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The synthesis of structured Pd/C hydrogenation catalysts by the chemical vapor deposition of Pd(allyl)Cp onto functionalized carbon nanotubes anchored to vapor grown carbon microfibers

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Abstract

Vapor grown carbon fibers (VGCF) were prepared by the iron-catalyzed decomposition of methane. The as-grown microfibers were treated by HNO_3, and iron nanoparticles were deposited onto the fiber surface by impregnation. Carbon nanotubes (CNT) were grown homogeneously as branches on the microfiber surface by tuning the process parameters of the methane decomposition. A composite carbon nanotube–carbon microfiber (CNT–VGCF) system was thus obtained and used as support for palladium nanoparticles. Oxygen-containing functional groups were introduced into the CNT–VGCF system by plasma treatment in a fluidized-bed reactor. The Pd/C catalyst was prepared by chemical vapor deposition on the CNT–VGCF support using Pd(allyl)Cp as a precursor (MOCVD) in a fixed-bed reactor. The effects of the surface treatment and the deposition of palladium were investigated by X-ray photoelectron spectroscopy (XPS). Only traces of palladium were detected after deposition on as-grown fibers, whereas a significantly higher concentration was found on plasma-treated fibers. The catalytic activity of the Pd/C catalyst was evaluated by the hydrogenation of cyclooctene in a fixed-bed microreactor under plug-flow conditions. The CNT–VGCF system was found to be a suitable structured support for Pd nanoparticles.

Keywords: Carbon nanotube; Carbon microfiber; Palladium nanoparticles; Functionalization

1. Introduction

Tailoring of a supported catalyst remains a challenge especially when the structure of the metals as well as the support is considered. The objective is to obtain structurally well-defined catalysts with nanoparticles of a known structure, which are bound to the support in a controlled manner. Metal-organic chemical vapor deposition (MOCVD), one of the most effective methods for achieving supported nanoparticles, allows for direct and complete deposition of active metals onto supports by the reaction between functional groups at the surface (such as the OH groups) and a suitable volatile organometallic precursor [1]. This method avoids steps such as impregnation, washing, drying, calcinations, and activation involved in solvent-based catalyst preparations.

The selective hydrogenation of alkynes and olefins is an important process for the purification of feed streams in the petrochemical industry. Supported palladium catalysts are known to be highly active and selective for these reactions [2–4]. The hydrogenation reactions are very sensitive to the metal particle size. A high dispersion of Pd particles is favorable in general [5,6]. The vapor deposition of the precursor may either be carried out in the presence of a reducing agent, resulting in the immediate reduction of the adsorbate at the same temperature, or in inert gas followed by reduction as a separate step. We showed recently that the latter tended to result in smaller Pd particles and higher catalytic activity [7].

The vapor grown carbon fibers (VGCF) can be prepared by decomposing hydrocarbons over transition metal catalysts such as iron, nickel or their alloys at high

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temperatures [8]. VGCFs are widely recognized as a promising support for heterogeneous catalysts because of their high purity, chemical stability and high mechanical strength [9]. Modifying the morphology of VGCFs by growing nanofibers or nanotubes (CNT) has been reported recently [10,11]. The modification of morphologies of supported catalysts can effectively improve catalytic reactions by achieving both a lower pressure drop as well as improved mass and heat transfer. In addition, the difficulties associated with catalyst separation can be overcome. In this communication, we present the preparation of palladium catalysts supported on structured carbon nanotubes, i.e., the CNT–VGCF system and its characterization.

