to produce the powder catalysts. By optimizing the composition ratios of Fe, In (between 10 and 33% of Fe), and Sn (less than 3.3% of Fe), carbon nanocoils could be grown in high yield. From the study of optimizing the compositions of In and Sn and the study of crystal structures of the catalysts using X-ray diffraction measurements, it was also found that Sn in the catalysts was required to grow carbon nanocoils and that In plays roles in increasing the yield of carbon nanocoils and controlling the coil diameters. This study will lead to the mass production of carbon nanocoils and therefore widen their applications.

I. Introduction

Carbon coils are expected to have applications such as nanosprings,^{1,2} electromagnetic wave absorbers,³ and field emission displays⁴ due to their unique shape. They can be synthesized by catalytic thermal chemical vapor deposition (CCVD) using Co, Fe, Ni,^{5–7} Ni/Cu alloys,⁸ or iron-coated indium–tin–oxide (ITO) substrates⁹ as catalysts. Especially, iron-coated ITO substrates can synthesize nanosized coils in high yield.⁹ Thin film catalysts such as iron-coated ITO substrates are problematic for the mass production of carbon nanocoils because carbon nanocoils are grown only on the substrate supporting the film catalyst. For the mass production of carbon nanocoils, it is essential to produce catalysts in other forms, and it is found that the powder form is best for this purpose. Another advantage of powder catalysts is that they can be used for the synthesis of carbon nanocoils in the gas phase. Here, we have developed powder catalysts containing oxides of iron (Fe), indium (In), and tin (Sn) produced by using a coprecipitation technique. The coprecipitation technique used in this study makes it possible to mass-produce powder catalysts in a simple way without requiring a vacuum system, unlike the production of thin film catalysts. To find the optimum composition ratios of Fe, In, and Sn for the growth of carbon nanocoils, we have produced powder catalysts with various composition ratios, and CCVD was performed using these catalysts. At the same time, the roles of In and Sn in the catalysts have also been studied with the measurements of crystal structures of the catalysts using X-ray diffraction (XRD).

II. Experiment

Fine particle catalysts used in this study were produced as follows.¹⁰ Iron chloride (FeCl₃), indium chloride (InCl₃), and tin chloride (SnCl₄) were first dissolved in deionized water with the same concentration (0.1 mol/L), and then these solutions were mixed with appropriate ratios. At this point, the aqueous solution of Fe³⁺, In³⁺, and Sn³⁺ ions was prepared, and the composition ratio of the catalyst was determined in accordance with the amount of the aqueous solutions mixed. An alkaline solution, an aqueous solution of ammonium carbonate ((NH₄)₂CO₃) in this study, was added to this ion solution to “precipitate simultaneously” hydroxides of iron, indium, and tin. The mixture of the hydroxides was rinsed with deionized water several times to remove ammonium chloride (NH₄Cl), which was produced in the precipitation process, and dried at 110 °C. Then, the dried hydroxide was milled to produce fine particles. After milling, the fine particles were heated at 600 °C for 2 h to remove ammonium chloride further and form oxides of Fe (Fe₂O₃), In (In₂O₃), and Sn (SnO₂) by dehydration.

The CCVD growth of carbon nanocoils was performed in a flow reactor at atmospheric pressure. Fine particle catalysts were put in the quartz reactor and then heated to 700 °C in a helium (He) atmosphere at the flow rate of 200 sccm. After heating to 700 °C, acetylene (C₂H₂) gas was supplied at the rate of 60 sccm for 30 min to perform CCVD growth. After CCVD, the deposits were analyzed by a scanning electron microscope (SEM).

III. Growth of Carbon Nanocoils from Particle Catalysts

To investigate whether Fe–In–Sn–O fine particle catalysts can grow carbon nanocoils in high yield, the fine particle catalysts whose molar composition ratio (from now on, composition ratio is defined as molar composition ratio in this study)

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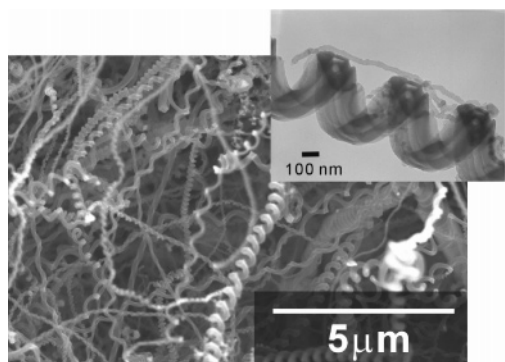


Figure 1. SEM image of carbon nanocoils grown from an Fe-In-Sn-O powder catalyst (composition: Fe/ITO = 3:1). The inset is the TEM image of a carbon tubule nanocoil.

