Structural and chemical characterization of ribbon-like particles in Co/Mn/Al/Mg multi-metal catalyst

L. D. Yao[1], J. P. Tessonnier[1], D.S. Su[1] and R. Schlögl[1]

M. Becker[2], W. Xia[2], and M. Muhler[2]

1. Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany
2. Laboratory of Industrial Chemistry, Ruhr-University Bochum, Universitaetsstr. 150, 44780 Bochum, Germany

yao@fhi-berlin.mpg.de
Keywords: multi-metal catalyst, ribbon-like particle, CNTs, microstructure

Carbon nanotubes (CNTs) have attracted great interest of researchers over the last decade due to their exceptional properties, such as very high electrical and thermal conductivity as well as high mechanical strength. In any case, it is desirable to grow high quality CNTs with high yields. Developing high-efficiency catalysts is one strategy to achieve this goal. So far, transition metals like Fe, Co and Ni have been used as commercial catalyst for the synthesis of CNTs at an industrial scale. It was demonstrated that the catalytic performance, in the case of Co, can be optimized by adding promoters like Mo, W, etc. The synergistic effect of the mixture compared to pure Co further increases the yield of CNTs [1]. However, there are few reports related to multi-metal catalysts for the growth of CNTs. Recently, we have successfully prepared a class of multi-metal catalysts Co/Mn/Al/Mg containing numerous nano-scale ribbon-like particles, and investigated the variation of morphology of the catalyst before and after CNTs growth. It will be helpful in not only understanding the effect of morphology on the catalytic activity, but also exploring the mechanism of CNT growth.

A multi-metal (Co/Mn/Al/Mg) catalyst was prepared by discontinuous precipitation of the corresponding nitrate salts with NaOH. CNTs were grown by catalytic chemical vapor deposition at 485°C with an ethylene/hydrogen mixture. Microstructural and chemical characterization of the catalyst was carried out on Hitachi S-4800 SEM, Philips CM200-FEG and CM200-LaB_6 TEM.

The structure of the sample after calcination was analyzed by means of X-ray diffraction (XRD), showing that the catalyst mainly consists of some phases with a spinel-like structure (AB_2O_4 type). Here, A site may be occupied by Mg, Co and Mn ions, while B site may be occupied by Al, Co and Mn ions. According to the XRD pattern, except for AMn_2O_4 type compounds which have a tetragonal spinel structure, it is hard to specify the chemical composition of the cubic spinel structures due to the similar lattice parameters among these compounds.

From a morphology point of view, the sample contains catalyst particles with various shapes, many of them looking like thin ribbons, as shown in Fig. 1a. The ribbon-like particles are clearly visible in Fig. 1b, which yield widths of about 5 to 8 nm and lengths between 30 and 50 nm. It is roughly estimated that the content of the ribbon particles accounts for 50-60% in the catalyst. According to the observations of high resolution TEM (HRTEM), these ribbon-like particles are single crystals. As an example (see Fig. 1c), the extended direction of ribbon parallel to the $(111)_c$ plane for the cubic spinel structure or the $(101)_t$ plane for the

W. Grogger, F. Hofer, P. Pölt (Eds.): MC2009, Vol. 3: Materials Science,
DOI: 10.3217/978-3-85125-062-6-556 ,

tetragonal spinel structure. Co, Mn, Al, Mg and O elemental mappings demonstrate their homogeneous distribution in the catalyst, as shown in Fig. 1d.

