COMPARISON OF THE CATALYTIC EFFICIENCY OF NATURAL AND SYNTHETIC MONTMORILLONITES FOR THE GROWTH OF CARBON NANOTUBES

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Abstract

We demonstrate the synthesis of two composites consisting of carbon nanotubes and clay mineral montmorillonite. Synthetic and natural montmorillonites were examined as a matrix for synthesis of carbon nanotubes by hot filament chemical vapour deposition. Synthesis of carbon nanotubes on natural forms of montmorillonite but also on its synthetic form can only be achieved by incorporation of a catalytic phase. We have observed that there is no significant difference between natural and synthetic forms of montmorillonite as for the final carbon phase. In both cases the surface of the mineral is covered by a dense network of carbon nanotubes.

Keywords: Carbon nanotubes, montmorillonite, chemical vapour deposition

1. INTRODUCTION

Synthesis of carbon nanotubes (CNTs) on minerals provides new fibrous nanomaterials which could be used as ceramic reinforcement [1-3]. In the presented work we follow up our optimized method of catalytic synthesis of nanocomposites based on CNTs and minerals [4-7]. We examine synthetic and natural montmorillonite used as a matrix for *in situ* synthesis of CNTs in a hot filament chemical vapour deposition reactor (HF CVD). The aim of the present work is to compare the catalytic efficiency of these two matrices for the growth of CNTs.

2. EXPERIMENTAL MATERIALS AND TECHNOLOGY

Two different types of montmorillonite (MMT) - natural and synthetic - were used as substrates for CNTs synthesis. Natural MMT was isolatedfrom bentonite. Bentonite comes from Stará Kremnička, Jelšový potok in the Kremnica Mountains, Slovakia[8].The size of particles wasbelow 2 μm.The samples taken from natural MMT were impregnated by iron from an aqueous solution of $Fe(NO_3)_3$. Synthetic MMT was prepared by 6 day lasting hydrothermal synthesis in an autoclave (Lampart, Hungary) with a volume of 1 litre at a temperature of 300 °C and pressure 8.8 MPa. The starting compounds were aluminium nitrate, magnesium nitrite, ferric nitrite and amorphous silicon dioxide with particles of 5 to 50 nm in size (Aerosil, Evonik Industries, France). The ratios of SiO_2, Al_2O_3, MgO and Fe_2O_3 in the prepared product were 4 : 1 : 0.6 : 0.1. Synthetic MMT contained 5 wt% of Fe_2O_3. Synthetic MMT has a markedly higher content of iron than natural MMT. A sample taken from synthetic MMT was divided for use in two experiments. The first part was destroyed by milling in a common laboratory achate dish, while the second part was impregnated by iron in an aqueous solution of $Fe(NO_3)_3$. Suspensions of the minerals were deposited on a siliconsubstrate(1 cm × 1 cm, ON Semiconductor Ltd., Czech Republic) by a micropipette and dried first at room temperature and then in a drier at 110 °C. Synthesis of CNTs was carried out in the HF CVD reactor. The working atmosphere was a mixture of methane and hydrogen. The precursors are activated by five tungsten filaments heated up to 2200 °C. The pressure and temperature during deposition were 3000 Pa and approx. 600 °C, respectively, and the synthesis time was 25 minutes. The quality and nature of carbon deposited on the silicate and nanocomposite were examined by scanning electron microscopy (JEOL, Japan) and Raman spectroscopy (HORIBA Jobin Yvon, France).

3. RESULTS

Products of synthesis in the HF CVD reactor are shownin **Figs. 1, 2 and 3**. **Figs. 1 and 2** show nanotubes grown on natural and synthetic MMT impregnated by ferric ions, mostly by trivalent atoms Fe(III) [5]. The surfaces of the minerals are covered by non-aligned CNTs with various diameters and shapes. The length of single CNTs varies in a wide range, the longest CNTs have lengths from 20 to 30 μm and diameter from 5 nm to approx. 120 nm. SEM observations cannot confirm unambiguously that CNTs do not penetrate the interlayer spaces of MMT. A significant result of this study is that iron atoms which are part of the structure of montmorillonite did not show catalytic activity in the synthesis of CNTs on the amorphous substance obtained by milling of synthetic MMT (see **Fig. 3**). The degree of mechanical destruction was verified by X-ray diffraction.