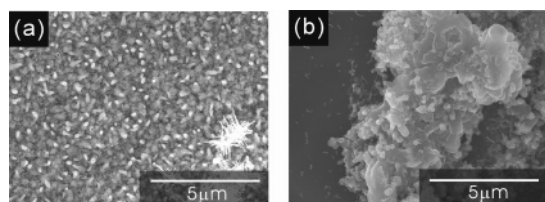


Figure 2. SEM images of the deposits grown from the powder catalysts without Fe (a) and without ITO (b).

of In and Sn is the same as that of ITO film (In/Sn = 1:0.05, in moles) used by Zhang et al.⁹ were produced, assuming that the optimum composition ratio of In and Sn for carbon nanocoil growth is that of the ITO substrate. The composition ratio of Fe and ITO was varied in order to find the optimum composition ratio of Fe and ITO in fine particle catalysts. An SEM image of carbon nanocoils grown from an Fe-In-Sn-O fine particle catalyst (composition ratio Fe/ITO = 3:1) is shown in Figure 1.

More than 95% of the deposits are carbon nanocoils with various coil diameters. Almost the same results were obtained when the composition ratios of Fe and ITO are between Fe/ITO = 1:1 and Fe/ITO = 10:1. From this result, it is seen that carbon nanocoils can be grown also with Fe-In-Sn-O powder catalysts produced using a coprecipitation technique when the composition ratio of Fe and ITO is correctly selected. As seen from the TEM image of a carbon nanocoil (see the inset of Figure 1), the fiber forming the carbon nanocoil was found to be hollow, and therefore the carbon nanocoils grown from the powder catalysts synthesized in this study can be called carbon tubule nanocoils. Using the catalyst without Fe, neither carbon nanocoils nor carbon fibers were grown, as shown in Figure 2a. This result implies that Fe is required to grow carbon nanocoils. On the other hand, when ITO was not included in the catalyst, it was also found that neither carbon nanocoils nor long carbon fibers were grown (see Figure 2b). This result is different from that with Fe/ITO film catalysts. When the film catalyst without ITO was used, only carbon nanotubes were grown.¹¹ Therefore, it was found that Fe was required to grow carbon fibers or nanotubes. The reason the catalyst particle without ITO used in this study could not grow carbon fibers or nanotubes may be the difference in the size of the catalysts. The thickness of Fe in the film catalysts was 15 or 100 nm, while the size of the powder catalyst used in this study was an order of micrometers. It is considered that the Fe₂O₃ particle (the powder catalyst without ITO synthesized in this study was found to be Fe₂O₃ from XRD measurement) with micrometer size was so large that it could not absorb carbon atoms enough to grow carbon fibers or nanotubes with the CCVD condition

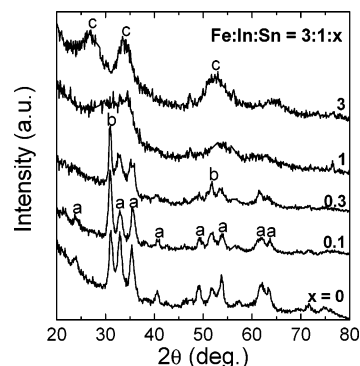


Figure 3. XRD patterns of the catalysts with various compositions of Sn (Fe/In is fixed to 3:1). The peaks marked by "a", "b", and "c" correspond to Fe₂O₃, In₂O₃, and SnO₂, respectively.

used in this study. However, the growth of carbon fibers and nanocoils was induced by adding ITO into Fe particles with micrometer size. The cause of this effect will be discussed in the next sections.

IV. Composition of Catalysts

In this section, the optimization of the composition ratio of In and Sn is carried out to grow carbon nanocoils in high yield. In addition, by changing the compositions of In and Sn independently, it may be possible to study the roles of In and Sn in the catalysts. In this study, the roles of In and Sn are discussed with XRD measurements of the catalysts before and after the CCVD process and SEM images of the deposits after CCVD.

