The two-step chemical vapor deposition of Pd(allyl)Cp as an atom-efficient route to synthesize highly dispersed palladium nanoparticles on carbon nanofibers

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Highly dispersed palladium nanoparticles supported on carbon nanofibers, which show high catalytic activity and stability in the hydrogenation of cyclooctene, were synthesized by the two-step metal organic chemical vapor deposition (MOCVD) of allylcyclopentadienylpalladium (Pd(allyl)Cp) as precursor at atmospheric pressure.

Since their discovery in 1991,[1] carbon nanotubes and nanofibers have attracted great scientific interest from a fundamental point of view and because of their potential applications such as structure reinforcement, nanoelectronic devices, and field emitters.[2] The novel nanostructured carbon materials are considered promising heterogeneous catalysts or catalyst supports due to their unique structural, electronic and mechanical properties.[3] Several studies report that the use of carbon nanofibers as catalyst supports can improve activity and selectivity in hydrogenation,[4] hydroformylation[5] and electrocatalysis.[6] The supported catalysts were prepared by various conventional methods such as impregnation, co-precipitation, and ion exchange. However, there are difficulties in controlling the preparation steps and in obtaining highly dispersed metal particles due to the various effects of the solvent on the adsorption process. MOCVD has been shown to be a powerful method for generating highly dispersed metal catalysts in a controlled and reproducible manner.[7] Recently, palladium was deposited onto mesoporous MCM materials by the grafting route, and the as-prepared catalysts showed remarkable activity in Heck reactions.[8] Also, palladium was deposited onto silica supports by MOCVD in a fluidized-bed reactor resulting in highly dispersed Pd nanoparticles.[9] However, the synthesis of well-dispersed metal particles on carbon nanofibers is challenging as only a few sites are available for the anchoring of the organometallic precursors.[10] Here, we report the synthesis of evenly distributed Pd nanoparticles supported on carbon nanofibers by MOCVD. The materials exhibit excellent activity for the hydrogenation of cyclooctene and may find additional applications in the synthesis of fine chemicals and in electrocatalysis.

The palladium deposition onto carbon nanofibers was achieved by the two-step chemical vapor deposition of Pd(allyl)Cp as a precursor with high vapor pressure in a fixed-bed reactor. Carbon nanofibers were supplied by Applied Sciences Inc. The outer diameter of the carbon nanofibers was 70–200 nm, the length was 20–100 μm, and the BET surface area amounted to 50–60 $m^2 g^{-1}$. The carbon nanofibers were functionalized for 3 h at reflux with 5 M HNO_3 prior to palladium deposition. The precursor was sublimed at 50 °C and adsorbed at 80 °C in He as carrier gas. The adsorbed precursor was reduced at 80 °C in diluted H_2 at atmospheric pressure. The level of Pd loading was found to depend on the degree of functionalization of the carbon nanofibers and on the amount of precursor provided in the sublimation chamber. Transmission electron microscopy (TEM) images did not reveal the presence of any Pd particles when the support was not functionalized by HNO_3 (Fig. 2, left). Instead, the deposition of Pd black was observed on the glass walls of the reactor due to the low amount of anchoring sites on the support in agreement with phenomena observed during the deposition of platinum onto carbon nanospheres, multi-walled carbon nanotubes or graphite.[10] Samples with Pd loadings of 2.04 wt% and 4.30 wt% (from ICP-OES) were obtained, when the designed loadings were 2.5 wt% and 5.0 wt%, respectively. Their X-ray diffraction (XRD) patterns shown in Fig. 1 only reveal a broad Pd(111) diffraction peak at about 40.2° for the 4.30 wt% Pd sample, indicating rather small Pd particles in addition to the diffraction peaks originating from the carbon nanofibers. The right part of Fig. 2 shows a TEM image of the functionalized sample with 2.04 wt% Pd. Highly dispersed and evenly distributed Pd particles with diameters of 2–4 nm are observed. The high degree of dispersion points to a strong interaction between the metal precursor and the carbon nanofibers, resulting in a large number of Pd nuclei. Similar