The results imply that synthesis of CNTs on both forms of MMT can only be achieved by artificial incorporation of a catalytic phase. This result could be expected also for other types of phyllosilicates. MMT has the ability to multiply its volume by water swelling. The existence of negative charge on the stack of MMT has the consequence that the colloidal particles of MMT in aquatic sediments behave as anions with ion exchange properties, thus in an aqueous solution of ferric salts MMT can be enriched with iron ions, hereby providing a matrix containing the Fe^{3+} (as well as Fe^{2+}) catalyst for the formation of nanocomposites. Based on our experimental knowledge we conclude that the catalytic activity of the silicates for synthesis of CNTs is not related solely to the ion exchange mechanism.

4. CONCLUSION

The surface of natural and synthetic montmorillonite was covered by a dense network of randomly oriented CNTs. One could observe various types of CNTs. They exhibit different shapes, diameters and lengths. On the surface of some CNTs one could also see impurities**-** probably amorphous carbon. Synthesis of CNTs on the natural forms of MMT but also on its synthetic form can only be achieved by incorporation of a catalytic phase. No significant difference has been observed between natural and synthetic forms of montmorillonite compared as for the final carbon phase.The iron atoms which are part of the structure of montmorillonite did not show catalytic activity in the synthesis of CNTs, not even after degrading this structure by milling.

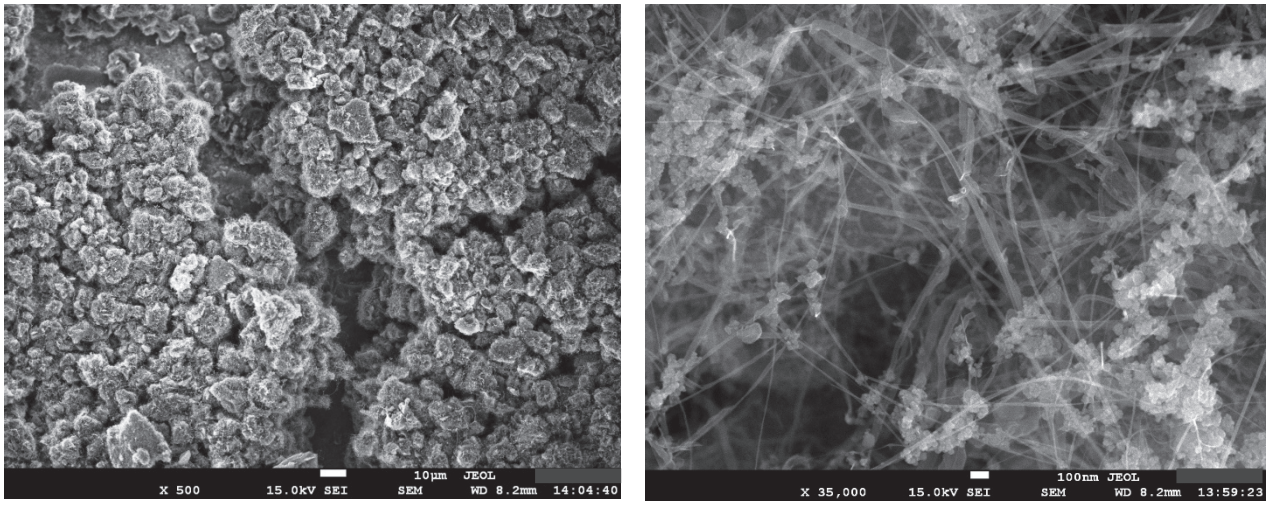

Fig. 1 The surface of natural montmorillonite additionally enriched with iron after carbon deposition on the silicate. Right **-** detail view, CNTs are incorporated into the mineral layer and create a 3D network