A. Optimization of the Composition of Sn. To optimize the composition of Sn, we synthesized fine particle catalysts with various compositions of Sn, assuming that the optimum composition ratio of Fe and In was Fe/In = 3:1. Namely, we produced the powder catalysts with the composition ratios of Fe/In/Sn = 3:1:0, 3:1:0.1, 3:1:0.3, 3:1:1, and 3:1:3.

To investigate how the crystal structures of the catalyst are changed by the addition of Sn, the XRD patterns of the catalysts with various Sn compositions before CCVD were measured and were analyzed by MDI JADE analysis software. The results are shown in Figure 3. The XRD patterns of Fe₂O₃ (marked by "a" in Figure 3), In₂O₃ (marked by "b"), and SnO₂ (marked by "c") were seen in Figure 3, and these patterns were dependent on the composition of Sn.

When Sn is not included in the catalyst, only XRD patterns of Fe₂O₃ and In₂O₃ were seen. On the other hand, a small amount of Sn in the catalyst ($0.1 \leq x \leq 0.3$, in Figure 3) broadened the XRD patterns of Fe₂O₃, while the sharpness of the XRD pattern of In₂O₃ was not changed. The half-width of the XRD patterns of Fe₂O₃ slightly increased from 1.0 degree in case of the catalyst without Sn ($x = 0$) to 1.8 degree in the case of $x = 0.3$, while the half-width of the XRD patterns of In₂O₃ was kept at 0.8 degree. This indicates that SnO₂ reduced the crystalline size of Fe₂O₃ but not that of In₂O₃. In addition to this, the angular shifts of the XRD patterns of both Fe₂O₃ and In₂O₃ were not seen in Figure 3. This implies that solid solutions of Fe and Sn, In and Sn, and their oxides were not formed in the catalysts synthesized in this study. From these results, it is considered that SnO₂ compressed Fe₂O₃ and reduced the crystalline size of Fe₂O₃, while the crystalline size of In₂O₃ was not changed by only a small amount of Sn. The reason the XRD pattern of SnO₂ was not seen in the catalysts with Fe/In/Sn = 3:1:0.1 and 3:1:0.3 is that the amount of SnO₂ was too small and its crystalline size was also too small to detect with

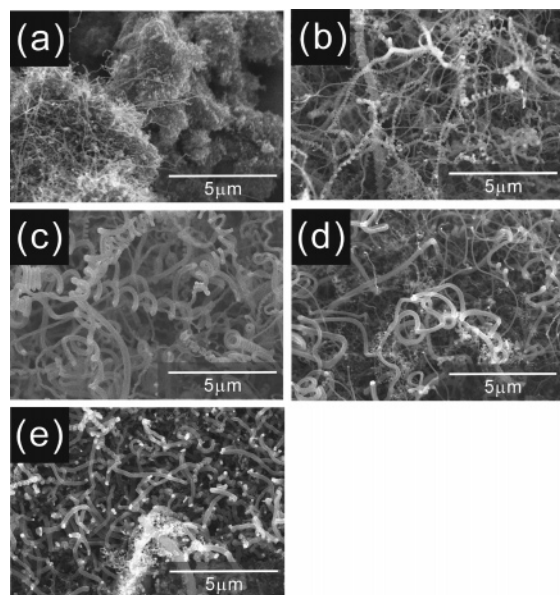


Figure 4. SEM images of the products after CCVD ((a) Fe/In/Sn = 3:1:0, (b) Fe/In/Sn = 3:1:0.1, (c) Fe/In/Sn = 3:1:0.3, (d) Fe/In/Sn = 3:1:1, and (e) Fe/In/Sn = 3:1:3).

XRD measurements, rather than that Sn and In_2O_3 formed solid solutions. This is because the angular shifts of the XRD patterns of In_2O_3 and Fe_2O_3 were not seen in Figure 3, and only the XRD pattern of Fe_2O_3 was broadened by adding a small amount of Sn.

As the composition of Sn increases further to Fe/In/Sn = 3:1:1, the XRD patterns of both In_2O_3 and Fe_2O_3 disappear and two broad peaks were seen between $2\theta = 27^\circ$ and 36° and between 50° and 60° . These broad patterns probably came from the broadened XRD patterns of Fe_2O_3 and In_2O_3 in addition to the XRD patterns of SnO_2 . This implies that the crystalline sizes of both In_2O_3 and Fe_2O_3 particles are reduced by SnO_2 when the composition of Sn is large. When Fe/In/Sn = 3:1:3, only the XRD pattern of SnO_2 is seen, although it is broad. This broad XRD pattern may be because SnO_2 was also compressed by Fe_2O_3 and In_2O_3 .

