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Application of Homogeneously Precipitated Nanosized Fe-Doped Alumina Powders to Carbon Nanotube Growth

Yasemin Çelik and Ender Suvaci*†
Department of Materials Science and Engineering, Anadolu University, 26480 Eskisehir, Turkey

Emmanuel Flahaut,† Alicia Weibel,† and Alain Peigney†‡
†Université de Toulouse, UPS, INP, Institut Carnot Cirimat, 118, route de Narbonne, F-31062 Toulouse cedex 9, France
‡CNRS, Institut Carnot Cirimat, F-31062 Toulouse, France

Homogeneous precipitation of hydroxides was investigated as an alternative method to synthesize Fe-doped aluminium oxide ($\alpha$-$\text{Al}_2\text{O}_3$) particles over which carbon nanotubes (CNTs) were grown via a catalytic chemical vapor deposition (CCVD) method. Performance of the homogeneously precipitated particles for CNT growth was quantitatively compared with that of the combustion-synthesized ones. The main advantage of the homogeneous precipitation of hydroxides and subsequent calcination process against to the combustion synthesis and other commonly practiced chemical routes is the ability to tailor the Fe-doped $\alpha$-$\text{Al}_2\text{O}_3$ precursor powder characteristics such as size and specific surface area (SSA) without requiring any milling step and also to control the phase composition of the oxide powder with high Fe content, and subsequently the quality and quantity of CNTs during CCVD process. The particle size of the precipitated and calcined $\alpha$-$\text{Al}_2\text{O}_3$-Fe$_2$O$_3$ powders varies between ~50 and 400 nm for 5–10 cat.% Fe-containing systems. The monodispersed particle size distribution and optimum phase composition of the homogeneously precipitated powders, particularly for a 10 cat.% Fe content in the starting oxide, and their much higher SSA than similar materials prepared by other chemical routes lead to production of high amounts of good quality CNTs.

1. Introduction

Carbon nanotubes (CNTs) are very promising materials in the field of nanotechnology due to their unique and exceptional properties. Therefore, they can find many applications, such as in electronic devices and their incorporation in polymer–matrix, metal–matrix, or ceramic–matrix composites. The obtained nanocomposites generally exhibit improved electrical and/or mechanical properties. The difficulty to prepare a nanocomposite is to achieve a homogeneous dispersion of the CNTs in the matrix.

Mechanical mixing and chemical methods are the common approaches that have been utilized for dispersion of CNTs. Both of these methods allow to select the type and purity of CNTs before the dispersion process. However, such methods bring some potential hazard issues due to handling free CNTs. The mixing of CNTs with the ceramic powders by commilling processing requires long times and usually damages the CNTs and aggressive chemical functionalization may introduce structural defects in nanotubes. An alternative to these methods is synthesis of CNTs on the surface of ceramic particles. Peigney et al. have developed a catalytic route for the in situ formation of CNTs over a composite Fe–$\alpha$-$\text{Al}_2\text{O}_3$ powder by reduction of an alumina–hematite solid solution powder in $\text{H}_2$–$\text{CH}_4$ atmosphere. This simple and scalable technique can be applied to a wide range of matrices and provides a very homogeneous dispersion of CNTs in the CNT–Fe–$\alpha$-$\text{Al}_2\text{O}_3$ nanocomposite powder, while avoiding the hazardous effect of free CNTs. Previous studies showed that, in order to obtain a noteworthy amount of CNTs with a good quality in the nanocomposite powder system, the starting oxide powder should be crystallized in the stable, monophased $\alpha$-form (Fe-doped aluminum oxide ($\alpha$-$\text{Al}_2\text{O}_3$–Fe$_x$O$_y$)) and have a very high specific surface area (SSA). Moreover, increasing Fe content in the starting oxide powder provides more catalytic particles available for CNTs growth. However, $\text{Fe}_2\text{O}_3$ (hematite) phase segregation, which results in the formation of carbon nanofibers (CNFs), should be avoided in the catalytic materials to be utilized for CNTs synthesis, although $\alpha$-$\text{Fe}_2\text{O}_3$ may lead to smaller particle-sized corundum ($\alpha$-$\text{Al}_2\text{O}_3$) by lowering the $\gamma$ to $\alpha$-$\text{Al}_2\text{O}_3$ transformation temperature. In previous works, the alumina–hematite starting powders for CNT synthesis have been mostly prepared by the mixed-oxalate, oxinate, and combustion routes with maximum Fe content of alumina ≤10 cat.% (i.e., $x \leq 0.1$ in $\text{Al}_{2-x}\text{Fe}_x\text{O}_3$). Unfortunately, the reported SSA values for the calcined $\alpha$-$\text{Al}_2\text{O}_3$–Fe$_x$O$_y$ powders prepared by these methods are relatively low ($< 10 \text{ m}^2/\text{g}$), which is a limiting factor for the production of large amount of CNTs over the Fe–$\alpha$-$\text{Al}_2\text{O}_3$ composite powders. Consequently, the synthesis of monophased $\alpha$-$\text{Al}_2\text{O}_3$–Fe$_x$O$_y$ powders with high SSA (i.e., $> 10 \text{ m}^2/\text{g}$) remains a challenge in order to obtain higher amount of good quality in situ synthesized CNTs over alumina matrix nanocomposite powders.