2. Experimental

2.1. Preparation of the CNT–VGCF support

Both the parent fiber and the nanotubes in this work were grown from the iron-catalyzed decomposition of methane. The reactor used for the growth of fibers and nanotubes consisted of a horizontal quartz tube with a length and inner diameter of 100 and 3 cm, respectively. The feed gases had the following purities: CH_4 99.995%, H_2 99.99999%, and He 99.9999%. The flow rate of the feed stream was regulated by mass flow controllers, and the methane concentration in the exhaust gas stream was monitored on-line by a non-disperse infrared photometer (BINOS, Leybold-Heraeus). The conversion of methane (X) was derived from the methane mole fractions in the feed (y_0) and the exit gas stream (y) taking into account the increasing volumetric flow rate due to the decomposition of methane ($CH_4 \rightarrow C + 2H_2$):

$$X = \frac{1}{(1+y)} \frac{(y_0 - y)}{y_0}$$

The parent fibers used as support for the growth of nanotubes were grown at 1423 K on graphite foil (Grafoil®, Union Carbide), which had been impregnated by iron nitrate in advance. The average length and diameter of the strongly anchored parent VGCFs were 25 mm and 6 μm, respectively. The parent fibers were treated with concentrated nitric acid for 72 h at room temperature in order to introduce oxygen-containing groups onto the surface, which is essential for the successful impregnation of iron catalysts [12]. The nitric acid-treated fibers were dried at room temperature and then immersed in an iron nitrate solution for 3 h. The mixture was dried by circulating air at room temperature. The iron-loaded VGCFs were oxidized in air for 2 h at 623 K in order to stabilize the iron-containing particles. Subsequently, iron oxide was reduced by hydrogen and nanotubes were grown from CH_4 diluted by He (50% CH_4, 150 ml min^{-1} (STP)) for 20 min at 1173 K.

2.2. Preparation of supported palladium catalysts by MOCVD

The iron particles were removed from the CNT–VGCFs using diluted nitric acid. The CNT–VGCFs were then treated by an oxygen plasma (120 W, radio frequency generator) for 7 min in a fluidized-bed reactor. The Pd/CNT–VGCF catalysts were prepared by MOCVD of Pd(allyl)Cp in a fixed-bed reactor with a diameter of 10 mm. The reactor was first filled with 0.2 g CNT–VGCF support. A predetermined amount of precursor corresponding to the desired palladium loading of 5.0 wt.% was transferred into the sublimation chamber. The reaction chamber was kept at 333 K and the sublimation chamber at 323 K. Helium was used as carrier during the dissociative adsorption (first step). After 4 h, hydrogen diluted in helium (30% H_2) was introduced for the reduction (second step). The total flow rate was kept at 35 ml min^{-1} (STP) during the whole sequence of steps.

2.3. Characterization

The CNT–VGCFs were studied by scanning electron microscopy (Philips ESEM XL 30). The BET surface area was determined by nitrogen adsorption at 77 K. The samples were outgassed at 573 K until the pressure was lower than 500 Pa. The palladium loading was determined by ICP-OES (Pye Unicam 7000 ICP-OES Spectrometer). All X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum set-up equipped with a Gammadata-Scienta SES 2002 analyzer. Monochromatic Al Kα (1486.6 eV; anode operating at 14 kV and 55 mA) was used as incident radiation. XP spectra were recorded in the fixed transmission mode. In this work, a pass energy of 200 eV was chosen, resulting in an energy resolution better than 0.5 eV. Charging effects were compensated by the usage of a flood gun. Binding energies were calibrated based on the main C 1 s peak at 284.5 eV. The CasaXPS program was used for data treatment (peak fitting, content evaluation).

2.4. Determination of catalytic activity

The gas phase hydrogenation of cyclooctene was chosen as a test reaction, which was conducted in a laboratory-scale fixed-bed reactor under atmospheric pressure in the temperature range from 313 to 353 K using nitrogen as a carrier gas. The molar ratio of nitrogen, hydrogen and cyclooctene was 100:1:1, and the total flow rate was 300 ml min^{-1} (STP). The supported catalyst was hand-milled and diluted with quartz powder (25 mg Pd/CNT–VGCF catalyst in 2 g quartz powder) in the reactor in order to achieve plug-flow conditions and to avoid full conversion. The products were analyzed by on-line gas chromatography using a Chrompack CP-WAX 52 B column and a flame ionization detector.