The SEM images of products with various compositions of Sn after CCVD are shown in Figure 4. No carbon nanocoil was grown from the catalyst without Sn (Fe/In/Sn = 3:1:0), as seen in Figure 4a. Only a few carbon fibers were grown. This shows that In did not have an ability to grow carbon nanocoils.

With only a small amount of Sn included (namely, Fe/In/Sn = 3:1:0.1), carbon nanocoils are grown in high yield, as shown in Figure 4b. From this result, it is seen that only a small amount of Sn in the catalyst particle induced the growth of carbon nanocoils. This tendency is opposite to that of the study by Pan et al.¹¹ In the study by Pan et al.,¹¹ it was found that In was required to grow carbon nanocoils. The cause of this difference may be the fact that a small amount of Sn adsorbed at the reactor wall in the former deposition process might be included in catalysts during CCVD, and it might be assumed that only a small amount of Sn should not influence the result in their study. When the composition of Sn is slightly increased to Fe/In/Sn = 3:1:0.3, the yield of carbon nanocoils dropped (Figure 4c). It is also found that the majority of carbon nanocoils grown with this catalyst had coil diameters of above 500 nm. The reason for this will be discussed later.

When the composition of Sn is increased much more (Fe/In/Sn = 3:1:1, 3:1:3), little carbon nanocoils were grown. Instead, curly short fibers and straight long fibers with larger

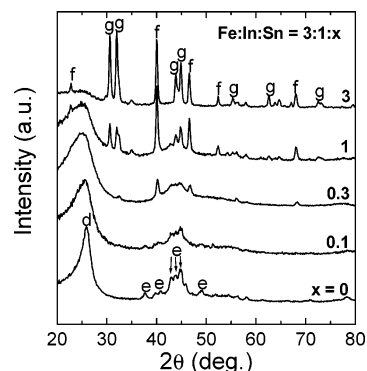


Figure 5. XRD patterns of the catalysts with various Sn compositions after CCVD. The peaks marked by “d”, “e”, “f”, and “g” correspond to graphite, Fe_3C , Fe–In–Sn–C, and Sn, respectively.

fiber diameters (≈ 200 nm in average) than those of carbon nanocoils grown from the catalyst with smaller Sn composition (Fe/In/Sn = 3:1:0.1) (≈ 30 – 100 nm) were seen, as shown in Figure 3d,e. Considering that Sn is required to grow carbon nanocoils, more Sn in the catalyst should grow carbon nanocoils in higher yield than when the composition of Sn is small. However, the result showed the opposite tendency.

To investigate the cause of this tendency further, XRD patterns of the catalysts with various Sn compositions after CCVD were also measured. They are shown in Figure 5. Only the XRD patterns of graphite (carbon fibers) (marked by “d” in Figure 5) and cementite Fe_3C (marked by “e”) were seen when no Sn is included (case of $x = 0$ in Figure 5) in the catalysts. Any patterns of substances including In were not clear.

With a small amount of Sn included ($x = 0.1$ in Figure 5) in the catalyst, the XRD patterns of Fe_3C were broadened. For example, the peak at $2\theta = 38^\circ$ clearly seen in the case of $x = 0$ (no Sn included) became broad and was not clearly seen when $x = 0.1$. This also indicates that the crystalline size of Fe_3C was reduced by Fe–In–Sn–C (this substance was not clearly seen in the XRD pattern of $x = 0.1$ because the amount of this substance was too small and its crystalline size was also too small).

