



Internal field ^{59}Co NMR study of cobalt-iron nanoparticles during the activation of CoFe_2/CaO catalyst for carbon nanotube synthesis



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ABSTRACT

CoFe_2/CaO catalysts for multi-walled carbon nanotubes (MWCNT) were characterized during the activation period ($T = 670\text{ }^\circ\text{C}$; $\text{C}_2\text{H}_4/\text{Ar} = 1:1$, 400 sccm) by internal field ^{59}Co nuclear magnetic resonance. During this induction period, although C_2H_4 is already reacting, the MWCNT yield remains negligible. The NMR spectra of the catalysts revealed the occurrence of several structural and magnetic species. They were not detectable by conventional X-ray diffraction but the heterogeneity of the metal particles was corroborated by high-resolution transmission electronic microscopy coupled with energy dispersive X-ray spectroscopy. Two samples quenched at different activation time contained, beside non-reacted pure metal Co particles, strong and weak ferromagnetic alloys. During activation, the pure Co metal content dropped and an increase of the ordering of the cobalt-iron alloy in the catalyst was evidenced thus revealing a multistage activation mechanism for the reaction. We propose this ordering process during the induction period to be an intermediate step between the strong ferromagnetic Co rich alloy and the weak ferromagnetic Fe rich one and that it favors the onset of MWCNTs growth.

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1. Introduction

The catalytic growth of carbon nanotubes by catalytic carbon vapor deposition (CCVD) can be performed on variety of Co, Fe, and Ni catalysts [1–8]. It is typically a three-step process where an induction period is followed by a steady-state growth and finally an asymptotic approach to the maximal tube length (Fig. 1) [9]. This kinetic behavior can be rationalized in terms of carbon dissolution, diffusion and assembly on restructuring metal particle surfaces [10,11]. The kinetic and deactivation study of these catalysts have been performed in some recent papers [12,13]. However, the transition between induction and growth is not yet fully understood. A visualization of such period on pure Co catalyst is carried out in Ref. [14] and Monte Carlo simulations of CNT growth on Ni catalyst are reported in Ref. [5]. How the

carbon and the metal interact together in time can be modeled by numerical methods, but this obviously requires a prior knowledge of the composition of the metal particle under reaction conditions [15,16]. It is thus of importance that this knowledge is still lacking for bimetallic catalysts such as CoFe.

Recent advances in structural characterization methods have permitted the study of MWCNT nucleation despite its rapid and complex nature [17]. A variety of relatively conventional techniques has been implemented such as transmission electron microscopy (TEM) [11], X-ray photoelectron spectroscopy (XPS) [18,19], Raman spectroscopy [20–22], and X-ray diffraction (XRD) [23–27]. However, new knowledge can still be gained by the mobilization of more exotic techniques. Among them, internal field ^{59}Co nuclear magnetic resonance (IF-NMR), also known as ferromagnetic nuclear resonance (FNR), is a relatively new approach in the field of metal catalysis and it has been successfully implemented to study Fischer-Tropsch synthesis (FTS) catalysts [28–32] and ceramic composite catalysts [33]. ^{59}Co IF-NMR can follow bimetallic catalysts structural changes during activation,

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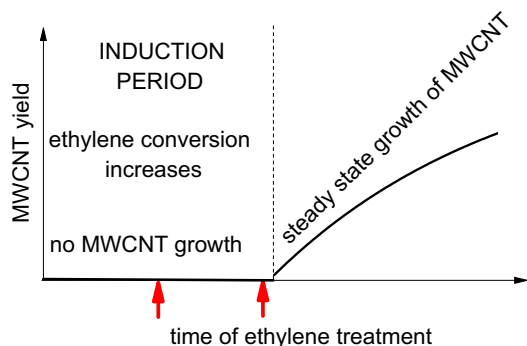


Fig. 1. General scheme of the succession of events occurring during the activation of the catalyst for carbon nanotubes growth by catalytic carbon vapor deposition (CCVD). The first step is an induction period during which ethylene conversion increases progressively to its maximum value but the MWCNT remains close to zero. During the second step, the ethylene conversion rate drops while the MWCNT conversion reaches a steady state. To better understand the mechanism at stake during the induction period, ^{59}Co IF-NMR has been performed on catalysts quenched at times (red arrows) corresponding approximatively to the middle or the end of the induction period (22 and 44 s, see experimental section for details and Ref. [46] for actual experimental values).

by quenching the metal particles after a controlled reaction time period.

In the appropriate range of temperature and size, iron and cobalt metal nanoparticles are ferromagnetic opening the unique possibility to perform ^{59}Co or ^{57}Fe NMR in the internal field of the particles [34,35]. Looking at the resonances of nuclei in ferromagnets has been largely exploited to study the bulk properties of alloys or the local structure and interfaces in metallic thin films [36,37]. Comparatively, the potential of internal field NMR has been somewhat ignored in a field where metal alloys play a large role, namely heterogeneous catalysis. Building on recent publications by us [38,39] and others [28,40], we mobilize the potential of the method in catalysis. Here, we report how the nuclear magnetic resonance of ^{59}Co in the internal field of cobalt-iron bimetallic nanoparticles expresses the evolution of the active phase of CoFe_2 catalysts during the well-known induction period [12] of multi-walled carbon nanotube (MWCNT) synthesis. In particular, it can shed new light on what happens during the first tens of seconds in the reactor.