3. Results and discussion

3.1. Preparation and characterization of parent fibers and secondary filaments

The fiber morphology can be tuned by a variety of parameters, including the growth temperature, the time on stream, the concentration of the feed gas, the catalyst loading, etc. We studied the growth of VGCFs as well as carbon fibers of different dimensions grown on VGCFs [13]. To optimise the growth conditions for different morphologies, the methane conversion was investigated as a function of temperature. It can be seen in Fig. 1 that the onset of the conversion was at about 1130 K. A local maximum appeared at about 1250 K, which is identified as resulting from catalytic conversion [14]. Carbon filaments originated from catalytic growth at lower temperature and were thickened by pyrolytic carbon decomposition at higher temperature into microfibers. Two temperature regimes can be distinguished based on the conversion curves, i.e., a regime between 1130 and 1250 K (dominated by the fiber initiation) and a lengthening and thickening-dominated regime above 1250 K. In order to achieve nanotubes on VGCFs, a temperature of 1173 K (just above the fiber-initiation temperature) was selected as the growth temperature for nanotubes, thus avoiding the main thickening process.

The parent fibers used in this work were grown from an iron-catalyzed decomposition of methane on graphite foil at 1423 K. Prior to the fiber growth, the graphite foil was impregnated by an iron nitrate solution and subsequently dried. Deposition of metal particles onto the surface of the parent fibers is a necessary step in order to grow secondary filaments, and a small catalyst particle size is essential for the growth of nanotubes. This remains, however, a challenge due to the hydrophobic and inert nature of the fibers.

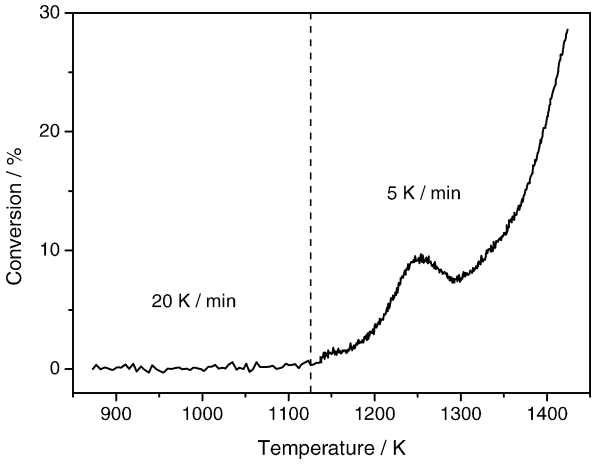


Fig. 1. Conversion of CH_4 as a function of temperature during the growth of fibers on the iron-loaded graphite foil. A feed mixture consisting of 30% CH_4 and 70% H_2 was supplied to the reactor using a flow rate of 250 ml min^{-1} (STP).

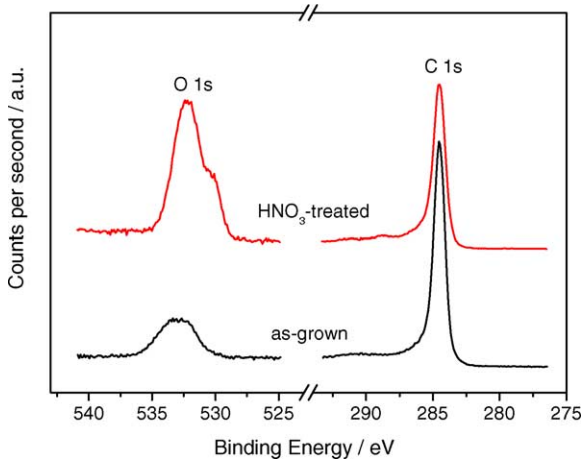


Fig. 2. XP spectra of as-grown and HNO_3-treated parent VGCFs. The O 1s peaks were multiplied by a factor of 3.