Homogeneous precipitation from aqueous salt solutions in the presence of a precipitating agent has been demonstrated as a simple and effective method for the production of metal hydroxide particles with controllable size and shape. The slow and uniform release of the precipitating agent in the reaction mixture allows production of dense and pure particles with uniform size distribution as well as tailorability of the surface area. The research objective of this study was to investigate the homogeneous precipitation of hydroxides as an alternative method for the preparation of Fe-doped alumina powders ($\alpha$-$\text{Al}_{1-x}\text{Fe}_x\text{O}_3$, $x \leq 0.1$) for the CNTs–Fe–$\alpha$-$\text{Al}_2\text{O}_3$ nanocomposite powder manufacturing.
II. Experimental Procedure

(1) Preparation of \( \alpha \)-Al\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) Powders

In this study, aqueous solutions of aluminum sulfate octadecahydrate (Al\(_2\)(SO\(_4\))\(_3\)·18H\(_2\)O, Merck (Darmstadt, Germany), extra pure) and iron(III) nitrate nonahydrate (Fe(NO\(_3\))\(_3\)·9H\(_2\)O, Merck, GR for analysis) were prepared with varying molarities depending on aluminum and iron fractions in the target solid solutions. 0.05M Al\(_2\)(SO\(_4\))\(_3\)·18H\(_2\)O and required amount of Fe(NO\(_3\))\(_3\)·9H\(_2\)O were dissolved in distilled water separately and then mixed together in a beaker. pH was decreased to 2.0 by addition of 5 wt.% HNO\(_3\) aqueous solution. The solution was heated while it was being stirred at ~600 rpm. When the temperature of the solution reached 70°C, hexamethylene tetramine (C\(_6\)H\(_{12}\)N\(_2\), HMT) was added and some turbidity, indicating the formation of particles, was immediately observed in the solution. The system was heated to 90°C for the complete activation of HMT. After stirring the suspension for 1.5 h at 90°C, the supernatant was removed by centrifugation; this step was repeated five times by refreshing the distilled water. The powders were then dried in a freeze-dryer. Thermogravimetric analysis and differential thermal analysis (DTA) were performed to determine the calcination temperature of the as-synthesized powders to obtain a stable \( \alpha \)-phase. Accordingly, the powders were heated in laboratory air at 5°C/min up to 1000°C ≤ T ≤ 1070°C. They were held at these temperatures for 1–60 min. The amount of the powder that was obtained after calcination is ~0.5 g for each batch. Calcined solid solutions were denoted as xFeTyZt, where x, y, and z refer to the cationic percent of Fe in the Al\(_{2-x}\)Fe\(_{y}\)O\(_3\) (x = 0.05, 0.07, and 0.10), calcination temperature (°C), and calcination time (minute) of the starting oxide powders, respectively.

In order to compare efficiency of the homogeneously precipitated powders for CNTs synthesis, Al\(_1.8\)Fe\(_0.2\)O\(_3\) (10 cat.% Fe-doped) powder was also produced by combustion route, which was described in detail by Cordier et al.\(^{13}\) In this process, the required proportion of aluminum nitrate nonahydrate (Al(NO\(_3\))\(_3\)·9H\(_2\)O, Merck, extra pure) and iron nitrate nonahydrate (Fe(NO\(_3\))\(_3\)·9H\(_2\)O, Merck, GR for analysis) were dissolved in distilled water in a Pyrex\(_b\) beaker. A mixture of citric acid and urea (75% citric acid and 25% urea) was used as fuel, in a quantity equal to twice the stoichiometric ratio.\(^{13}\) The required amount of citric acid and urea were dissolved in distilled water and then added into the nitrate solution. The solution was stirred at 600 rpm and ca. 120°C for 1 h. The Pyrex\(_b\) beaker was then placed in a preheated furnace, at 550°C, and kept there for at least 20 min. The as-synthesized amorphous powder was subjected to two-stage calcination process: it was first heated at 5°C/min up to 600°C, 1.5 h of dwell time in order to remove the residual carbon and then at 15°C/min up to 1100°C, 20 min of dwell time to obtain the \( \alpha \)-phase. It is possible to produce up to 4 g of calcined powder for each batch with the conditions utilized in this study. After calcination, the powder (~25 g of batch) was attrition milled at 250 rpm for 4 h in distilled water by using ~480 g of yttria-stabilized ZrO\(_2\) balls, 3 mm in diameter. Carbon content and attrition milled Al\(_1.8\)Fe\(_0.2\)O\(_3\) solid solution powder obtained by the combustion route is denoted as CS throughout the text.