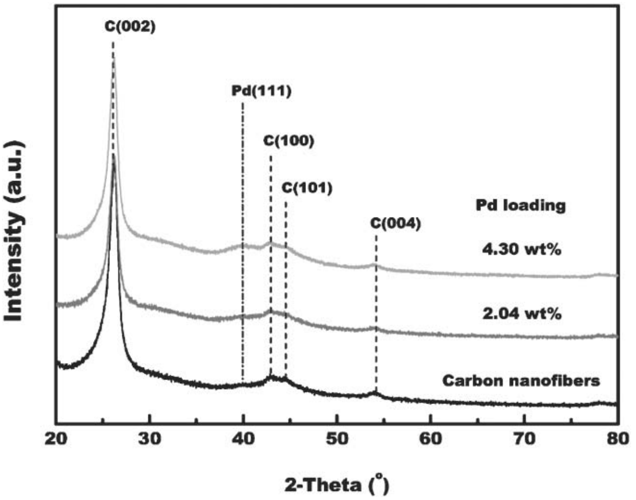

Fig. 1 XRD patterns of the functionalized carbon nanofibers prior and subsequent to Pd MOCVD.

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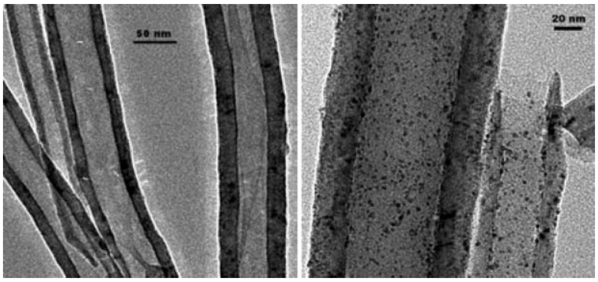

Fig. 2 TEM images of untreated (left) and functionalized carbon nanofibers (right, 2.04 wt% Pd) subsequent to Pd MOCVD.

observations were reported by Pham-Huu *et al.* for carbon fiber-supported Pd catalysts synthesized by incipient wetness impregnation.[4b] However, the distribution of the Pd particles achieved in this way was in the range from 1 to 9 nm compared with the distribution in the range from 2 nm to 4 nm (Fig. 2), clearly demonstrating the advantages of MOCVD.

The two-step chemical vapor deposition was also studied by on-line mass spectroscopy taking the fragmentation patterns into account. During the first step (Fig. 3, top), Pd(allyl)Cp was adsorbed dissociatively on the surface of the carbon nanofibers. We simultaneously observed the formation of cyclopentadiene (m/z = 66) and propene (m/z = 41). However, only cyclopentadiene was detected during the adsorption when silica was used as support.[9] It is known that the functionalization of carbon nanofibers under strongly acidic conditions results in the formation of carboxylic, hydroxylic and carbonyl groups at defect sites in the approximate ratio of 4 : 2 : 1.[11] The carboxylic groups are assumed to be mainly responsible for the dissociative adsorption of the precursor replacing the roughly equally strongly bound allyl and Cp ligands. Obviously, it depends on the reactivity of the surface groups as to which ligand is dissociated off. On silica hydroxyl groups are considered as the anchoring sites of Pd(allyl)Cp.[8,9] During the reduction step (Fig. 3, bottom), cyclopentane (m/z = 70) and propane (m/z = 29) were obtained simultaneously. It is not possible to decide whether the alkanes originate from hydrogen-assisted elimination or from subsequent olefin hydrogenation over metallic Pd particles within the fixed bed.

