Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: http://oatao.univ-toulouse.fr/
Eprints ID: 10719

Identification number: DOI:10.1111/j.1151-2916.2002.tb00513.x
Official URL: http://dx.doi.org/10.1111/j.1151-2916.2002.tb00513.x

To cite this version:

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@inp-toulouse.fr
(Mg,Co)O Solid-Solution Precursors for the Large-Scale Synthesis of Carbon Nanotubes by Catalytic Chemical Vapor Deposition

Revathi R. Bacsa,† Christophe Laurent,‡ Alain Peigney,* † Thibaud Vauggien,† Emmanuel Flahaut,† Wolfgang S. Bacsa,‡ and Abel Rousset†

Laboratoire de Chemie des Matériaux Inorganiques, Centre Interuniversitaire de Recherche et d’Ingénierie des Matériaux, Université Paul-Sabatier, and Unité Mixte de Recherche Associée au Centre National de la Recherche Scientifique, 31062 Toulouse Cedex, France

Laboratoire de Physique des Solides de Toulouse, Université Paul-Sabatier, 31062 Toulouse Cedex, France

Since their discovery in 1991 by Iijima, carbon nanotubes have found potential application as electronic components, reinforcement materials, and hydrogen storage devices.1,2 Efforts are being made by various groups for the large-scale production of carbon nanotubes using chemical vapor deposition (CVD) techniques.3 Flahaut et al.4 have reported the formation of carbon nanotubes by the generation of cobalt-catalyst nanoparticles in situ from Mg1−xCoxO solid solutions. Selective reduction of the transition-metal ion can be effected, leaving the solvent to act as a combination of a matrix and a support. The nanometric particles of cobalt formed at 800°–1000°C on the surface of the oxide grain during the reduction in methane and hydrogen atmosphere catalyze the formation of carbon nanotubes. The system Mg2CoO is of particular interest because of its solubility in dilute HCl, which permits the extraction of the nanotubes from the support matrix. It is, therefore, of interest to develop inexpensive, large-scale production methods for high-surface-area Mg1−xCoxO solid-solution powders to increase catalytic activity and yield.

Solid solutions of transition-metal ions in insulating oxides have been used in the past as catalysts in dehydrogenation reactions.5 Although MgO and CoO form a series of continuous solid solutions obeying Vegards law, the multiple oxidation state of cobalt leads to the stabilization of Co3O4 unless long reaction times or high temperatures are used.6 In this context, we report results on the synthesis of (Mg,Co)O solid solutions with surface areas of the order of 30–65 m²/g using combustion synthesis and on their application for the production of single- and double-walled carbon nanotubes using catalytic decomposition of methane. The advantages of combustion synthesis are low reaction time, high-surface-area crystalline products, inexpensive reactants, and suitability for large-scale synthesis because of low-energy input requirement.

Combustion synthesis of oxides was developed by Kingsley and Patil7 for the synthesis of fine Al2O3 particles using the combustion of Al(NO3)3 with urea as fuel. The process has been used for the preparation of a variety of complex oxides.8,9 In all these preparations, the quantity of fuel used was based on calculations wherein the compositions of the redox mixtures were adjusted to give an equivalence ratio of unity (i.e., oxidant/fuel = 1). Zhang and Stangle10 studied the effect of the fuel content on the phase and surface area in the system CuO–Fe3O4 prepared by combustion synthesis. However, for the fuel contents used, a single crystalline phase could not be obtained, and increased fuel content decreased the specific surface area of the product.

In this article, we report results on the effect of varying the fuel content on the phase and microstructure of Mg1−xCoxO solid solutions. Analogous to the findings of Zhang and Stangle, we find that stoichiometric quantities of the fuel (urea in our case), as calculated in Refs. 7–9, are not sufficient for the formation of a single crystalline phase. Doubling the fuel content results in a single phase but decreases the surface area. Further increase in fuel content to 3 and 4 times the stoichiometric amount leads to higher-surface-area solid solutions until the solid solution is partially demixed to CoO-Co2O3 and Mg1−xCoxO (y < x). The presence of Co3O4 or CoO causes the reduction of the oxide solid solution at lower temperatures, thus decreasing the selectivity of the nanotube formation process.

II. Experiment Procedure

Magnesium and cobalt nitrates were mixed in the appropriate ratio. Urea was used as the fuel. The cobalt content was varied between 2.5 and 20 mol% in the solid solution. The amount of urea was varied in multiples of the stoichiometric amount. The stoichiometric amount [U] was calculated using the total oxidizing and reducing valences of the components that served as numerical coefficients for stoichiometric balance, as described by Kingsley and Patil.2 For a mixture of magnesium and cobalt nitrates, these amounts corresponded to a nitrate/urea molar ratio of 1/1.666. The variations in fuel content were denoted by 1[U], 2[U], 3[U], 4[U], and 6[U] (this corresponded to ~27%–165% of total mass). The mixture was stirred with a small amount (2–5 mL) of water at 80°C to form a clear solution. The solution was introduced into a furnace maintained at 550°C. The solution underwent dehydration and caught fire after 1.5 min, resulting in large quantities of gases. The mixture foamed and glowed to incandescence, after which it filled the reaction vessel and formed a porous mass. After 5 min the products were removed and crushed lightly to a fine powder.