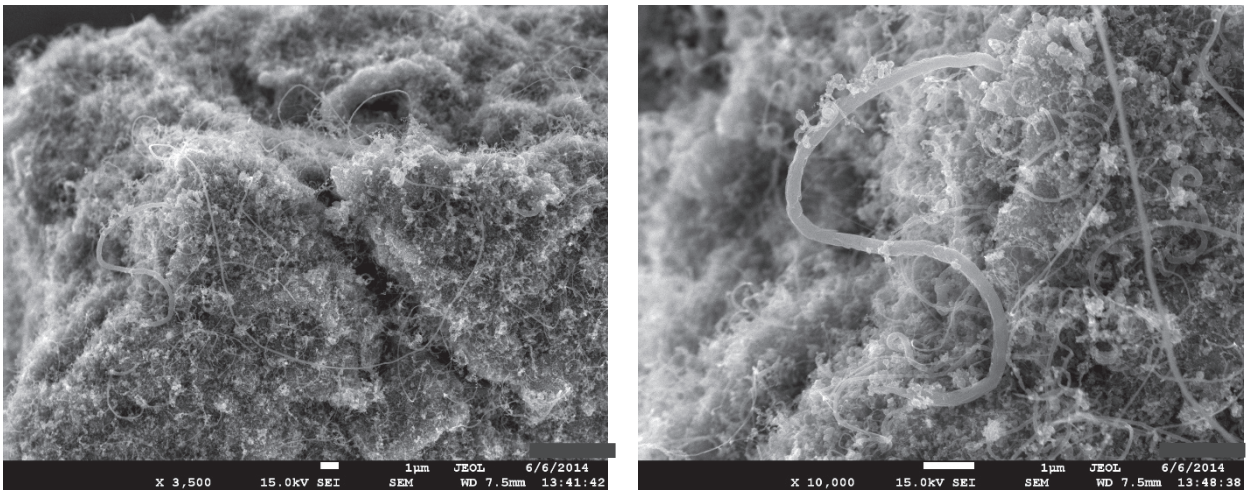

Fig. 2 SEM images of synthetic crystalline MMT additionally enriched with iron after synthesis of CNTs. Right - detail view, randomly oriented CNTs with various shapes and lengths

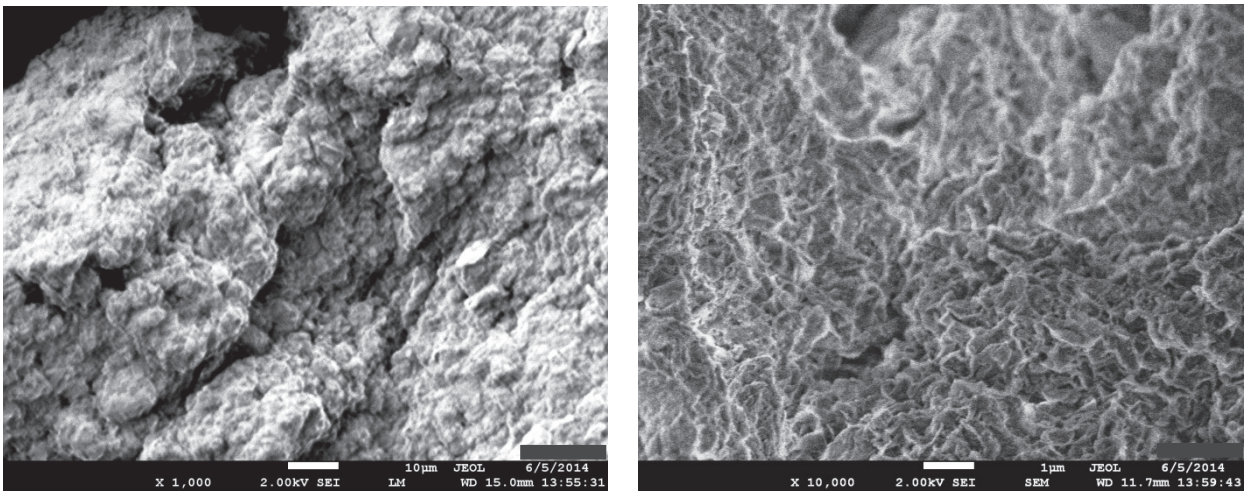

Fig. 3 SEM images of synthetic MMT destroyed by milling.
The absence of CNTs after its exposure in HF CVD reactor is obvious

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