When the composition of Sn x increases to more than 0.3, three peaks at $2\theta = 40^\circ$, 47° , and 68° (marked by “f”) became visible. These peaks correspond to Fe_3SnC or $\text{Fe}_3\text{InC}_{0.5}$, according to the database of the analysis software (Note: the XRD patterns of $\text{Fe}_3\text{InC}_{0.5}$ and Fe_3SnC are similar, and therefore it was difficult to distinguish from measured XRD patterns). This XRD pattern became dominant in the case in which the composition of Sn x is quite large ($x \geq 1$). This indicates that most of the Fe reacted with Sn by being incorporated with C, and then most of the catalyst became the substance represented by this XRD pattern. For the film catalysts of Fe-coated ITO, the peak at 40° clearly appeared at the beginning stage of CCVD, and then this intensity decreased when carbon nanocoils are grown.¹² Thus, it is reasonable to ascribe the plateau at 40° when Fe/In/Sn = 3:1:0 to $\text{Fe}_3\text{InC}_{0.5}$. Thus, we express the substance whose XRD pattern is marked by “f” in Figure 5 as $\text{Fe}_3\text{In}_{1-m}\text{Sn}_m\text{C}_n$. It is also found in Figure 5 that the XRD pattern of Sn (marked by “g”) was seen when $x \geq 1$. This shows that SnO_2 not reacted with Fe and C was reduced by C_2H_2 gas and became Sn during CCVD.

B. Roles of Sn. As shown in the previous sections, the composition of Sn in the catalysts had to be small to grow carbon nanocoils in high yield. This probably makes the distribution of the composition ratios of Fe and Sn formed in the catalyst easier than when the composition of Sn is large.

According to Nakayama,¹³ the growth of carbon nanocoils is tip-growth, and the mechanism of carbon nanocoil formation is that the composition of the catalyst particle at the tip of the carbon nanocoil is not uniform and thus causes the difference in the extrusion velocities of carbon network between inner and outer sides of the carbon nanocoil. When the composition of Sn is small, it is easy for Sn to be localized in the catalyst; therefore, the gradient of the composition of Sn is easily formed in the catalyst particle at the tip. From the XRD patterns shown in Figure 5, it is estimated that the part of the catalyst particle where the Sn composition is large becomes $\text{Fe}_3\text{In}_{1-m}\text{Sn}_m\text{C}_n$ while the part where the Sn composition is small becomes Fe_3C . In addition, the extrusion velocities of the carbon network of $\text{Fe}_3\text{In}_{1-m}\text{Sn}_m\text{C}_n$ and Fe_3C should be different. For these reasons, most of the products grown from the catalysts with smaller Sn compositions become carbon nanocoils.

On the other hand, if the composition of Sn is too large, the composition of Sn in the catalyst particle becomes more uniform; therefore, the catalyst particle at the tip becomes $\text{Fe}_3\text{In}_{1-m}\text{Sn}_m\text{C}_n$ only during CCVD, as seen from Figure 5. Consequently, it is difficult for the catalyst particle to generate the difference of extrusion velocities of carbon network between inner and outer sides of the catalyst particle; thus, only thick carbon fibers were grown from the catalysts with large Sn composition (see Figure 4e).

As discussed in the previous section, the coil diameter of the carbon nanocoils grown from the catalyst with the composition ratio $\text{Fe}/\text{In}/\text{Sn} = 3:1:0.3$ was larger than that of carbon nanocoils from the catalyst with the smaller Sn composition ($\text{Fe}/\text{In}/\text{Sn} = 3:1:0.1$) than $\text{Fe}/\text{In}/\text{Sn} = 3:1:0.3$, although the yield was low. This may also be because the composition of Sn in the catalyst with $\text{Fe}/\text{In}/\text{Sn} = 3:1:0.3$ is more uniform than that in the catalyst with $\text{Fe}/\text{In}/\text{Sn} = 3:1:0.1$. In this case, the difference of the extrusion velocities of the carbon network between the inner and outer sides of carbon nanocoils are smaller when $\text{Fe}/\text{In}/\text{Sn} = 3:1:0.3$ than that when $\text{Fe}/\text{In}/\text{Sn} = 3:1:0.1$. The smaller the difference of the extrusion velocities between inner and outer sides of carbon nanocoils is, the larger the radius of the curvature of carbon fibers forming carbon nanocoils becomes.

For better understanding, the roles of Sn discussed above are visualized in Figure 6.

