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Identification of key parameters for the selective growth of single or double wall carbon nanotubes on FeMo/Al_2O_3 CVD catalysts

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Abstract

The successive organometallic chemical vapor deposition of metallic molybdenum and then iron from their carbonyl precursors at 220 °C on γ-alumina results in the formation of a bi-layered film on the alumina surface. These catalysts might be active for the selective synthesis of single or double wall carbon nanotubes from methane at 900 °C provided that (i) a fine tuning of the activation step is performed and (ii) the gas phase composition is carefully controlled. The negative influence of nitrogen on the selectivity towards SWCNT and DWCNT has been evidenced. Addition of hydrogen is harmful to SWCNT growth, whereas a low partial pressure of hydrogen is necessary to grow selectively DWCNT. These results can be rationalized in terms of kinetics of reduction of the active catalytic species. Based on XRD, Raman spectroscopy, XPS, FESEM/EDX and TEM analyses, a general pathway for SWCNT formation on the FeMo/Al_2O_3 CVD catalysts is proposed that involves the active mixed $FeMoO_4$ oxide phase.

Keywords: Carbon nanotubes; Chemical vapor deposition; Iron molybdenum catalysts

1. Introduction

The use of carbon nanotubes (CNT) in the field of nanotechnology is now well established, and for multiwall carbon nanotubes (MWCNT), the existence of large scale and selective synthetic processes have allowed to develop at the industrial or semi-industrial scale some innovative applications such as field emission display and conductive or/and reinforced polymers [1]. Single wall carbon nanotubes (SWCNT) are often considered as perfect 1D nanostructures that present attractive electronic and mechanical properties, and the presence of a single graphene layer allows to reach comparable or better performances than MWCNT with lower carbon loadings. As far as production techniques are concerned, catalytic chemical vapor deposition (C-CVD) appears to be the most promising one in view of selective large scale preparations of SWCNT. However, the selective production of carbon nanotubes with a controlled number of walls (SWCNT, DWCNT) is still a challenge and nowadays several tedious steps are required to separate SWCNT not only from the catalyst but more especially from the other undesired carbonaceous products [2]. Indeed, the synthesis of SWCNT or DWCNT is a very sensitive process and two specific aspects should be carefully controlled: (i) the catalyst preparation followed by its activation, and (ii) the tuning of the operative conditions.

Concerning the catalyst, a large variety of preparation routes have already been explored [3]. Usually, iron, cobalt or nickel can be used in association with a large variety of supports; alternatively, these metals can be doped by molybdenum [4–6] in order to improve the selectivity. The difficulty in catalysts preparation for selective SWCNT growth lies in the high temperatures (800–1000 °C) production of small size nanoparticles. Most of the classical methods as impregnation [7,8], coprecipitation [9,10], sol–gel process [11–13] as well as more sophisticated ones (colloidal solutions [14], or combustion processes [15–17]) have already been explored for the catalytic growth of SWCNT. Curiously, chemical vapor deposition, a well established technique for the production of highly-dispersed supported metal catalysts [18,19], has not been

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extensively used for CNT catalysts preparation [20,21]. Recently, we reported the use of FeMo/Al_2O_3 systems prepared by organometallic CVD (OMCVD) from $[Fe(CO)_5]$ and $[Mo(CO)_6]$ for the growth of SWCNT [22].

As far as the C-CVD operative conditions for SWCNT growth are concerned, different parameters have to be considered [3]. Usually, short reaction times and temperatures between 850 and 950 °C are adapted to SWCNT growth, and the carbon supply rate influences dramatically the SWCNT selectivity, high selectivity being achieved for high carbon supersaturations. This latter parameter is difficult to control as it is interconnected with the other ones. Concerning the reactive gas mixture used for SWCNT growth, it generally contains: (i) a carbon source, (ii) an inert gas used for dilution and (iii) hydrogen introduced to clean up the catalyst surface through native carbon gasification. In some cases, a soft oxidant such as water or carbon dioxide can also be introduced to gasify contaminating carbon [23,24]. Several hydrocarbons as well as carbon monoxide or alcohols have been successively used as carbon source. The carrier gas generally consists of nitrogen or argon but the use of helium, that presents a high thermal conductivity, has also been reported [25]. Even if it is commonly admitted that, according to the carbon source and to the temperature, the presence of hydrogen is beneficial to SWCNT and DWCNT growth, some authors have excluded it from the gas phase but no explanation was yet given [26,27].

