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Low-temperature catalytic oxidation of multi-walled carbon nanotubes

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ABSTRACT

When in a pure form, carbon nanotubes are known to be stable in air up to ~800 K making them attractive for a large variety of applications. In this work, we report a significant decrease of ignition temperature (in some cases occurring at ~500 K) and a reduction in the apparent activation energy for oxidation in air as a result of impregnation with nanoparticles (<2 nm) of metal (Pt, Pd, Ni and Co) acetylacetonates or by decoration with corresponding oxides. Surprisingly, defects introduced by partial oxidation of the carbon nanotubes do not in practice have any influence on the enhancement of further oxidation. Reduction temperatures of metal oxides with H_2 were close to those of other carbon supported catalyst materials. However, the carbon nanotubes showed a tendency for low temperature gasification in the presence of hydrogenation catalyst metals (Pt, Pd).

1. Introduction

Carbon nanotubes (CNTs) have similar outstanding properties to those of graphite (crystallinity, good electrical and thermal conductivity) and activated carbon (large specific surface area, optionally functionalized surface). They also enable hierarchical assemblies [1,2] and template-based structures [3] that thus offer the possibility of combination with other materials to form heterostructures [4–6] or composites [1,7]. Metal and/or metal oxide nanoparticles supported on carbon nanotubes have given rise to a new family of nanocomposites during the past few years [8–23]. Catalyst materials have been demonstrated for hydrogen production by reforming (ethanol [9], methane [10]), oxidation reactions (carbon monoxide [11], methanol [12]), hydrogenation/dehydrogenation of hydrocarbons [3,13,14], Fischer–Tropsch synthesis [15] and coupling reactions [16,17]. They may also be applied in large area catalytic electrodes for fuel cells [18–21] and active sensing layers for gas detection [22,23] , thus demonstrating the versatility of CNT based support materials.

The prerequisites of a good catalyst are high activity/selectivity, reasonable cost, reusability in batch operations and long lifetime in continuous reactors [24]. Catalyst deactivation, caused by either chemical or physical changes on the catalyst, is a major problem. When exposed to high temperatures the support material may sublimate, recrystallize and coarsen leading to sintering. It is a slow process, but when it occurs it is very difficult or even impossible to reverse. In

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the case of carbon and organic polymer based support materials, oxidation is a further challenge that also comes into play.

Before applying CNTs in industrial technologies, the behavior of material under various synthetic and operation conditions should be studied and assessed [25,26]. Despite the emerging applications of CNTs as catalyst support, only a few reports have dealt with the limitations of such flammable materials. For example, photo-ignition of single-wall carbon nanotubes has been reported when exposing powder samples to a camera flash, due to their excellent optical absorption and the subsequent rapid local temperature increase [27]. In a set of publications [28,29], Ci and co-workers have recently demonstrated a novel technique to remove carbon atoms from the surface of highly-oriented pyrolitic graphite using nickel nanoparticles at various temperatures ranging from ~1020 to 1370 K. In addition, the effect on the oxidation of catalyst residuals of CNT synthesis has been studied by thermogravimetric analysis (TG). The catalyst type, the crystallinity and size of the metal nanoparticles as well as the process temperature have all been found to influence the oxidative stability of CNTs [30–34].

In this paper, we present a systematic study of the stability in an oxidizing atmosphere of MWCNTs impregnated with metal catalyst precursors, or decorated with different nanoparticles of metals and their oxides. The effect of metal nanoparticles on the ignition temperature and on the activation energy of oxidation have been assessed by thermal gravimetry and calculated using the Horowitz–Metzger method [35]. To make the study more complete, reduction of metal oxide nanoparticles with H_2 in the presence of carbon nanotubes has also been investigated using temperature programmed reduction (TPR).

The results reported here shed light on the practical temperature window for synthesis and the use of carbon nanotube based support materials. As we show, the presence of metal/metal oxide and metal acetylacetonate nanoparticles on the surface of nanotubes can induce an oxidative degradation of the support at temperatures well below 800 K, i.e., below the temperature usually associated with the onset of oxidation of pure nanotubes [36–39].