C. Optimization of the Composition of In. To optimize the composition of In, we produced the powder catalysts with various compositions of In, fixing the composition ratio Fe/Sn to 3:0.1, which is found to be the optimum composition ratio of Sn and Fe in the previous experiment. The crystal structures of the catalysts with various compositions of In before CCVD were investigated by XRD measurements, which are shown in Figure 7. It should be noted first that the XRD patterns of Fe-In , In-Sn , and Fe-In-Sn alloys were not seen even if the composition of In is changed. In addition, no angular shift was seen in the XRD pattern. When no or a small amount of In ($\text{Fe}/\text{In}/\text{Sn} = 3:0:0.1$ or $3:0.3:0.1$) is included in the catalyst, only an XRD pattern of Fe_2O_3 (marked by "a" in Figure 7) was seen. When In is included as $\text{Fe}/\text{In}/\text{Sn} = 3:1:0.1$, the XRD pattern of In_2O_3 (marked by "b") was seen in addition to the XRD pattern of Fe_2O_3 . The peaks due to In_2O_3 became intense when the composition of In is increased to $\text{Fe}/\text{In}/\text{Sn} = 3:3:0.1$ and $3:9:0.1$.

The SEM images of the products grown from the catalysts with various compositions of In are shown in Figure 8. When the catalyst without In is used, some carbon nanocoils were seen, which also confirms that Sn is a metal required to grow carbon nanocoils. The average diameter of straight fibers (≈ 80

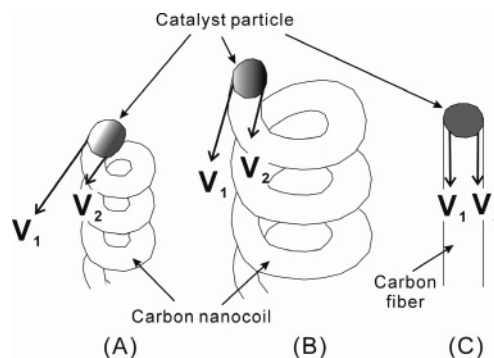


Figure 6. Schematic of carbon nanocoils and fibers grown from various Sn compositions. (A), (B), and (C) are the carbon nanocoils and carbon fibers grown from the catalyst with small, medium, and large Sn compositions, respectively. The darker part of the catalyst particle represents the area where Sn is included. V_1 and V_2 are the extrusion velocities of the carbon network at the outer and inner part of the carbon nanocoil, respectively. In (A), the gradient of the Sn composition is so large that V_1 becomes much larger than V_2 . Therefore, carbon nanocoils with a smaller coil diameter is grown. In (B), as the gradient of Sn composition is not as large as that of (A), the difference between V_1 and V_2 is not as large as that of (A) as well. In this case, carbon nanocoils with a larger coil diameter are grown. In (C), the composition of Sn is uniform, and therefore $V_1 \approx V_2$. In this case, carbon fibers are grown.

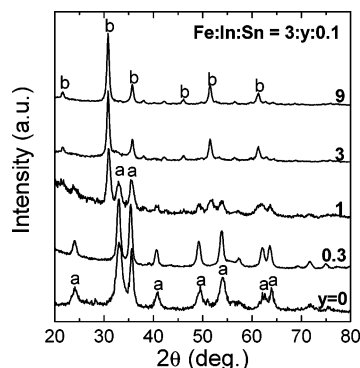


Figure 7. XRD patterns of the catalysts with various In compositions (Fe/Sn is fixed to 3:0.1). The peaks marked by "a" and "b" correspond to Fe_2O_3 and In_2O_3 , respectively, which is the same as in Figure 3.

nm) seen in Figure 8a was smaller than that of short straight fibers (≈ 200 nm) grown by using the catalyst with large composition of Sn (see also Figure 4e). As shown in Figure 2a, the catalyst without ITO grew neither carbon nanocoils nor carbon fibers. Here, it is found that the growth of carbon nanocoils and carbon fibers was induced by adding only a small amount of Sn in the catalysts. To investigate the crystal structures of the catalysts with and without Sn, the XRD patterns of the catalysts with and without Sn were measured. Figure 9 shows the results.

As shown in Figure 9, the XRD pattern of the catalyst with Fe only was much sharper than that of the catalyst with Fe and Sn, indicating that the crystalline size of Fe_2O_3 without Sn is larger than that of the catalyst with Sn. Considering that the catalyst particles prepared by a coprecipitation technique are mainly cohered particles, this result shows that the particle size of Fe_2O_3 in the catalyst particles was reduced by SnO_2 , and this size reduction increased the catalyst activity of Fe_2O_3 .