(2) Production of CNT–Fe–Al\(_2\)O\(_3\) Nanocomposite Powders

The prepared powders were placed in alumina boats in the middle of a catalytic chemical vapor deposition (CCVD) chamber and then reduced in H\(_2\)-CH\(_3\)OH gas mixture (82 mol% H\(_2\) as reducing gas and 18 mol% CH\(_3\)OH as carbon source) at 1000°C with a heating and cooling rate of 5°C/min (no dwell) to produce CNTs–Fe–Al\(_2\)O\(_3\) nanocomposite powders.\(^{5,10}\) These nanocomposite powders are presented with an “R” at the beginning of the initial code of the sample, i.e., R-wFeTyZt or R-CS.

(3) Characterization

To determine the temperature of the exothermic transformation from the cubic phase to the stable \( \alpha \)-form, DTA were performed in air up to 1200°C with a heating rate of 10°C/min on the homogeneously precipitated powders. Phase analyses of the powders were performed by XRD (Rigaku Rint 2200, Tokyo, Japan) with CuK\(_\alpha\) radiation. To get additional information about the substitution of Al\(^{3+}\) by Fe\(^{3+}\) cations as a function of Fe content and calcination temperature and/or time, the cell parameters were determined from the XRD data using silicon as a reference standard. The morphology of the as-synthesized and calcined powders was examined by field-emission-gun scanning electron microscopy (FESEM, Zeiss Supra 50 VP, Oberkochen, Germany). The SSA of the Al\(_{2-x}\)Fe\(_y\)O\(_3\) powders (S\(_p\)) was measured by Brunauer–Emmett–Teller (BET) method (Micromeritics FlowSorb II 2300, Micromeritics Instrument Corporation, Norcross, GA) using N\(_2\) adsorption at liquid N\(_2\) temperature. The accuracy of the measurements is estimated to be ±3%. Effects of the calcination temperature and time on the SSA of the obtained \( \alpha \)-Al\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) powders and role of the SSA of these powders on CNTs synthesis were investigated. In addition to BET, the crystallite size of the \( \alpha \)-Al\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) powders were determined according to Scherrer’s equation\(^{17}\) via an X-ray based calculation and the corresponding SSA values were calculated assuming the particles as equivalent spheres. In the calculations, (01–12) peak of corundum was utilized as reference peak while (111) peak of silicon was used for correction as internal standard.

The CNTs–Fe–Al\(_2\)O\(_3\) nanocomposite powders were characterized by FESEM (Jeol JSM 6700F, Tokyo, Japan). Carbon content analysis and SSA measurements were carried out in order to get quantitative data about CNTs synthesis efficiency. The carbon content (C\(_w\)) of the nanocomposites, which shows the amount of carbon species deposited during CCVD, was determined by flash combustion method with an accuracy of ±2%. The SSA of the CNTs–Fe–Al\(_2\)O\(_3\) nanocomposite powders (S\(_w\)) was measured by the BET method. Then, the nanocomposites were oxidized at 900°C for 2 h in order to remove all carbon species and the SSA of the oxidized powders (S\(_o\)) was measured. These results were then used for calculating the parameters representing the quantity (AS, ΔS = S\(_o\)–S\(_w\)) and the quality (ΔS/C\(_w\)) of the CNTs.\(^{6}\) The CNTs–Fe–Al\(_2\)O\(_3\) nanocomposite powders were also characterized by Raman spectroscopy and transmission electron microscopy (TEM). The Raman spectra were recorded at 632.82 nm and 7 mW using a DilorXY (JY Instruments, NJ) micro-Raman set-up with back-scattering geometry. TEM analyses were performed on the CNTs–Fe–Al\(_2\)O\(_3\) nanocomposite powders with a Jeol JSM 1011 operated at 100 kV. The samples were prepared by sonicking the nanocomposite powder in ethanol and then dropping that suspension on a copper grid coated with a lacey carbon film.

III. Results

(1) Oxide Powders Produced by Homogeneous Precipitation and Calcination

DTA results (not shown) revealed that the transition from cubic to corundum phase occurs at 1105°C, 1070°C, and 1050°C for the powders containing 5, 7, and 10 cat.% Fe, respectively. The decrease in the transformation temperature into stable form with increasing Fe content is in agreement with the previous studies.\(^{10,11}\) Accordingly, to complete the transformation of the precipitated powders into the corundum phase as well as maintaining high SSA, the powders were heat treated at 10°C/5°C below these transformation temperatures for some period of time (Table I).

