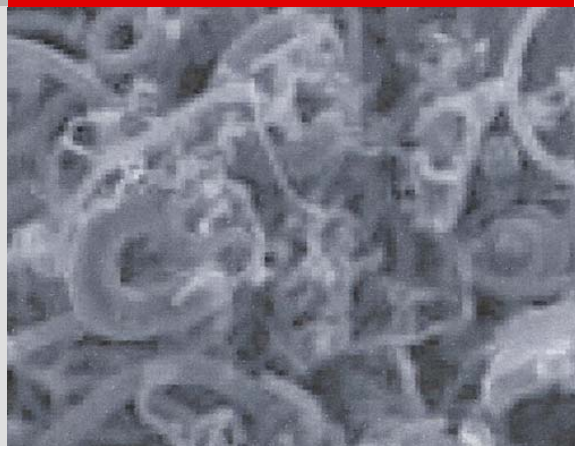
Anton Paar



Graphitic nano-fibers

A candidate for hydrogen storage

1 Introduction

For many years nano-structured carbon materials have been intensely studied [1-4] and are used for various applications, e.g. as catalyst support, for Li-ion-batteries and as emitter materials.

They are also of major interest as media for hydrogen storage. Fig.1 shows different structures of carbon to be used in this respect and their hydrogen storage capacities [5-7, 9]

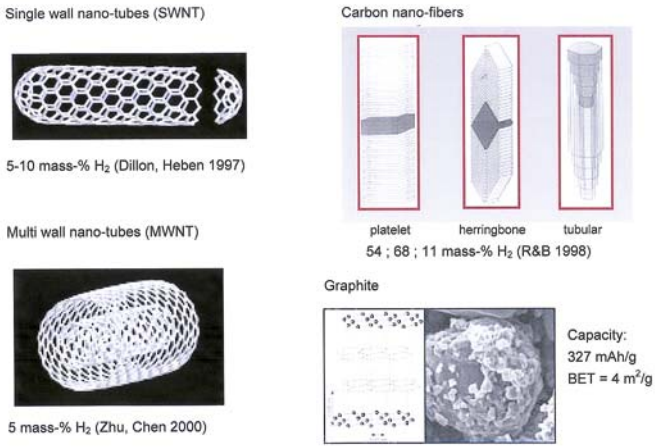


Fig. 1 Carbon nano-structures for hydrogen storage

Nano-structured carbon materials can be produced by different procedures, among them catalytic chemical vapour deposition (CCVD).

In this work in-situ X-ray diffraction (XRD) studies were performed to investigate the CCVD synthesis of graphitic nano-fibers (GNF) and their potential as hydrogen storage material. In this respect, the behavior of the synthesized fibers during high temperature activation and during adsorption/desorption of hydrogen was investigated.

Thermodesorption spectroscopy (TDS/MS) was used to analyze the amount of adsorbed hydrogen as well as the surface species of the different carbon materials.

The morphology of the fibers was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The in-situ X-ray diffraction studies were performed with the XRK 900 reactor chamber by Anton Paar [8].

2 XRK 900 heating attachment

The XRK 900 is a reactor chamber for X-ray diffraction experiments up to 10 bar gas pressure. It can be fitted to all common diffractometers instead of the standard sample holder. In-situ investigations of solid state reactions can be carried out from room temperature up to 900 °C, with excellent temperature uniformity in the sample. The design of the chamber permits rapid and reliable flushing with reaction gas and gas flow through the sample to perform studies of solid state – gas reactions.

3 Experimental

The XRD investigations were carried out in the angular range between 15 and 65° 2Θ at temperatures up to 900 °C, pressures up to 5 bar and loads up to 10.000 v/vh.

4 Results and Discussion

The NiO/CuO catalyst (Ni:Cu=98:2 weight%) was first formed in an H_2/N_2-gas stream at 350 °C (reducing conditions). The reduction of NiO to metallic Nickel was finished after 2 hours.

The catalyst was diluted with silicon to contain formation of the graphitic nano-fibers. Silicon also acted as internal calibration standard.

After catalyst formation, the graphitic nano-fibers were prepared by catalytic CVD in an atmosphere of $C_2H_4/H_2/N_2$ at 600 °C.

The diffraction patterns of the catalyst and the synthesized nano-fibers are shown in Fig.2.

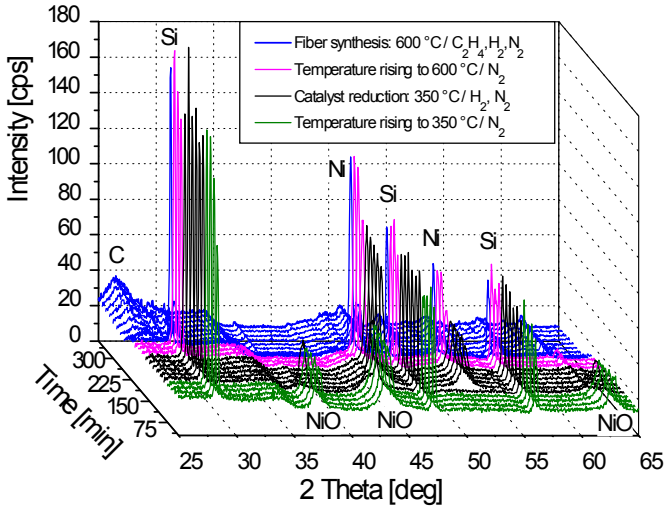


Fig. 2 Diffraction patterns of the catalyst and the nano-fibers depending on atmosphere and temperature

Fig.3 shows some SEM/TEM pictures of various carbon fibers that were synthesized using different catalysts and reaction gases.

