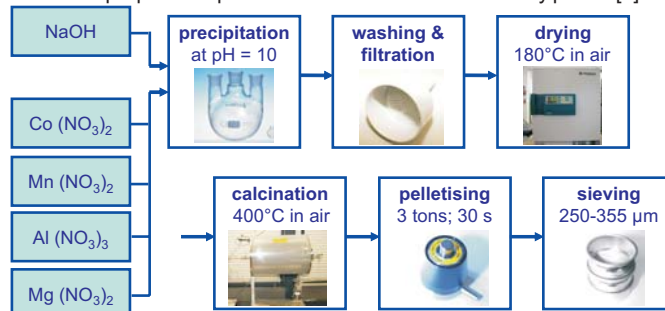


Introduction

Multiwalled carbon nanotubes (MWCNT) expose several extraordinary properties, e.g. electric conductivity, unique geometry and high mechanical strength [1,2]. The growing field of potential applications results in an increasing demand of cost-effective CNTs. Catalytic chemical vapor deposition (CCVD) of hydrocarbons over Fe-, Co- or Ni-based catalysts is the most promising synthesis route towards a large scale CNT production [3, 4]. Based on patent literature [5], an industrially applied Co-Mn-Al-Mg-catalyst was synthesized in a small-scale precipitation. The MWCNTs were achieved by decomposition of ethylene over the reduced catalyst. In this work the quaternary catalyst and the obtained CNTs are characterized. The focus is placed on the chemical state of the catalyst during the pretreatment and the early stages of the CNT synthesis. Additionally, the impact of Mn on the catalytic activity is investigated. The aim of this work is to draw correlations between catalyst properties and CNT structure.

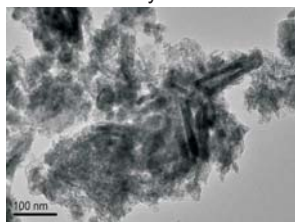
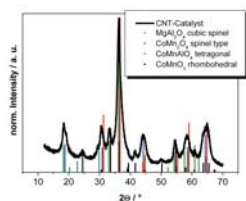
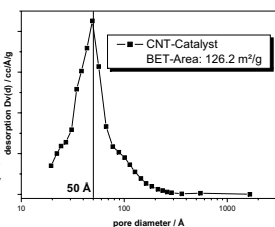
Catalyst Preparation

Aqueous solutions of nitrate salts were discontinuously precipitated with NaOH. The preparation procedure was based on an industry patent [5].



Characterization

The CNT-catalyst was studied by a combination of XRD, elemental analysis, TEM and N₂ physisorption. The mixed oxide consists basically of a cubic spinel with the general formula A^{II}B^{III}O₄, where site A^{II} is occupied by Mg²⁺, Co²⁺ or Mn²⁺ and site B^{III} by Al³⁺, Co³⁺ or Mn³⁺. Additionally, tetragonal and rhombohedral phases can be assigned. The mean pore diameter is 5 nm. Mainly a ribbon-like particle shape are observed by TEM measurements.



Elemental analysis by ICP-OES

Co wt-%	Mn wt-%	Al wt-%	Mg wt-%
31.0	26.0	3.4	3.6

CNT Yield

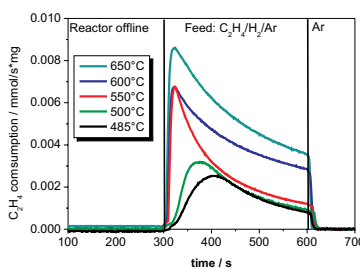
The CNT were prepared in a tubular quartz reactor using ethylene as carbon source. After reducing the catalyst samples in hydrogen, the yield was determined after 120 min growth at 650°C using a mixture of ethylene and hydrogen as feed gas. The reaction conditions were taken over from an industry patent [5].

Yield CNT-Catalyst: **171.8 g_{CNT}/g_{Cat}**

$$\text{CNT yield} = (m_{\text{total}} - m_{\text{Cat}}) / m_{\text{Cat}}$$

Variation of Temperature

The consumption of ethylene during the initial stage of the CNT growth reaction was monitored by an IR gas detector. The amount of deposited carbon increases with higher temperature. Strong hints of pore diffusion limitations for particle sizes above 250 µm were found at 650°C.

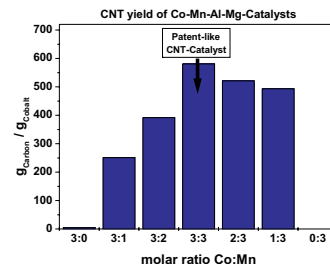
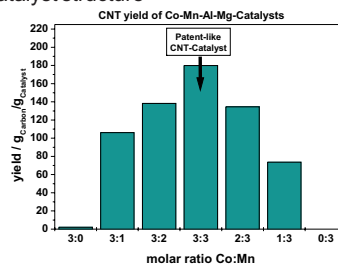


Acknowledgment

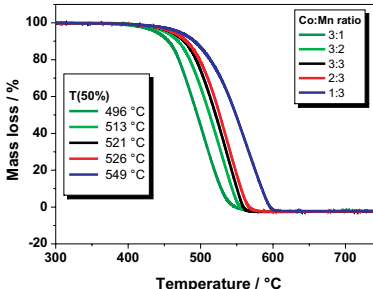
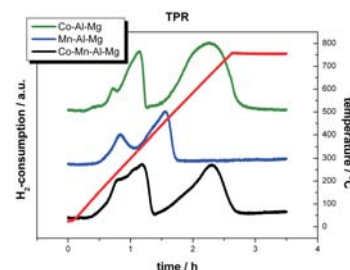
Financial support by the Federal Ministry of Education and Research (BMBF) of the „CarboScale“ project within the scope of „Inno.-CNT“ is gratefully acknowledged. The author thanks the Fritz-Haber-Institute of MPG for electron microscopy analysis.

Variation of the Co/Mn-Ratio

The Co/Mn-ratio was varied in order to study the impact on the catalytic activity and catalyst structure



The highest CNT yield was achieved by the patent-like Co-Mn-Al-Mg sample with a ratio of Co:Mn 3:3. Only a very low yield was obtained using Co-Al-Mg as catalyst. The sample containing Mn-Al-Mg showed no activity. The results of temperature-programmed reduction (TPR) demonstrate that the Co is not fully reduced at 650°C. The presence of Mn is known to hamper the reducibility of Co [6].



The oxidation stabilities of the CNT were tested by a temperature-programmed oxidation (TPO) in air using thermogravimetry (TG) in order to observe the mass loss with increasing temperature. The CNT combusted between 400 to 600°C. The temperature of 50% mass loss increases with a higher Mn content in the catalyst. The FWHM of the differential TG curve was about 70 K for all samples.

Conclusions

- Mesoporous spinel Co-Mn-Al-Mg oxides were obtained by precipitation of nitrate salts.
- Remarkable high CNT yields were achieved from catalysts with an equimolar ratio of Co:Mn. The addition of Mn enhances the catalytic activity of Co by a factor of 84.
- Explosion-like CNT growth was observed during initial stage of the synthesis.
- Oxidation stability of the CNT increases with higher Mn content of the catalyst.

Literature

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