In order to investigate variations in the catalyst morphology and composition during the CNT growth, the catalyst was first reduced in H_2 at 650°C and then reacted with H_2 and a carbon source gas (C_2H_4) diluted in Ar at relatively low temperature (485 ^{o}C) for only 30 seconds. TEM observations show that large amounts of CNTs were produced (see Fig. 2a), and that the average CNT diameter is of about 10 nm. Typically, CNTs grow from single nano-scale ribbon particle, as shown in Fig. 2b, and the interface between the CNTs and the ribbon particle can be imaged. Surprisingly, Co particles could not be observed or detected by elemental mapping after reaction (see Fig. 2d), although it is generally accepted that CNTs grow from metal nanoparticles and that the diameter of the CNTs is defined by the diameter of the Co particles. It appears that part of the oxygen atoms are removed from the spinel structure and crystal grains can therefore be divided into several fragments because of a large amount of oxygen vacancies. Polycrystalline particles in Fig. 2c support this hypothesis. We assume that CNTs grow from Co-terminated planes or from Co clusters. Further investigations are necessary in order to fully understand the growth mechanism in the case of these catalysts.

In summary, the Co/Mn/Al/Mg multi-metal catalyst exhibits interesting morphology containing numerous nano-scale ribbon particles. CNTs can grow based on the ribbon particles in the absence of pure Co particles. In addition, this kind of catalyst displays a high catalytic performance compared to traditional Co catalyst [2].

1. P. Landios et al., Carbon. **47** (2009) p789.
2. The authors thank the German ministry for education and research for financial support through the Inno.CNT project (BMBF grant 03X0040H).

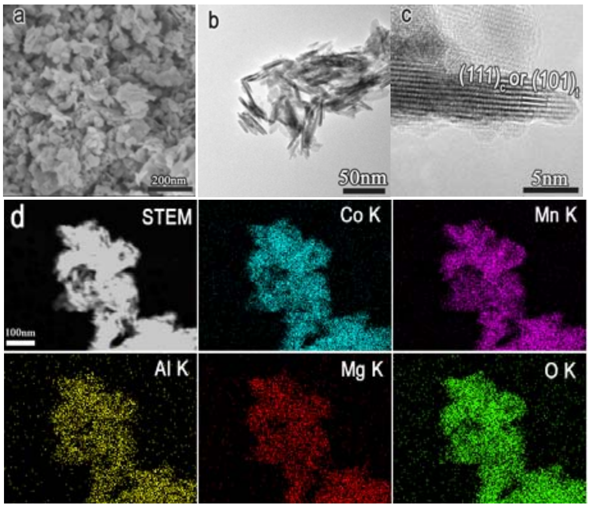

Figure 1. (a) SEM and (b) TEM images of multi-metal catalyst. (c) HRTEM image of single nano-scale ribbon particle. (d) STEM image together with EDX maps for multi-metal catalyst.

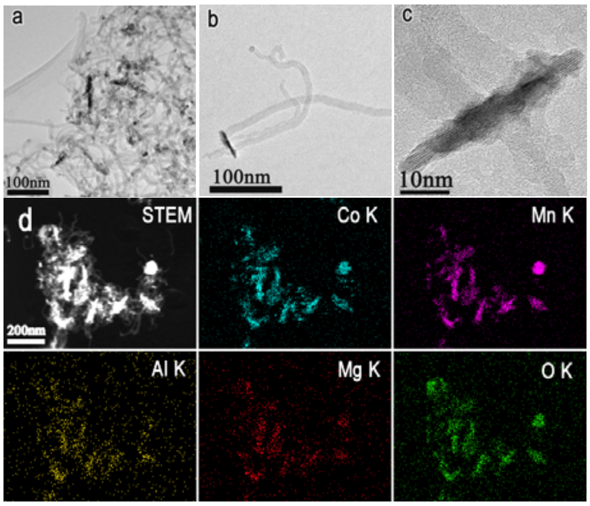

Figure 2. (a) and (b) TEM images of multi-metal catalyst after reaction. (c) HRTEM image of single nano-scale ribbon particle with CNTs. (d) STEM image together with EDX maps for multi-metal catalyst after reaction.

W. Grogger, F. Hofer, P. Pölt (Eds.): MC2009, Vol. 3: Materials Science,
DOI: 10.3217/978-3-85125-062-6-556 , © Verlag der TU Graz 2009