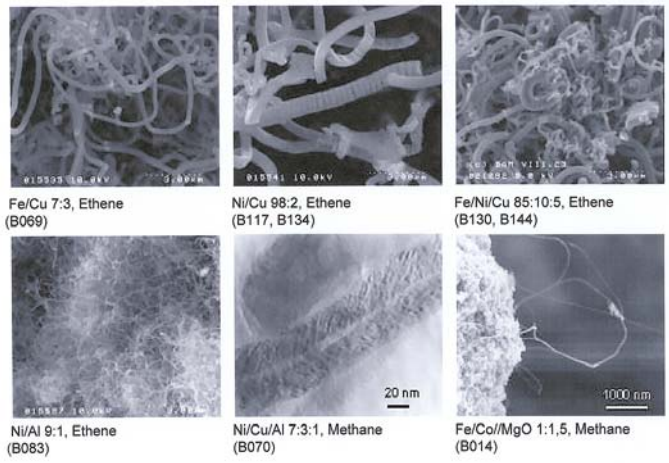


Fig. 3 SEM/TEM pictures of selected carbon fibers

In order to incorporate hydrogen in-between the graphite layers, the nano-fibers were treated with hydrogen at temperatures between 25 and 600 °C and at a pressure of 5 bar.

The hydrogen adsorption process was investigated with XRD by monitoring the (002) reflex of graphite and thus the lattice expansion in the c-direction.

A decrease of the diffraction angle of the (002) reflex and an increase of the d_{002}-value up to 0.03 Å was observed, upon treatment with hydrogen as well as temperature and pressure increase (25 to 600 °C; 1 to 5 bar).

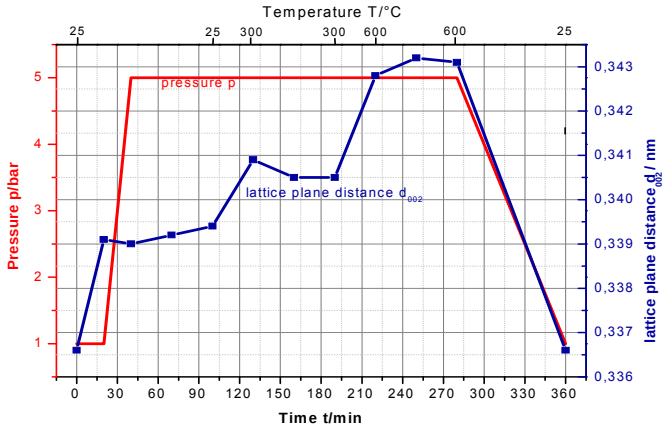


Fig. 4 Lattice distance d_{002} of the nano-fibers depending on temperature and hydrogen pressure

The lattice expansion and hydrogen adsorption was only observed during in-situ synthesis and characterization of the fibers in the XRK 900 under exclusion of air. The investigation and interpretation of this effect is still subject of further studies. One possible explanation is that upon contact with air, different gas molecules occupy the sorption sites of the fibers.

The desorption of hydrogen was monitored with thermodesorption spectroscopy (TDS/MS). The amount of desorbed hydrogen was found to be approx. 1 mass%. Higher adsorption values of a couple of mass% were achieved by surface modification of the fibers.

5 Summary

With the **XRK 900** reactor chamber in-situ X-ray diffraction studies of catalysts as well as of graphitic nano-fibers were performed.

After CCVD preparation of the nano-fibers, they were treated with hydrogen at 5 bar and 600 °C.

The amount of hydrogen adsorbed on the fibers was found to be approx. 1 mass%. The hydrogen storage leads to an increase of the d_{002} lattice distance of 0.03 Å due to

hydrogen incorporation between the graphite layers. The lattice expansion could only be observed when the synthesized fibers did not have any contact with air.

Thus the **XRK 900** is an essential analytical tool for in-situ XRD investigations at elevated temperatures and pressures.

The correlation between the structural changes of the nano-fibers and the amount of adsorbed hydrogen is the subject of further studies.

6 References

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Data provided by:

Prof. Klaus Richter, GNF Gesellschaft zur Förderung der naturwiss.-techn. Forschung e.V., Berlin-Adlershof

Contact Anton Paar GmbH:

Tel: +43 316 257-0
Fax: +43 316 257 257
info@anton-paar.com
www.anton-paar.com