1Centre Interuniversitaire de Recherche et d’Ingénierie des Matériaux.
2Laboratoire de Physique des Solides de Toulouse.
The composition and phase of the solid solutions were determined using chemical analysis and X-ray diffractometry (XRD). Lattice parameters were calculated from diffractograms with NaCl as the internal standard. Crystallite sizes were calculated from the full-width at half-maximum using the Scherrer equation. Surface areas were measured using adsorption of nitrogen at liquid-nitrogen temperature. The microstructure of the oxide was studied using scanning and transmission electron microscopies (SEM and TEM). The oxide powder was reduced in a methane and hydrogen reducing atmospheres, the diffusion of oxygen vacancies from the oxide phase increases with increasing urea content, and, above 6[U], the two phases are difficult to separate. For these compositions, XRD of the brown powder recovered from the center of the reaction vessel shows the presence of MgCoO or CoCO3. Infrared spectra confirm the presence of the carbonate ion. These results show that the solid solution is demixed at high urea contents. Measurement of lattice parameters for 0 < x < 0.2 has been conducted for solid solutions prepared using 3[U]. Figure 1(B) shows the lattice parameter as a function of x. Vegard’s law is obeyed for the range studied (0 < x < 0.2 mol), proving that complete solid solutions are formed. MgO prepared by the combustion of Mg(NO3)2 with urea has been used to determine the lattice parameter for x = 0.

Figure 2 shows the BET surface areas of the oxide solid solutions (the brown phase for starting compositions with >4[U]) as a function of the urea content in the reaction mixture. Increase in urea content to 2[U] decreases the surface area sharply, which is in accordance with the observations of Zhang and Stangle,10 who explain it to be due to the increase in the temperature of combustion, which increases the crystallite size. The increase in urea content is also required to avoid the formation of CoO. Thus, the amount of fuel required to react completely with the metal nitrates corresponds more to a fuel-rich composition rather than a stoichiometric composition of nitrate/urea for the MgO-CoO system. More probably, the simple assumption that the valence of nitrogen in the product species is zero (nitrogen gas) is not valid for our system.7

Increasing the urea content to 3[U] and 4[U] increases the surface areas of the oxide solid solutions until the appearance of the blue phase. The surface areas of the brown powder, which is the major reaction product, continue to increase with increasing urea content, whereas the blue powder has a surface area of ~ 35 m2/g, which does not vary with the fuel content. An increase in fuel contents increases the time required for combustion and the volume of the final product. For 6[U], 3 g of solid solution occupy the entire 500 mL crystallization dish at the end of the combustion.

A fuel content of 3[U] is ideal for maximum surface area before the onset of demixing of the solid solutions. The demixing of the solid solution in the system (Mg,Co)O has been widely studied.12,13 It has been proposed that, at low grain sizes and in highly reducing atmospheres, the diffusion of oxygen vacancies from phases of CoO, Co3O4, and Co2O3 occurs. Complete solid solutions are formed for 2[U] and 3[U]. When urea contents of 4[U] and greater are used, a blue powder is formed on the walls of the crystallization dish in which combustion is conducted. The main product of the reaction is the solid solution, which is brown. The quantity of the blue phase increases with increasing urea content, and, above 6[U], the two phases are difficult to separate. For these compositions, XRD of the brown powder recovered from the center of the reaction vessel shows the presence of MgCoO or CoCO3. Infrared spectra confirm the presence of the carbonate ion. These results show that the solid solution is demixed at high urea contents. Measurement of lattice parameters for 0 < x < 0.2 has been conducted for solid solutions prepared using 3[U]. Figure 1(B) shows the lattice parameter as a function of x. Vegard’s law is obeyed for the range studied (0 < x < 0.2 mol), proving that complete solid solutions are formed. MgO prepared by the combustion of Mg(NO3)2 with urea has been used to determine the lattice parameter for x = 0.