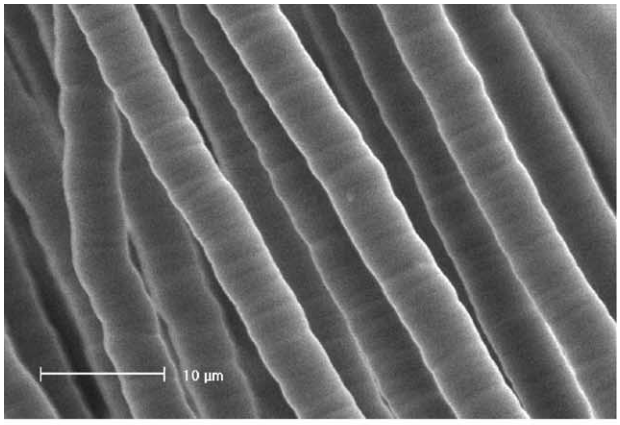
A variety of surface treatment methods were reported including nitric acid treatment, plasma treatment, oxidation in air, supercritical fluid treatment, etc. [15–17]. Nitric acid treatment was chosen for the modification of parent VGCFs.

The XPS studies showed that the concentration of oxygen-containing species on the fiber surface increased significantly due to the HNO_3 treatment (Fig. 2). In addition to the film of molecular water contributing to the O 1s peak at about 532 eV, a second peak at about 530.5 eV is clearly identified originating from oxygen-containing surface functional groups [18]. Table 1 summarizes the surface composition of as-grown and treated fibers derived from the XPS measurements. A more detailed XPS study including the deconvolution of the O 1s and C 1s peaks is in progress. Heating will be performed in the directly attached XPS preparation chamber to simulate the conditions prior to and during nanotube growth, and XP spectra will be acquired to monitor the changes on the fiber surface as a function of temperature and gas phase composition.

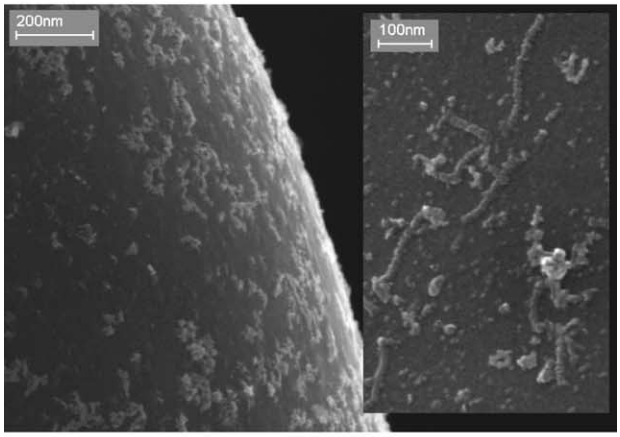
Fig. 3a shows an SEM image of as-grown parent microfibers. To achieve nanoparticles, HNO_3-treated parent fibers were soaked in a diluted iron nitrate solution of predetermined amounts. The mixture was dried by circulating air at room temperature, and on the fibers an iron loading of 0.36 wt.% was achieved. The loaded fibers

Table 1
Atomic concentration of oxygen and palladium on the fiber surfaces derived from the XP spectra

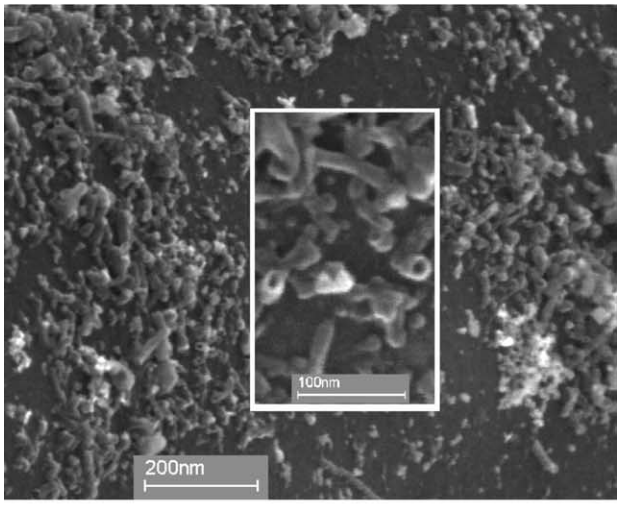
Sample	Atomic concentration on the fiber surface (%)	
	Oxygen	Palladium
As-grown VGCF	6.1	–
HNO_3-treated VGCF	18.4	–
Plasma-treated VGCF	14.5	–
Pd/as-grown VGCF	–	0.05
Pd/plasma-treated VGCF	–	3.9



(a)



(b)



