Preparation and catalytic behaviour of vanadium oxide nanowire-carbon nanotube composites

Z. P. Zhu,[a,b] D. S. Su,[a] G. Weinberg,[a] G. Mestl,[c] R. Schlögl[a]

[a]Department of Inorganic Chemistry, Fritz-Haber-Institute of MPG, Faradayweg 4-6, D-14195 Berlin, Germany. [b]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, CAS, 030001 Taiyuan, China. [c]NanoScape AG, Butenandt Str. 11(E), D-81377 Munich, Germany.

1-D nano-sized fibrous and tubular inorganic structures have attracted special attention due to their outstanding structural flexibility and unique chemical and physical properties. Vanadium oxide wires are of specially interest for catalytic science due to their intrinsic highly variable valency and excellent redox properties.[1] Vanadium oxides and related compounds are frequently employed as the catalysts for partial oxidation or dehydrogenation of alkanes.[2,3] Most of these reactions are highly exothermic. The reaction-released heat hoards on the catalyst surfaces and thus declines the catalytic activity or selectivity, because the thermal conductivities of both active catalysts and the normally employed supports are very low. Such a problem is possibly solved by employing special supports with high thermal conductivity[2], which act as heat sinks to extract the heat from the catalyst surface and reactor. Carbon nanotubes (CNTs) have an excellent thermal conductivity, high surface area, and high thermal and chemical stabilities. Furthermore, it is well known that carbon material themselves, including nanofibres,[4] are also active and selective for some catalytic oxidation reactions. Therefore, combining vanadium oxides with CNTs is expected to produce a novel catalytic material and to improve the catalytic behavior. In this work, we report a novel approach for the preparation of vanadium oxide nanowires (VONWs) and CNT composites and for their thermal stability and catalytic behavior for butane oxidation.

Multi-walled tubes with diameters of 10-50 nm were obtained by a detonation of mixed picric acid, paraffin, and cobalt acetate[5]. To synthesize the VONW-CNT composites, the CNTs are pre-oxidized by 6 M HNO_3 solution at refluxing temperature for 12 h to partially remove the impurities (cobalt and amorphous carbon particles) and to modify oxygen-containing groups on the tube surface. 100 ml solution of NH_4VO_3 (0.04-0.08 M) containing 100 mg oxidized CNTs was refluxed for 5 h with magnetic stirring. After the refluxing, the suspension was filtrated, washed with deionized water and ethanol, and dried at 110 ^oC overnight.

The hydrolysis of NH_4VO_3 can effectively produce vanadic acid or VO_x at refluxing temperature but leads to heavy aggregation – formation of irregular micrometer large particles, rendering the control of size and shape difficult. When surface-modified CNTs are introduced into an aqueous NH_4VO_3 solution, the hydrolysis leaves behind well-grown VONWs, with lengths of up to 20 μm and widths of 5-15 nm (Figure 1a). The VONWs are often separated from the CNTs and are normally organized as bundles. Previously reported CNT-assisted production of 1-D V_2O_5 nanostructures applied molten V_2O_5 or HVO_3 gel on tube surfaces and/or filled internal cavities, such that CNTs act as geometric templates.[6] In the present approach towards VO_x nanowires, however, CNTs serve as inducers by partially providing their curved surfaces (Figure 1b) for inducing the nucleation of the VO_x nanostructures. This is well confirmed by the detailed TEM observations of wire morphologies and wire-tube existing

states.

The VOx nanowires exhibit an average O/V atomic ratio of 3.8 as revealed by EDX analyses. V L-edge and O K-edge EELS reveal two types of electronic structures for different individual wires, associated with V^{5+} and V^{4+} oxides. X-ray powder diffraction confirms the mixed composition of $V_2O_5 \cdot H_2O$ and $6VO_2 \cdot 5H_2O$. The crystals are well structured and exhibit the (001) planes normal to wire axis (HRTEM), suggesting that the nanowires grow along [010] direction.

Thermal stability of vanadium oxide nanostructures is crucial for their practical applications in catalysis. Unlike the tubular nanostructures obtained by an organic amine-directed hydrothermal route, decomposing above 250 ^oC,[7] the present nanowires are rather stable in morphology at temperatures as high as 400 ^oC in air, although the wire surfaces become rough and most of the water molecules in the crystals are lost after the heating treatments.

The catalytic behavior of the obtained VONW-CNT composites was primarily tested for butane oxidation at 180-220 ^oC. The results showed that about 60% butane is converted. Although 80% of the converted butane is oxidized into CO and CO_2, the remained 20% products seem very interesting. Investigation of their real structures and natures are in progress.

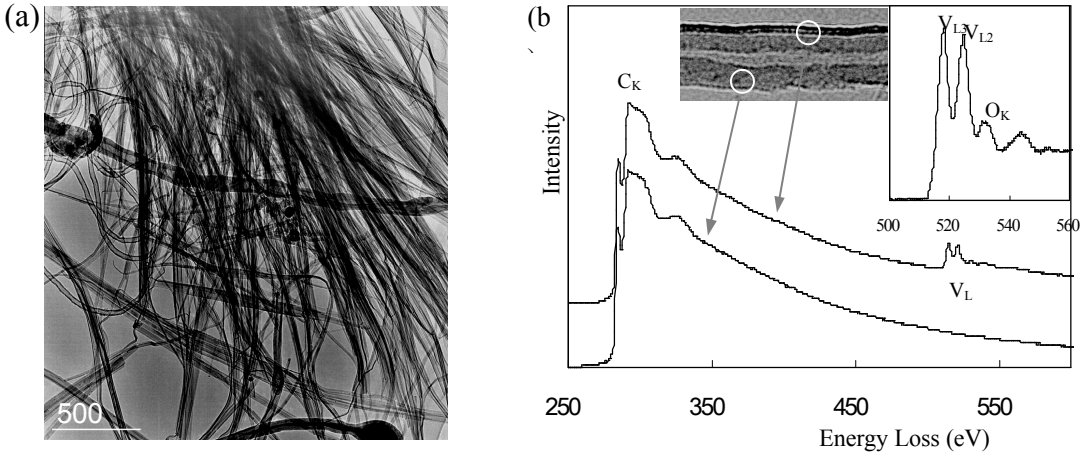

Figure 1. (a) TEM image of the materials obtained from NH_4VO_3 hydrolysis in the presence of CNTs. (b) EELS obtained on two different sides of a carbon tube (left inset). One side is coated with a thin film of vanadium oxide, while the other side shows no vanadium. The right inset is the magnification of the vanadium oxide spectrum.

Acknowledgment:
This work is performed in frame of ELCASS and SFB 564 of DFG. Z.P.Zhu thanks Alexander von Humboldt Foundation for scholarship support.

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