Figure 1(a) shows the effect of Fe content on the phase development of 5Fe1050T60t, 7Fe1050T60t, and 10Fe1050T60t powders. A shift of the main peak positions toward lower 2θ values with respect to pure Al\(_2\)O\(_3\) indicates substitution of Al\(^{3+}\) cations by Fe\(^{3+}\) in the corundum lattice to form an \( \alpha \)-Al\(_{2-x}\)Fe\(_y\)O\(_3\) solid solution. Furthermore, this shift increases with increasing Fe content. Besides the \( \alpha \)-Al\(_{2-x}\)Fe\(_y\)O\(_3\) peaks, hematite-rich secondary phase is detected for the 10Fe1050T60t powder. As the Fe content is decreased to 7 and 5 cat.%,
The cell parameter calculations (Table II) showed that the $c$ parameter of 10 cat.% Fe-doped powders increased with increasing calcination time up to 30 min, indicating substitution of more Al$^{3+}$ cations by Fe$^{3+}$, as in agreement with the shift observed in the XRD patterns. The $c$ parameters for 10Fe1000T30t and 10Fe1050T60t are similar. This suggests that the amount of Fe$_2$O$_3$ dissolved in the Fe-doped Al$_2$O$_3$ matrix reaches a saturation value after calcination at 1000°C for 30 min. However, further analysis is required to test this hypothesis. The 10Fe1000T1t powder contains some transition Al$_2$O$_3$ phase, therefore, cell parameter measurements may not give reliable results. The 5Fe1070T60t powder has a lower $c$ parameter than the 10 cat.% Fe-doped powders, due to lower Fe content. The $c$ parameter of the CS powder is higher than homogeneously precipitated powders as expected, because no $\alpha$-Fe$_2$O$_3$ peak (i.e., all Fe is distributed in the alpha alumina lattice) was detected in its XRD pattern. The higher solubility of iron in alumina for the $\alpha$-Fe$_2$O$_3$ peaks are observed. However, broad peaks of transition ($\gamma$ or $\theta$) Al$_2$O$_3$ phase appears in this case, probably due to insufficient calcination temperature and/or time (Fig. 1(a)). Increasing the calcination temperature of 5 cat.% Fe-doped powder to 1070°C allows obtaining a monophased $\alpha$-Al$_2$Fe$_{0.1}$O$_3$ powder with neither transitional alumina- nor hematite-rich phases (Fig. 1(b)), while $\alpha$-Fe$_2$O$_3$ peak was detected in 7 cat.% Fe-doped powder when its calcination temperature was increased to 1060°C. Figure 1(c) shows the XRD patterns of 10 cat.% Fe-doped powders, which were calcined at 1000°C for 1 and 30 min. It is observed that both powders contain hematite-rich secondary phase. Additionally, the powder calcined for 1 min (10Fe1000T1t) contains transitional Al$_2$O$_3$ phase. The XRD pattern of the CS powder (10 cat.% Fe-doped) synthesized by the combustion route and calcined at 1100°C, 20 min (Fig. 1(d)), revealed only the peaks of $\alpha$-Al$_{1.8}$Fe$_{0.2}$O$_3$.

Fig. 1. XRD patterns of homogeneously precipitated Al$_{2.2}$Fe$_2$O$_3$ powders showing the effect of (a) Fe content (the powders were calcined at 1050°C for 60 min), (b) calcination temperature (5Fe1050T60t and 5Fe1070T60t), and (c) calcination time (10Fe1000T1t and 10Fe1000T30t) on the phase development. (d) XRD pattern of CS powder (combustion-synthesized Al$_{1.8}$Fe$_{0.2}$O$_3$ powder calcined at 1100°C for 20 min and then attrition milled).
The SSA (S₅, Table I) of the 10 cat.% Fe-doped Al₂O₃ powders decreases with increasing calcination temperature and/or time (38.7, 19.1, and 12.9 m²/g for 10Fe1000T1t, 10Fe1000T30t, and 10Fe1050T60t, respectively). The exceptionally high S₅ value of the 10Fe1000T1t arises probably from the presence of transitional Al₂O₃ phase. Surprisingly, it is observed that the SSA of the Al₁₋ₓFeₓO₃ powders increases with simultaneously increasing the calcination temperature and decreasing the Fe content (12.9, 29.3, and 34.0 m²/g for 10Fe1050T60t, 7Fe1060T60t, and 5Fe1070T60t, respectively). These results can be attributed to the reduction in the Fe content, which shifts the crystallization of the solid solution toward higher temperatures. The SSA measurements of the 5 and 10 cat.% Fe-doped alumina powders, which were calcined at 1050°C for 60 min, show that the SSA increases with decreasing Fe content. The SSA values of 10Fe1050T60t and 5Fe1050T60t powders are 12.9 and 31.9 m²/g, respectively. The SSA of CS samples decreases with increasing calcination temperature and/or time as in agreement with the SSA values (38.7, 19.1, and 12.9 m²/g, respectively) measured by BET method. The difference between the calculated and measured SSA values of the 10Fe1000T30t and 10Fe1050T60t probably arises from neck formation (i.e., the first stage of sintering) between particles during the calcination process, which causes a lower SSA in BET. The crystallite size of 5Fe1070T60t (39.7 nm) is smaller than that of 10 cat.% Fe-doped powders, although it was calcined at a higher temperature. The calculated SSA (37.3 m²/g) of the 5Fe1070T60t is very close to the measured value (34.0 m²/g).