(c)

Fig. 3. SEM images of parent fibers supported nanotubes: (a) as-grown parent microfibers; (b) part of a fiber covered by as-grown nanotubes with a diameter of about 15 nm. The inset shows an image with a higher magnification. (c) The same sample after washing by 1 M HNO_3 in order to remove the iron catalyst particles. The open ends of nanotubes can be seen clearly in the inset.

were oxidized in air at 623 K in order to stabilize the catalyst particles. The parent fibers were then heated from room temperature up to the growth temperature of 1173 K in hydrogen. During the heating in hydrogen, the iron oxide particles were reduced to the metallic state. The nanotubes were grown for 20 min from methane diluted by helium (50% CH_4, 150 ml min^{-1} (STP)) at 1173 K. Fig. 3b shows the as-grown nanotubes on the VGCFs. It can be seen in the inset that the diameter of the nanotubes amounts to a few tens of nanometers whilst the length surpasses 100 nm. Catalyst particles can also be seen in the inset. By washing with 1 M HNO_3, the catalyst particles were removed and nanotubes appear with open ends (Fig. 3c). The BET measurement yielded a specific surface area of 8.7 $m^2\ g^{-1}$ for the CNT–VGCF, which is much higher than about 0.4 $m^2\ g^{-1}$ derived from the mean diameter of the parent fibers. Due to the large dimensions of the parent fibers (average diameter of 6 μm), a further increase of the BET area can only be achieved by reducing the size of the parent fibers and increasing the number of anchored CNTs as shown by our ongoing studies.

3.2. Preparation and characterization of supported palladium catalysts by MOCVD

To employ carbon fibers as a catalyst support, it is important to modify their surface, for instance, by the introduction of oxygen-containing surface groups [19]. Due to oxidation, the hydrophobic carbon surfaces become more hydrophilic. The wetting properties are very important in both catalyst preparation and application. Furthermore, a stronger interaction of the fibers with catalyst precursor complexes can be achieved, and oxygen-containing species can be used as anchoring sites for the immobilization of larger molecules such as metal–ligand systems. It is reported that oxygen-containing functional groups can be effectively enhanced by oxygen plasma treatment [20]. Hence, the surface of the VGCFs and the CNT–VGCFs was modified by oxygen plasma in a fluidized-bed reactor after the iron catalyst particles had been removed by diluted nitric acid.

In a recent study we showed that the deposition of palladium from Pd(allyl)Cp using a two-step method, consisting of the dissociative adsorption of the Pd precursor followed by its reduction, was more effective to prepare highly active catalysts than the reductive CVD of the precursor in H_2, i.e., in one step [7]. The Pd particle size appeared to be smaller in the two-step method, and the catalysts turned out to be highly active for the hydrogenation of cyclooctene. Therefore, the two-step CVD process was used for the preparation of Pd/C catalysts. The MOCVD of palladium was performed on both as-grown and plasma treated microfibers and on plasma-treated CNT–VGCF samples.

The XP spectra of the as-prepared Pd/VGCF catalysts are shown in Fig. 4. Only traces of palladium were detected on the as-grown sample, whereas the palladium peak increased significantly on plasma-treated catalysts (Table 1). The

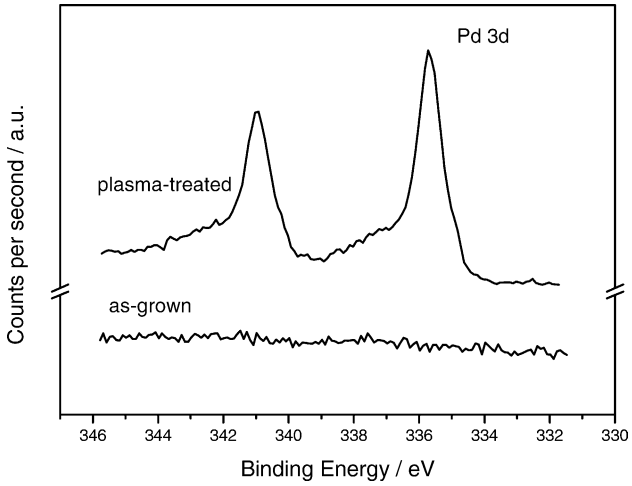


Fig. 4. Pd 3d XP spectra of as-grown Pd/VGCF and plasma-treated Pd/VGCF samples.