In this work, we report the marked influence of the gas phase composition on the selective growth of SWCNT or DWCNT from methane on FeMo/Al_2O_3 OMCVD catalysts. A detailed characterization of the catalytic system at different stage of the process allows us to propose a general pathway for SWCNT growth.

2. Experimental

2.1. Catalyst preparation

Caution: $[Fe(CO)_5]$ is a highly toxic compound—all manipulation should be carried out under a well ventilated fume-hood.

Fluidized bed CVD of iron and molybdenum on γ-Al_2O_3 (158 $m^2\,g^{-1}$, Aldrich) starting from iron pentacarbonyl $[Fe(CO)_5]$ and molybdenum hexacarbonyl $[Mo(CO)_6]$ was performed in a specially designed glass vessel reactor (Fig. 1). For FeMo/Al_2O_3 systems, $[Mo(CO)_6]$ was introduced as a powder in the sublimator and the liquid $[Fe(CO)_5]$ precursor into a bubbler. A mass of grains of alumina (100–125 μm) was poured into the column. Deposition experiments were performed under reduced pressure (20 mTorr) at 220 °C. The temperatures of the sublimator and the bubbler were kept at 80 °C and 25 °C, respectively. The precursors decomposition was assisted by introduction of a low partial pressure of water in the reactor. Most of the bimetallic systems were prepared by depositing firstly molybdenum and then iron. The catalyst was removed from the column under an argon atmosphere.

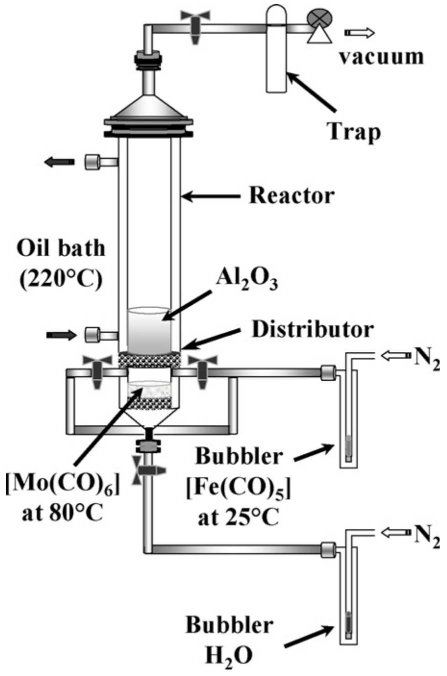

Fig. 1. OMCVD apparatus for the preparation of supported bimetallic catalysts.

2.2. Carbon nanotubes synthesis

The experiments were carried out in a conventional horizontal quartz CVD reactor (i.d. = 2.3 cm). Hundred milligrams of catalyst were placed in an alumina cup in the isothermal zone of the reactor and heated under nitrogen (100 sccm) up to 900 °C to activate it. Subsequently, a $N_2/H_2/CH_4$ or $Ar/H_2/CH_4$ mixture (50/150/100 sccm) was introduced at the same temperature for 30 min. After reaction, the oven was cooled down to room temperature under a N_2 flow (200 sccm).

Beside this set of conditions, two additional activation steps have been performed: the direct oxidation of the catalyst in an oven by air (250 sccm) from 25 to 900 °C at 15 °C min^{-1}, and the multi-step oxidation, that consists of 10 h in an oven at 200 °C under air (250 sccm) followed by 10 h at 400 °C under air, before the direct oxidation of the catalyst in air from 25 to 900 °C at 15 °C min^{-1}. Finally, for the influence of the gas phase composition, we have used different $Ar/H_2/CH_4$ gas mixtures: between 50/150/100 and 200/0/100 sccm.

The productivity was expressed as X ($g_C/g_{catalyst}$) and the activity as A^* (g_C/g_{Fe}/h). The amount of carbon on the composite powder was measured by TGA and the metal loading was evaluated by ICP-MS.

2.3. Characterization

Thermogravimetric analyses (TGA) were conducted on a Setaram thermobalance. The samples were heated in air from 25 to 1000 °C at 10 °C min^{-1}, followed by a 30 min isotherm. The TEM micrographs were obtained using a Philips CM12 microscope operating at 120 kV. The catalysts were observed with a HITACHI S 4500 I microscope and analysed by EDX.