The SEM image of the 10Fe1000T30t powder (Fig. 2(a)) shows the spherical, nanosized Fe-doped Al₂O₃ particles that range between ~50 and 200 nm in diameter, more or less aggregated due to partial sintering during the calcination process. Because the primary particle size was small enough, no subsequent milling step was applied to the calcined homogeneously precipitated powders. The SEM image of the CS powder (Fig. 2(b)) reveals a wider particle size distribution, from 100 nm to ~1.5 μm. The milling parameters used for this powder seem to be a good compromise to obtain a large SSA (32.9 m²/g).

**Table II. Cell Parameter Values (nm) of Calcined Fe-Doped Alumina Powders**

<table>
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<th>d</th>
<th>e</th>
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<tr>
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<td>1.3028</td>
<td>1.3042</td>
<td>1.3044</td>
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<td>Hematite</td>
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<td>1.3028</td>
<td>1.3042</td>
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</tbody>
</table>

Data for corundum and hematite were taken from JCPDS Files No. 10-173 and No. 33-664, respectively.

CS powder could arise from the faster reaction kinetics during combustion synthesis, which allows the production of a metastable solid solution.

The SEM image of the 10Fe1000T30t powder (Fig. 2(a)) shows the spherical, nanosized Fe-doped Al₂O₃ particles that range between ~50 and 200 nm in diameter, more or less aggregated due to partial sintering during the calcination process. Because the primary particle size was small enough, no subsequent milling step was applied to the calcined homogeneously precipitated powders. The SEM image of the CS powder (Fig. 2(b)) reveals a wider particle size distribution, from 100 nm to ~1.5 μm. The milling parameters used for this powder seem to be a good compromise to obtain a large SSA (32.9 m²/g).

(2) CNTs–Fe–Al₂O₃ Nanocomposite Powders

The SEM images of the CNTs–Fe–Al₂O₃ nanocomposite powders show the CNTs and/or the CNTs bundles covering the matrix particles evenly (Fig. 3). In the 5Fe1070T60t system (Fig. 3(a) and (b)), CNTs are either individual or in very small diameter bundles and the quantity remains low in spite of the high SSA of the starting powder. There is a clear increase in the amount of CNTs, and in the diameter of CNTs bundles, as the Fe content in the starting oxide increases from 5 to 7 cat.% and then to 10 cat.% (Figs. 3(a), (c), and (e)). No CNF was detected in the R–5Fe1070T60t (Figs. 3(a) and (b)), while a few CNFs were observed in the R–7Fe1060T60t (Fig. 3(d)) and R–10Fe1000T30t (Fig. 3(e)) systems. Higher amounts of CNFs and carbon nanoribbons (CNRs) were observed both in the R–7Fe1050T60t (Fig. 3(f)) and R–10Fe1050T60t (Fig. 3(h)). In the former system (Fig. 3(g)), CNFs and CNRs form large aggregates in some regions of the powder. Similar to the R–5Fe1070T60t system, no CNF was detected in the SEM micrograph of the R–CS powder (Fig. 4).

The SEM observations provide only qualitative information about the CNTs and/or other forms of carbon such as CNFs in the nanocomposites. Therefore, to analyze such characteristics quantitatively, carbon content (Cᵣ) analyses and SSA measurements were performed on the following nanocomposite powder systems: R–5Fe1070T60t, R–7Fe1070T60t, R–10Fe1000T1t, R–10Fe1000T30t, R–10Fe1050T60t, and R–CS. The Cᵣ analyses results, which range between 7.3 and 13.9 wt.%, are summarized in Table I.

The SSA of the nanocomposite powders (S₅, Table I) increased severely after being subjected to the CCVD. The SSA values of the R–10Fe1000T1t, R–10Fe1000T30t, and R–5Fe1070T60t powders after elimination all the carbon species via oxidation (31.1, 15.1, and 30.0 m²/g, respectively) are lower than the initial surface area of the corresponding starting oxides (S₅; 38.7, 19.1, and 34.0 m²/g, respectively). The SSA of R–CS
after oxidation (11.0 m\(^2\)/g) is three times smaller than that of the corresponding starting oxide powder (32.9 m\(^2\)/g).