When In is included between 10 and 33% of Fe (namely, $\text{Fe}/\text{In}/\text{Sn} = 3:0.3:0.1$ and $3:1:0.1$, respectively), the yield of carbon nanocoils became much higher than in the case in which no In is included. It seems that In somehow induced the growth of carbon nanocoils. As the composition of In increases to 100%

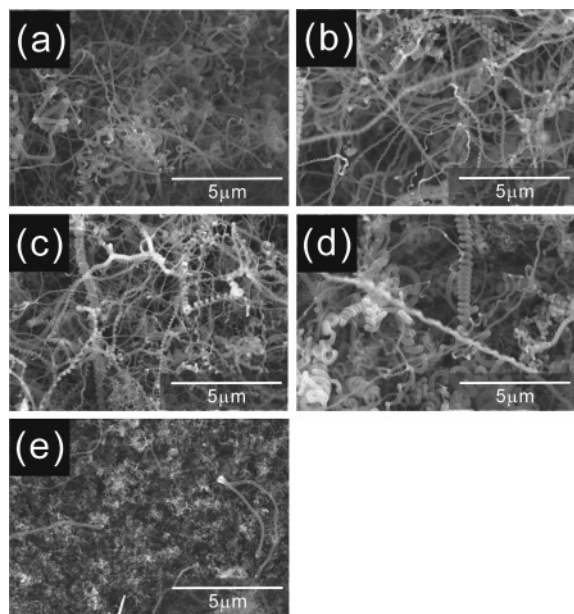


Figure 8. SEM images of the products with various compositions of In after CCVD ((a) Fe/In/Sn = 3:0:0.1, (b) Fe/In/Sn = 3:0.3:0.1, (c) Fe/In/Sn = 3:1:0.1, (d) Fe/In/Sn = 3:3:0.1, and (e) Fe/In/Sn = 3:9:0.1).

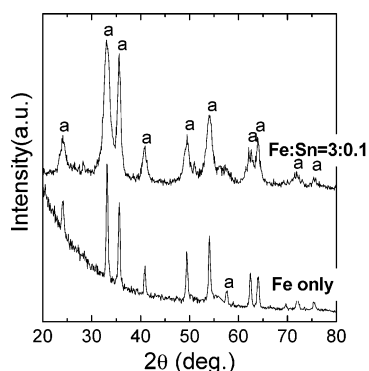


Figure 9. XRD patterns of the catalysts with Fe only and with Fe and Sn before CCVD. The peak marked by “a” corresponds to Fe_2O_3 .

of Fe (namely, Fe/In/Sn = 3:3:0.1), fewer carbon nanocoils were seen and their coil diameters were found to be larger (above 500 nm in most carbon nanocoils) than those grown from the catalysts with lower compositions of In. Further increasing the composition of In (Fe/In/Sn = 3:9:0.1), the catalyst did not grow carbon nanocoils, as seen in Figure 8e.

D. Roles of In. To discuss the roles of In in detail, the XRD patterns of the catalysts with various In compositions after CCVD were measured; these patterns are shown in Figure 10. When In is not included, the XRD patterns of graphite (marked by “d” in Figure 10) and Fe_3C (marked by “e”) were seen, the same as that when Sn is not included but In is (in Figure 5). The XRD pattern of Fe_3C is broadened when a small amount of In is included in the catalyst (Fe/In/Sn = 3:0.3:0.1 ($y = 0.3$) and 3:1:0.1 ($y = 1$)). This means that the crystal size of Fe_3C became smaller than that when In is not included. The cause of this reduction may also be because In_2O_3 compressed Fe_2O_3 and reduced its crystalline size before CCVD.

As the composition of In increased up to Fe/In/Sn = 3:3:0.1, the XRD pattern of Fe_3C became sharper again compared to that when Fe/In/Sn = 3:0.3:0.1 and 3:1:0.1 (especially see the peaks at $2\theta = 38^\circ$ and 44° in the inset of Figure 10). Moreover, the peak at $2\theta = 40^\circ$, representing Fe–In–Sn–C (marked by “f”), is visible. These show that In