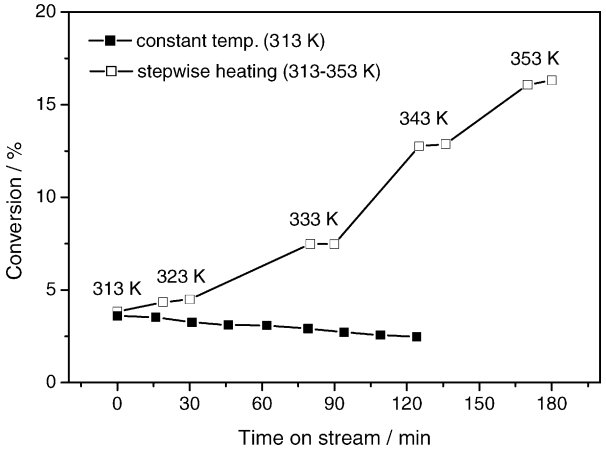


Fig. 5. Conversion of cyclooctene to cyclooctane over the Pd/CNT–VGCF catalyst (1.12 wt.% Pd) as a function of time on stream at constant temperature (313 K) and during heating (313–353 K). The ratio H_2:COE:N_2 amounted to 1:1:100 at a total flow rate of 300 ml min^{-1} (STP).

integrated XPS data reveal that the atomic concentration of palladium on the surface of the as-grown Pd/VGCF sample was about 0.05% (Table 1). However, no palladium was detected in the same sample by ICP-OES measurement. We assume that this is due to a very low palladium concentration in the sample. The surface atomic concentration of palladium derived from the XPS measurement for the plasma-treated sample was 3.9% (Table 1). Thus, oxygen-containing functional groups introduced by plasma treatment on the surface are essential to achieve a high Pd loading. The Pd $3d_{5/2}$ binding energy of 335.7 eV is somewhat higher than that of bulk metallic Pd. In addition, oxidized Pd species are present giving rise to a broad shoulder at about 337 eV [21]. Further studies are in progress including an additional hydrogen treatment in the preparation chamber to achieve a consistent deconvolution of the Pd 3d spectra.

3.3. Catalytic activity for the hydrogenation of cyclooctene (COE)

The loading of palladium in the plasma-treated Pd/CNT–VGCF sample determined by ICP-OES was found to be 1.12 wt.%. A degree of COE conversion of about 3.6% was achieved using 25 mg catalyst at 313 K (Fig. 5). The degree of conversion using the same amount of as-grown Pd/CNT–VGCF was below the detection limit. When the reactor temperature was increased in steps of 10 K, the conversion was found to increase correspondingly up to 16.3% at 353 K. Our on-going work shows that the palladium particle size and distribution can be well tuned on carbon nanotubes [22], and a highly active hydrogenation catalyst comparable with the Pd/silica catalyst reported in our former work [7] can be achieved. To fully develop the application of Pd/C catalysts, we are at present improving the BET area of the CNT–VGCF system and trying to avoid all synthesis steps involving liquids, i.e., our final aim is to develop a total gas-phase synthesis of Pd/CNT–VGCF catalysts. In addition, characterization of the palladium particles on the CNT–VGCFs by TEM is in progress.

4. Conclusions

1. Carbon nanotubes with a diameter of a few tens of nanometers were successfully grown on carbon microfibers. The distribution of the nanotubes was found to be homogeneous by SEM.
2. Palladium catalysts were prepared by MOCVD using the CNT–VGCF composite as support. Oxygen-containing functional groups were found to be essential for the deposition of palladium on the surface of the composite. The application of an oxygen plasma proved effective for functionalization of the carbon surfaces.
3. The catalytic activity of the Pd catalysts was tested by hydrogenating cyclooctene. Pd supported on the composite CNT–VGCF support was found to be an active hydrogenation catalyst.

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