When \(S_a\) is subtracted from \(S_m\), the obtained \(\Delta S\) value (Table I) shows the SSA of carbon per gram of the nanocomposite powder, which corresponds mainly to the surface area of CNTs, because it is considered that other forms of carbon (particularly CNFs and CNRs) are in minor quantity and/or have much smaller SSA than CNTs.\(^6\) Therefore, \(\Delta S\) value represents

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**Fig. 3.** FEG-SEM micrographs of the carbon nanotube-Fe–Al\(_2\)O\(_3\) nanocomposite powders showing the carbonaceous materials formed over the powders during the catalytic chemical vapor deposition process: (a,b) R–5Fe1070T60t, (c,d) R–7Fe1060T60t, (e,f) R–10Fe1000T30t, (g) R–10Fe1000T1t, and (h) R–10Fe1050T60t. Arrows point to carbon nanofibers (CNF) and carbon nanoribbons (CNR).
the quantity of CNTs or CNT bundles in the nanocomposite powder.6 ΔS calculations revealed that among the homogeneously precipitated powders, the highest CNTs quantities were achieved with the 10 cat.% Fe-doped powders, especially for the R–10Fe1000T30t (30.9 m²/g). This result is in agreement with the SEM observations of the nanocomposite powders (Figs. 3(a), (c), and (e)). It was also observed that the ΔS value of the R–CS system (37.6 m²/g) is higher than the nanocomposites prepared from the homogeneously precipitated powders.

ΔS/Cn (Table I), which represents the CNTs quality, corresponds to the SSA of carbon if it is assumed that the SSA of the other species remains almost constant during the nanocomposite oxidation.9 Higher ΔS/Cn value means smaller average tube diameter and/or tubes with fewer walls and/or more carbon in tubular form.5 In homogeneously precipitated powder systems, this parameter ranges from 143–356 m²/g, including the experimental uncertainty. The highest ΔS/Cn value among these systems is calculated as 329 ± 27 m²/g for the R–10Fe1000T30t. For the R–CS system, this CNTs quality value is 459 ± 31 m²/g (Table I).

Figure 5 shows the Raman spectra of the R–10Fe1000T30t and R–CS nanocomposite powder systems. The intense bands observed in the low-frequency range (100–300 cm⁻¹) of the Raman spectrum are assigned to the radial breathing modes (RBM),18 which correspond to the atomic vibration of C atoms in the radial direction, as if the tube was breathing.19 Each RBM signs the presence of a specific tube diameter in the sample according to the relations between the RBM frequency and the tube diameter.18 In Fig. 5(a), the RBM peaks are observed for both samples, suggesting that at least a part of the CNTs have only few walls. The diameters, which are calculated from the frequency of the RBM peaks,20 are in the ranges 1.02–1.76 and 0.83–1.83 nm for the R–10Fe1000T30t and R–CS nanocomposite powders, respectively. However, it should be noted that it is not possible to scan all the diameters of the CNT population in the sample with only one wavelength because a specific excitation wavelength enhances the signal for only some of the CNTs.21 The high-frequency region of the Raman spectra shows the so-called D-band (∼1320 cm⁻¹) and the G-band (∼1586 cm⁻¹) (Fig. 5(b)). The D-band to G-band intensity ratio (ID/IG) is 26% for the R–10Fe1000T30t and 35% for the R–CS nanocomposite powder. D-band is induced from disorder in graphitic materials and the G-band originates from the tangential vibrations of sp² carbon atoms along the tube axis.19 The ID/IG ratio is commonly used to characterize different kinds of disordered sp² carbon (e.g., carbon fibers)22 and an increasing ID/IG value is generally attributed to the presence of more structural defects. Therefore, the measured ID/IG values suggest that the R–10Fe1000T30t system contains fewer amounts of undesired carbon phases (CNFs or CNRs and/or disorganized carbon) with respect to the R–CS.

TEM images of the R–10Fe1000T30t and R–CS nanocomposite powders (Fig. 6) show that both samples contain isolated CNTs, 1–5 nm in diameter and CNTs bundles, about 10 nm in diameter, i.e. composed of only few CNTs. Some CNFs have been marginally detected in the R–10Fe1000T30t, as in agreement with the SEM observations, but also in the R–CS for which such a carbon form has not been evidenced by SEM, but suggested by the Raman spectroscopy.
homogeneously precipitated powders, only the $\text{Fe}_3\text{O}_4$ phase in the starting oxide powder. Peigney et al. related with higher quantity of hematite-rich secondary phase in the R–10Fe$_{1050}$T$_{60t}$, the higher CNFs and CNRs content is correlated with higher quantity of hematite-rich secondary phase in the nanocomposites prepared from the Fe-doped combustion-synthesized Al$_2$O$_3$ powder (CS). Arrows indicate the diameters of individual CNTs, large Fe catalyst nanoparticles and carbon nanofibers.