Figure 2 shows the BET surface areas of the oxide solid solutions (the brown phase for starting compositions with >4[U]) as a function of the urea content in the reaction mixture. Increase in urea content to 2[U] decreases the surface area sharply, which is in accordance with the observations of Zhang and Stangle,10 who explain it to be due to the increase in the temperature of combustion, which increases the crystallite size. The increase in urea content is also required to avoid the formation of CoO. Thus, the amount of fuel required to react completely with the metal nitrates corresponds more to a fuel-rich composition rather than a stoichiometric composition of nitrate/urea for the MgO-CoO system. More probably, the simple assumption that the valence of nitrogen in the product species is zero (nitrogen gas) is not valid for our system.7

Increasing the urea content to 3[U] and 4[U] increases the surface areas of the oxide solid solutions until the appearance of the blue phase. The surface areas of the brown powder, which is the major reaction product, continue to increase with increasing urea content, whereas the blue powder has a surface area of ~ 35 m2/g, which does not vary with the fuel content. An increase in fuel contents increases the time required for combustion and the volume of the final product. For 6[U], 3 g of solid solution occupy the entire 500 mL crystallization dish at the end of the combustion.
grain boundaries may be substantial and may result in concentration gradients because of the differences in the self-diffusion coefficients of cobalt and magnesium. This may cause the segregation of CoO in the fuel-rich compositions.

Figure 3(A) shows a TEM image of Mg$_{0.95}$Co$_{0.05}$O prepared with a fuel content of 3[U]. The particles have rectangular shape and a size distribution in the range 15–30 nm, although certain particles attain a size of 50 nm. The average grain size calculated from XRD is 30 nm. The combustion process thus produces powders with a distribution of grain sizes varying from 10 to 50 nm. The powder disperses readily in organic solvents and there is no agglomeration. Figure 3(B) shows SEM images of the porous Mg$_{0.95}$Co$_{0.05}$O solid solution after reduction in methane and hydrogen at 1000°C. Bundles of carbon nanotubes, 10–20 nm in width and >1 μm length occur. The porosity of the solid solution is maintained during reduction at 1000°C. High-resolution TEM images show that the bundles are composed of carbon nanotubes with diameters in the range 0.6–3 nm.

The BET surface areas of the solid solutions increase by a factor of 2 on reduction. In previous publications, we have shown that this increase in surface area ($\Delta S$) is principally due to the deposition of carbon, because there is little or no sintering of the solid solution under a hydrogen atmosphere. The increase in specific surface area on reduction divided by the weight of carbon nanotubes ($\Delta S/C$) is related to the yield of carbon nanotubes. Figure 4 shows a plot of $\Delta S/C$ as a function of the fuel content used during combustion for the precursor oxide Mg$_{0.8}$Co$_{0.2}$O. The yield of nanotubes continues to increase with an increase in the surface area of the precursor. However, because 4[U] and 6[U] conditions result in demixed solid solution, a fuel content of 3[U] is ideal for nanotube synthesis.

The increased yield of nanotubes with surface area of the precursor is due to an increase in the concentration of catalyst (cobalt nanoparticles) on the surface of the oxide grain. Previous experiments have shown that only nanoparticles of cobalt present on the surface of the reduced oxide grain catalyze the decomposition of methane to form nanotubes, while those present in the interior of the grain remain inactive. The decrease in nanotube yield for precursor prepared using 1[U] is due to the incomplete formation of solid solution, which results in Co$_3$O$_4$, the presence of which results in larger-diameter multiwalled tubes with lower surface area (for a given mass of carbon, the surface area decreases with increasing diameter and number of walls, assuming that the tubes are closed). The formation of carbon nanotubes is further verified by Raman spectroscopy. Figure 5 shows the Raman spectra of carbon nanotubes formed by the reduction of Mg$_{0.95}$Co$_{0.05}$O prepared using 3[U] fuel content. The Raman spectrum shows an intense band at 1580 cm$^{-1}$ due to the optical phonons in curved graphite sheets. The curvature induces a splitting of the in-plane degenerate optical mode in graphite, which results in two major bands (1570 and 1594 cm$^{-1}$). These spectroscopic features agree with observed Raman spectra of carbon nanotubes.
IV. Conclusions

Solid solutions of Mg$_{1-x}$Co$_x$O have been prepared by variation of urea content during combustion synthesis. Doubling the urea content avoids the formation of parasite Co$_3$O$_4$ but decreases the surface area. Further increase in urea content increases the surface area to 60 m$^2$/g but causes a demixed solid solution. Vegard’s law is obeyed in the range of concentration studied for solid solutions prepared using a urea content 3 times the stoichiometric amount.

On reduction at 1000°C in a methane and hydrogen atmosphere, single- and double-walled carbon nanotubes are produced with high yield. Presence of Co$_3$O$_4$ decreases the selectivity of the nanotube formation process, leading to tubes with more than 10 walls. The yield of carbon nanotubes decreases with an increase in surface area of the oxide precursor, and a urea content of 3[U] is ideal for carbon nanotube synthesis, as shown by surface-area measurements and Raman spectroscopy.

Acknowledgments

The authors thank Mr. Lucien Datas for the electron microscopy analysis which was conducted at the Service Commun de Microscopie Electronique à Transmission, Université Paul Sabatier.

References