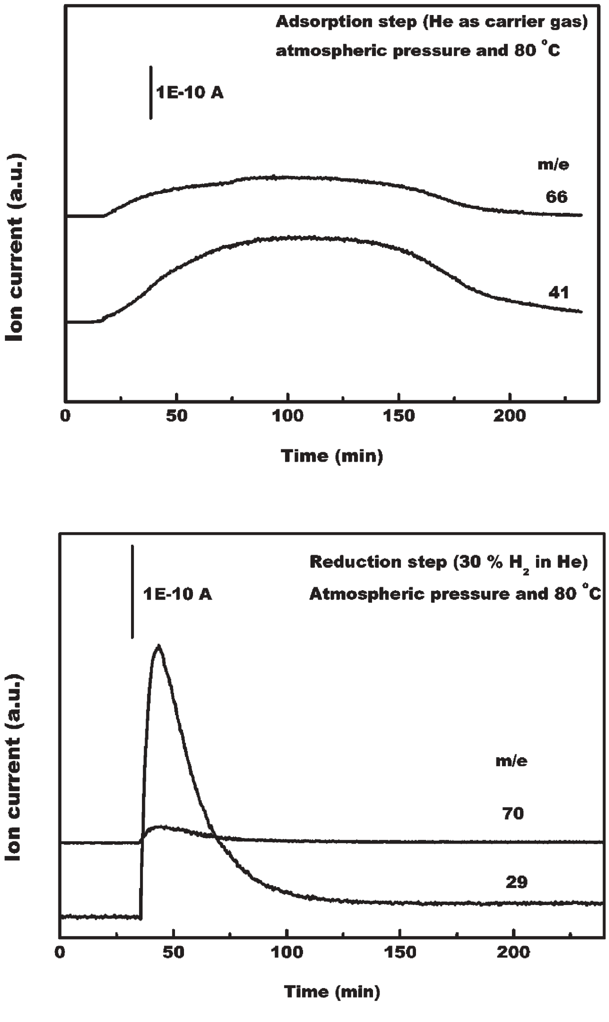

Fig. 3 Mass spectroscopy data obtained during the adsorption of the precursor in He (top) followed by the reduction in 30% H_2 (bottom).

The hydrogenation of cyclooctene was carried out in a fixed-bed reactor at 40 °C under atmospheric pressure using N_2 as carrier gas. The molar ratio of N_2 to H_2 to cyclooctene was 100 : 1 : 1. The catalyst weight was 25 mg to avoid full conversion. The total flow rate amounted to 300 $cm^3 min^{-1}$ (STP). The composition of the reactor effluent was analyzed by on-line gas chromatography using a Chrompack CP-WAX 52 CB column and a flame ionization detector. The catalytic activities of the catalysts with Pd loadings of 2.04 wt% and 4.30 wt% are shown in Fig. 4. Both catalysts are found to be highly active and stable, which is a significant improvement upon the catalysts produced by the impregnation methods. Jackson *et al.*[12a] observed rapid deactivation and a low hydrogenation rate for the catalysts produced by impregnation in agreement with results obtained by Okhlopkova *et al.*[12b] These results can presumably be attributed both to strong adsorption of cyclooctene on the catalysts and to the presence of micropores in the support. For carbon nanofibers, the high activity and stability can be attributed to the special interaction between the palladium nanoparticles and the carbon nanofibers, which has also been observed for Ni/CNFs[4b] and Ru/CNFs.[4c] In addition, the open structure of a fixed bed consisting of non-porous carbon

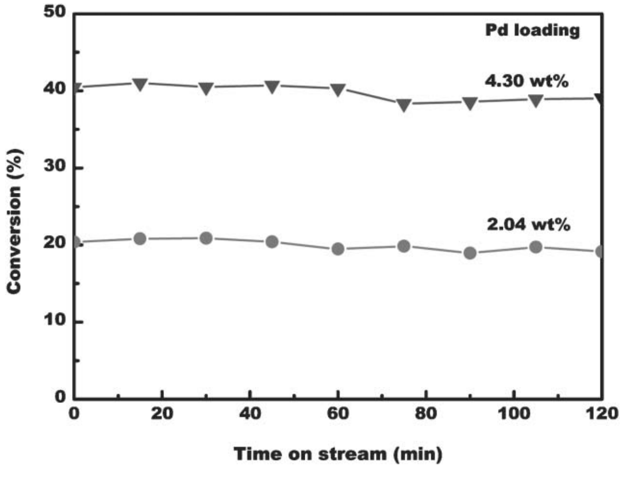

Fig. 4 Hydrogenation of cyclooctene over Pd supported on carbon nanofibers (atmospheric pressure and 40 °C).