**IV. Discussion**

The XRD pattern of the CS powder synthesized by the combustion route and calcined at 1100°C, 20 min showed that this powder crystallized in the monophased $\alpha$-Al$_2$Fe$_{0.2}$O$_3$ form; however, a complete transformation into the $\alpha$-form without any transition Al$_2$O$_3$ and/or hematite-rich secondary phase could not be achieved for 7 and 10 cat.% Fe-doped alumina powders prepared by homogeneous precipitation of hydroxides even after calcination. Muan and Gee$^7$ reported that $\sim$10 mol% hematite was the maximum dopant amount for retaining a monophased powder at temperatures below 1318°C. The XRD data obtained in the present study suggest that this maximum amount may vary depending on the synthesis route, which is in agreement with the previous studies.$^6$-$^9$,12,13 Among the homogeneously precipitated powders, only the 5Fe1070T60t system is free from the $\alpha$-Fe$_2$O$_3$ and transitional Al$_2$O$_3$ phases. No CNF was detected in the SEM analysis of the corresponding nanocomposite powder (R–5Fe1070T60t). A few CNFs were detected in the R–7Fe1060T60t and R–10Fe1000T30t nanocomposites, the corresponding oxides of which contain low amount of hematite-rich secondary phase. The amount of defective structures (CNFs and CNRs) in the nanocomposites increased, when the corresponding oxides contained higher amount of $\alpha$-Fe$_3$O$_4$ and/or transitional Al$_2$O$_3$ phase. For the R–10Fe1050T60t, the higher CNFs and CNRs content is correlated with higher quantity of hematite-rich secondary phase in the starting oxide powder. Peigney et al.$^7$ reported that $\alpha$-Fe$_3$O$_4$ phase segregation causes formation of too large Fe nanoparticles and consequently, result in the formation of CNFs. For the R–10Fe1000T11t, large aggregates of CNFs and CNRs could have been catalyzed by large Fe nanoparticles (diameter > 5 nm) formed probably during the CCVD process due to the presence of transitional alumina in the starting oxide powder. Laurent et al.$^7$ reported that larger catalyst nanoparticles were formed in the presence of amorphous or transition compounds due to coalescence of very small nanoparticles during the CCVD process which then leads to formation of inactive catalysts or CNFs, as in agreement with the results obtained in the present study.

The amount of carbon deposited during the CCVD is prone to increase with increasing Fe content, because higher amount of Fe means more catalytic nanoparticles.$^8$ Moreover, it has been shown that Fe nanoparticles are formed both within and at the surface of the alumina grains, and only the nanoparticles located at the surface immediately act as catalyst for the formation of CNTs.$^9$ Therefore, a very high SSA is desired, because it enhances the proportion of Fe nanoparticles located at the particle surface and thus increases the quantity of CNTs.$^3$ However, the $C_n$ values do not show a clear correlation with neither the Fe content nor the SSA values of the oxide powders ($S_i$) in the present work. The SEM results suggest that the high carbon content in the R–10Fe1000T11t (13.9 wt.%) and R–10Fe1000T60t (12.4 wt.%) can be attributed to the presence of significant amounts of CNFs and CNRs in these two powders because one of these filaments contains much more carbon than that of a CNT or a bundle of CNTs can contain.

Because the $C_n$ value includes all the carbon species deposited during the CCVD, it would be more meaningful to interpret this value by combining it with the SSA of the nanocomposite powder in order to extract quantitative information about only CNTs. The severe increase in the SSA of the powders after being subjected to the CCVD ($S_n$, Table I) indicates that a considerable amount of the carbon was deposited in the form of CNTs. The carbon is deposited especially in the form of CNTs upon the CCVD as long as the requirements for a successful CNTs synthesis are satisfied.$^7$–$^9$ The contribution of Fe and Fe$_x$C particles, which form at the surface of the matrix grains, to the increase in the SSA is expected to be at much smaller extent with respect to the contribution from CNTs.$^7$–$^9$ The SSA of oxidized powders are expected to be similar or slightly lower than their $S_i$ values, as reported by Laurent et al.$^7$; however, the SSA values of the R–10Fe1000T11t, R–10Fe1000T30t, and R–5Fe1070T60t powders after oxidation are lower than the initial surface area of their corresponding starting oxides. For the R–10Fe1000T11t, this could be due to crystallization of the remaining transition Al$_2$O$_3$ into the stable $\alpha$-form during the CCVD operated at 1000°C and/or during the oxidation at 900°C (local temperature is expected to be higher than 900°C due to the combustion process). Moreover, the decrease in SSA of the R–10Fe1000T30t and R–5Fe1070T60t powders may arise from the neck formation between fine particles during the CCVD and/or the oxidation treatment. The SSA of the R–CS after oxidation (11.0 m$^2$/g) is much lower than the initial SSA (32.9 m$^2$/g) of the CS powder, in comparison to the other nanocomposite and corresponding oxide powders. Because no transitional Al$_2$O$_3$ phase has been detected in the CS powder, this significant reduction in SSA may be due to sintering of the oxide particles, particularly the most reactive, i.e. the smaller ones whose the diameter is below 100 nm, during CCVD and/or oxidation. Therefore, although the maximum CNTs quantity ($\Delta S_i$ 37.6 m$^2$/g) was measured for the R–CS nanocomposite powder, this value probably includes the decrease in SSA due to sintering effect besides the SSA of CNTs and hence it may be misleading. Therefore, the quantity of CNTs could be lower than the value calculated based on the $\Delta S$ value. Moreover, the CNT quality of the R–CS system is probably much lower than that predicted $\Delta S/C_n$ value ($459 \pm 31$ m$^2$/g) due to the same reason. Therefore, $\Delta S/C_n$ is not very representative of the quality of CNTs for the R–CS. The R–10Fe1000T30t has a higher quality parameter ($\Delta S/C_n = 329 \pm 27$ m$^2$/g) than the other CNTs–Fe–Al$_2$O$_3$
nanocomposites prepared from homogeneously precipitated powders, in spite of the observation of a few CNFs in this sample. The quantity parameter was also very high ($\Delta S = 30.9 \pm 1.9$ m$^2$/g) for this sample. If these results are compared with the previously reported results,$^6$–$^9$ where the maximum achieved quality and quantity parameters were $314$ m$^2$/g and $19.6$ m$^2$/g,$^9$ respectively, it is obvious that the results obtained in this study are superior. It should be also noted that in the previous work where the best results were reported,$^5$ the SSA of the starting oxide was only $8.1$ m$^2$/g and the CCVD treatment was operated at $1050^\circ C$ ($50^\circ C$ higher than the present work). It is known that a higher temperature always favours the deposition of a higher quantity of carbon.