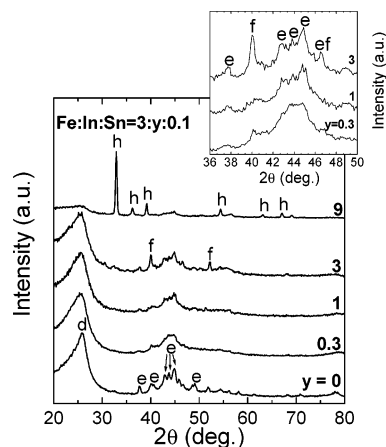


Figure 10. XRD patterns of the catalysts with various compositions of In after CCVD. The peaks marked by “d”, “e”, “f”, and “h” correspond to graphite, Fe_3C , Fe–In–Sn–C, and In, respectively. The inset shows the enlarged XRD patterns of the catalysts with the composition ratios Fe/In/Sn = 3:0.3:0.1, 3:1:0.1, and 3:3:0.1 after CCVD.

induced the crystallization of Fe_3C and Fe–In–Sn–C in such a large In composition. It is considered that this crystallization made active catalyst particles larger and consequently grew carbon nanocoils with larger coil diameters when Fe/In/Sn = 3:3:0.1. However, when catalyst particles become too large, the activity of catalyst particles may be lowered at the same time. This is probably the reason that the yield of carbon nanocoils dropped when Fe/In/Sn = 3:3:0.1. When the composition of In is increased to 300% of Fe (Fe/In/Sn = 3:9:0.1), the XRD pattern of In (marked by “h”) is seen after CCVD. This In was liquid during CCVD and reduces the activity of catalyst particles,¹² resulting in no growth of carbon nanocoils.

From the discussion above, it seems that In may adjust the crystalline size of Fe_3C and $\text{Fe}_3\text{In}_{1-m}\text{Sn}_m\text{C}_n$. By including In in the catalysts with appropriate composition (in the case of this study, this was between 10% and 33% relative to Fe composition), the crystalline sizes of Fe_3C and $\text{Fe}_3\text{In}_{1-m}\text{Sn}_m\text{C}_n$ were reduced so that the catalyst particles absorb enough carbon atoms to grow carbon nanocoils in high yield with the CCVD conditions used in this study. On the other hand, if the composition of In is too large, the crystalline sizes of these carbides also increases, and the catalyst particle cannot absorb enough carbon atoms to grow carbon nanocoils. As a result, the yield of carbon nanocoils is dropped when the catalyst with larger In composition is used.

However, when only In is included in the catalyst, it seemed that In played little role, as seen from Figure 4a. In Figure 4a, there were no carbon nanocoils and only a few carbon fibers were seen. In this case, it is considered that most of the In_2O_3 was reduced and In metal, which was produced by the reduction of In_2O_3 , disappeared before the formation of Fe_3C during CCVD. As a result, the migration of Fe_3C occurred during the CCVD process, and Fe_3C could not absorb enough carbon atoms to grow carbon fibers. The reason that a few thin carbon fibers were seen in Figure 4a may be because In_2O_3 remained during the formation of Fe_3C at the part of the catalyst where the carbon fibers were grown, and there it played its role.

V. Summary

Fe–In–Sn–O powder catalysts have been developed for the mass production of carbon nanocoils by using a coprecipitation technique, and these powder catalysts have been found to have the same ability as Fe/ITO thin film catalysts to grow carbon

nanocoils. The optimum composition of In and Sn have been found to be between 10 and 33% and below 3.3% (but not zero) relative to Fe composition, respectively. The roles of In and Sn in the catalysts have also been discussed by changing the compositions of Sn and In independently. Only with In_2O_3 and SnO_2 were neither carbon nanocoils nor carbon fibers grown. Therefore, it was found that Fe was required to grow carbon nanocoils and fibers. However, Fe_2O_3 by itself could not grow both carbon nanocoils and fibers, due to the size of Fe_2O_3 particles produced in this study. It has been found in this study that Sn was required to grow carbon nanocoils, and the composition of Sn should be small to grow carbon nanocoils in high yield. On the other hand, In increased the yield of carbon nanocoils by adjusting the crystalline sizes of Fe_2O_3 and SnO_2 . In and Sn also played a role in controlling the coil diameters by changing the crystal size of active catalyst particles in accordance with its compositions. The powder catalysts developed in this study can be used for the gas-phase growth of carbon nanocoils. In gas-phase growth, the powder catalyst must be supplied to the reactor continuously and kept in the reactor long enough to grow carbon nanocoils. Therefore, the development of powder catalysts for the growth of carbon nanocoils is a big step toward the mass production of carbon nanocoils.

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