It has been demonstrated that the formation of catalytically active metal particles largely conditions the nucleation mode of carbon as well as the selectivity and activity of the nanotube growth process, resulting in different diameter distributions [41], and structures [42] for the MWCNT. Thus, an investigation of the catalyst active component formation and of the carbon nucleation is of high importance for MWCNT production and selective processes design.

In this paper, we provide new clues with regard with the origin of the induction period during MWCNT growth on CoFe catalysts by following the alloy formation under reaction conditions (after quenching) by IF-NMR. We show that the nanoparticle composition is far from homogeneous and evolves significantly during the induction period.

2. Experimental

Co , and Co-Fe catalysts supported on CaO (Co:Fe ratio 1:2, total metal content 40 wt.%) were produced via the polymerizable complex route (Pechini method) [43,44]. Water solutions of metal nitrates (Fe , Co , and Ca) were mixed with citric acid and ethylene glycol. These mixtures were dried at 150°C to produce a 3D polymer matrix with metal ions evenly distributed in the bulk. The sub-

sequent heating of the dried mixtures in an air flow up to 550°C resulted in the removal of the organic matrix to give highly dispersed oxide systems containing metal ions in the form of CoFe_2O_4 spinel homogeneously distributed on calcium carbonate [45].

After the catalyst was heated to the reaction temperature (670°C) under an inert Ar atmosphere, about 300 mg of catalyst was activated *in situ* by introduction of a carbon feed (ethylene, $\text{C}_2\text{H}_4/\text{Ar} = 1:1$, 400 sccm) [25]. The samples were treated with a 5 (22 s reaction mixture pulse) or 10-fold (44 s reaction mixture pulse) carbon excess with respect to the full metal amount in the catalysts, i.e. the $[\text{mol C}_2\text{H}_4]/[\text{mol of (Fe-Co)}]$ ratio was equal to 5 and 10 for the 22 and 44 s reaction mixture pulses, respectively. These times were selected to represent the middle and the end of the induction period of the reaction according to the kinetics data previously reported [25,46]. The catalysts were then rapidly cooled to room temperature in an argon stream for 7 min (leading to a cooling rate far in excess of $50\text{ K}\cdot\text{min}^{-1}$), outgassed, and sealed-off in a glass ampoule of 8 mm outer diameter to quench and preserve the state of the metallic particles for further investigation by ^{59}Co IF-NMR. A reference sample of pure Co mono-component catalyst was also synthesized *via* the same procedure with an exposure time to the reaction mixture of 27 s (5-fold carbon excess).

^{59}Co IF-NMR experiments were carried out on a Bruker Avance III NMR spectrometer without application of an external field, i.e. outside of the magnet. A standard broadband static low Q NMR probehead was used during the experiments. The signal was acquired at room temperature point-by-point within a frequency range of 205–325 MHz with step of 1–2 MHz. At each frequency, the magnitude of two-pulses spin-echoes (two equal pulses of $1\ \mu\text{s}$, interpulse delay of $10\ \mu\text{s}$, 8000 transients) was recorded. The repetition rate was 200 Hz due to the very short T_1 relaxation time in ferromagnetic cobalt compounds. The spectra were corrected for the enhancement factor according to the procedure of Panissod et al. [36] More details on this issue and on peaks assignments can be found elsewhere [30,47,48].

The compositional heterogeneity of the CoFe particles was monitored under a JEM-2200FS (JEOL Ltd.) microscope using HAADF-STEM (High Angle Annular Dark Field Scanning Transmission Electron Microscopy) and EDX (Energy Dispersive X-ray spectroscopy). Samples were dispersed in ethanol and deposited on carbon-film-coated copper grids in a glove box under Argon. The elemental maps were obtained on O K (0.525 keV), Ca K (3.690 keV), Fe K (6.398 keV), Co K (6.924 keV) characteristic emission lines.

The XRD patterns were recorded on a D8 Advance diffractometer (Bruker, Germany) using $\text{CuK}\alpha$ radiation. Scanning was performed in the 2θ - angle range from 15° to 90° with a step of 0.05° and an acquisition time of 30 s for each step. Before acquisition, the samples were transferred in a glovebox under an Ar flow from an NMR ampule (i.e. the same sample was used for NMR and XRD experiments) into a tightly closing controlled atmosphere XRD cell to avoid sample oxidation.

Weight phase ratio and average crystallite size determination as well as the adjustments of lattice constants were obtained by Rietveld refinement using the TOPAS package. The ICSD database entries numbered 423,567 (CaCO_3), 180,198 (CaO), 161,509 ($\text{Ca}_2\text{-Fe}_2\text{O}_5$), 180,972 (FeO), 102,381 ($\text{Fe}_{0.5}\text{Co}_{0.5}$ alloy having bcc structure), 426,935 ($\alpha\text{-Co}$ with hcp structure) and 41,507 ($\beta\text{-Co}$ with fcc structure), were chosen as reference structures for the Rietveld simulations.

3. Results

The kinetics of the catalyst activation followed the expected sequence of induction, steady-state growth and asymptotic

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