The Raman and TEM analyses revealed the presence of CNFs in the R-CS system, although this carbon form has not been observed by SEM. Thus, although a hematite-rich secondary phase was not revealed by XRD for the corresponding starting oxide (CS), such a phase may still exist at a content below the detection threshold of this technique and result in the production of large quantities of CNFs. Additionally, while minimizing the amount of the hematite-rich secondary phase was only $8.1$ m$^2$/g and the CCVD treatment was operated at $1050^\circ C$ ($50^\circ C$ higher than the present work). It is known that a higher temperature always favours the deposition of a higher quantity of carbon.

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Consequently, the starting oxide powder containing 10 cat.% Fe, obtained by homogeneous precipitation of hydroxide and the optimized calcination ($1000^\circ C$ for 30 min) allows synthesis of much higher quantities of CNFs ($>5$ nm) (Fig. 6(b)) which catalyze the growth of a few CNFs.

In the present work, one of the main advantages of the starting oxide powders ($x$-$\text{Al}\text{Fe}_2\text{O}_3$) prepared by the homogeneous precipitation method followed by a calcination treatment is their higher SSA ($19–34$ m$^2$/g—Table I) when compared with the catalytic materials prepared by other chemical routes, also followed by a calcination treatment ($<10$ m$^2$/g).$^6$–$^9$–$^{12}$ Therefore, there is no need for milling and subsequently no potential of contamination. As in previous works, the main key is to find the appropriate calcination treatment (temperature and time) for the starting oxide powder with as high Fe content as possible to assure its complete crystallization under the corundum form while minimizing the amount of the hematite-rich secondary phase and maximizing the SSA. The consequence is the preparation of nanocomposite powders, with a reasonable quality, i.e., only very few CNFs, as shown for the R-10Fe1000T30t nanocomposite powder, the corresponding oxide powder of which was calcined at $1000^\circ C$ for 30 min, giving a SSA of $19.1$ m$^2$/g.

V. Conclusions

The results of this study show that nanodispersed Fe-doped alumina particles ($x$-$\text{Al}_{1-x}\text{Fe}_2\text{O}_3$) produced by the homogeneous precipitation of hydroxides are viable catalytic materials for the $\text{in situ}$ synthesis of homogeneously distributed CNTs in the Fe-Al$_2$O$_3$ matrix. One of the main advantages of the homogeneous precipitation and subsequent calcination process against to the combustion synthesis and other commonly practiced chemical routes is that physical and chemical characteristics of the Fe-doped Al$_2$O$_3$ powders can be tailored, which enables one to control the quality and quantity of CNTs during CCVD process. The homogeneously precipitated powders exhibit high SSA even after calcination and hence there is no need for milling and subsequently no potential of contamination. The calcination treatments of the starting oxides with high Fe contents (7 or 10 cat.%) must be optimized (temperature and time) to keep the SSA of the powder as high as possible while limiting the phase partitioning of the corundum form. Accordingly, the monodispersed homogeneously synthesized powders, particularly that containing 10 cat.% Fe content in the starting oxide, and their much higher SSA than similar catalytic materials prepared by other chemical routes result in the $\text{in situ}$ synthesis of larger quantities of CNTs with good quality in the nanocomposite powders.

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