2. Experimental

Multi-walled carbon nanotubes (MWCNTs, purchased from Sigma–Aldrich, >90% carbon basis, 10–15 nm (outer diameter) × 2–6 nm (inner diameter) × 0.1–10 μm (length)) were acid-treated to remove amorphous carbon and metal catalyst residuals of synthesis. In a typical process, a 5 g sample was sonicated for 1 h and then refluxed for 8 h in 250 ml 70% HNO_3 followed by washing with deionized water and drying. These nanotubes were used both as reference and as starting materials for the subsequent decoration experiments.

The pretreated nanotubes (~200 mg) were dispersed in 60 ml of toluene by ultrasonic agitation (3 h) then pre-defined amounts of metal acetylacetonate precursors (9 mg $Pt(acac)_2$ (Aldrich 99.99%), 12 mg $Pd(acac)_2$ (Aldrich, 99%), 18 mg $Ni(acac)_2$ (Aldrich, 95%) or 25 mg $Co(acac)_3$ (Aldrich, 98%) corresponding to 2 wt.% metal in the final product) were added and stirred at room temperature overnight. The solvent was evaporated at ~340 K under slow N_2 flow and the solids were dried at 353 K. Calcination of palladium and platinum precursor impregnated samples was carried out at 573 K for 1 h. Nickel acetylacetonate impregnated samples were annealed at 458 K for 2 h and at 653 K for 1 h, while nanotubes with cobalt precursor were calcined at 378 K for 45 min and then at 473 K for 45 min. Heating rates were set to 10 K/min.

Elemental contents were measured from five different locations of the samples with energy dispersive X-ray spectroscopy using a facility installed on a Zeiss Ultra *plus* field emission scanning electron microscope. Oxidation states of the metals in the samples were determined by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD electron spectrometer, monochromated Al K_α source operated at 150 W, charge neutralizer, analyzing area of $0.3 \times 0.7\ mm^2$). The average catalyst particle size was determined from electron micrographs taken by an energy filtered transmission electron microscope (EFTEM, Leo 912 Omega, 120kV, LaB_6 filament) assessing more than 200 particles from at least 3 different locations for each sample. Crystal sizes of the metal/metal oxides were determined with XRD (Bruker D8 Discover, Cu radiation source) by fitting a Lorenzial curve to measured reflections. Thermal gravimetric analysis was carried out with a Netzsch STA 409 PC Luxx facility (sample amounts of 5 to 12 mg were heated in air with a flow of 60 ml/min between 300 and 1023 K at a rate of 2 K/min). Temperature programmed reduction was studied with a Micrometrics Autochem 2910 equipment. First, approximately 100 mg of sample was placed in a U-shaped quartz tube and heated to 393 K at a rate of 10 K/min under He flow (50 ml/min) for half an hour. Before starting the reduction treatment the samples were cooled to room temperature. For TPR measurments the catalysts were heated to 923 K at a rate of 5 K/min for 30 min under a 1% H_2/Ar atmosphere.

3. Results and discussion

After impregnation, tiny particles of metal acetylacetonates (~1.5 nm) were formed and finely dispersed on the surface of nanotubes. Thermal decomposition of the precursor in air resulted in the formation of metal/metal oxide nanoparticles with a slightly larger size (<2 nm, Table 1). In the case of the cobalt decorated specimen the metal/metal oxide particles seemed to be somewhat smaller on average than the precursor salt particles. This is most likely caused by the Ostwald ripening of previously undetected $Co(acac)_3$ particles in the course of the decomposition experiment (Fig. 1). X-ray diffraction measurements showed broadened reflections of Pt and PdO phases in the corresponding powders, revealing an average crystal diameter of 7.2 ± 2.1 nm for Pt and 4.6 ± 0.3 nm for PdO as calculated by the Scherrer formula. The larger average crystal size values obtained by XRD compared to TEM are often seen for very small crystals [14,40]. In the case of the NiO_x/CNT and CoO_x/CNT samples, reflections originating from the catalyst nanoparticles were not observed indicating their very small size and/or amorphous nature (Figure S1 and Table 1).

Although the support material was acid treated to remove amorphous carbon and metal impurities, the presence of