nanofibers is beneficial to avoid mass transfer limitations. These effects are consistent with recent results reported by Pham-Huu *et al.* for the hydrogenation of cinnamaldehyde.[4b]

In conclusion, the two-step MOCVD can be efficiently used to synthesize highly dispersed Pd nanoparticles supported on carbon nanofibers under mild conditions. The functionalization of the carbon nanofibers is a necessary step to provide anchoring sites. The catalysts show high activity and stability in the hydrogenation of cyclooctene, presumably due to special metal–support interactions and the absence of micropores. Thus, the MOCVD route is of great potential in the controlled synthesis of carbon fiber-supported catalysts.

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Notes and references

1 S. Iijima, *Nature*, 1991, **354**, 56.

2 (*a*) R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787; (*b*) H. J. Dai, *Acc. Chem. Res.*, 2002, **35**, 1035.

3 (*a*) K. P. de Jong and J. W. Geus, *Catal. Rev. Sci. Eng.*, 2000, **42**, 481; (*b*) P. Serp, M. Corrias and P. Kalck, *Appl. Catal., A*, 2003, **253**, 337; (*c*) G. Mestl, N. I. Maksimova, N. Keller, V. V. Roddatis and R. Schlögl, *Angew. Chem., Int. Ed.*, 2002, **40**, 2066.

4 (*a*) J. M. Planeix, N. Coustel, B. Coq, V. Brotons, P. S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier and P. M. Aiayan, *J. Am. Chem. Soc.*, 1994, **116**, 7935; (*b*) C. Pham-Huu, N. Keller, M. J. Ledoux, L. Charbonnière and R. Ziessel, *Chem. Commun.*, 2000, **19**, 1871; (*c*) C. Park and R. T. K. Baker, *J. Phys. Chem. B*, 1998, **102**, 5168; (*d*) C. H. Liang, Z. L. Li, J. S. Qiu and C. Li, *J. Catal.*, 2001, **211**, 278.

5 (*a*) R. Gao, C. D. Tan and R. T. K. Baker, *Catal. Today*, 1999, **65**, 385; (*b*) R. Giordano, P. Serp, P. Kalck, Y. Kihn, J. Schreiber, C. Marhic and J. L. Duvail, *Eur. J. Inorg. Chem.*, 2003, 610.

6 (*a*) C. A. Bessel, K. Laubernds, N. M. Rodriguez and R. T. K. Baker, *J. Phys. Chem. B*, 2001, **105**, 1115; (*b*) E. S. Steigerwalt, G. A. Deluga, D. E. Cliffel and C. M. Lukehart, *J. Phys. Chem. B*, 2001, **105**, 8097; (*c*) W. Z. Li, C. H. Liang, J. S. Qiu, W. J. Zhou, H. M. Han, Z. B. Wei, G. Q. Sun and Q. Xin, *Carbon*, 2002, **40**, 787.

7 P. Serp and P. Kalck, *Chem. Rev.*, 2002, **102**, 3085.

8 C. P. Mehnert, D. W. Weaver and J. Y. Ying, *J. Am. Chem. Soc.*, 1998, **120**, 12289.

9 X. Mu, U. Bartmann, M. Guraya, G. W. Busser, U. Weckenmann, R. Fischer and M. Muhler, *Appl. Catal., A*, 2003, **248**, 85.

10 (*a*) P. Serp, R. Feurer, Y. Kihn, P. Kalck, J. L. Faria and J. L. Figueiredo, *J. Phys. IV*, 2002, **12**, 29; (*b*) P. Serp, R. Feurer, Y. Kihn, P. Kalck, J. L. Faria and J. L. Figueiredo, *J. Mater. Chem.*, 2001, **11**, 1980.

11 (*a*) T. Sainsbury and D. Fitzmaurice, *Chem. Mater.*, 2004, **16**, 2174; (*b*) T. G. Ros, A. J. van Dillen, J. W. Geus and D. C. Koningsberger, *Chem. Eur. J.*, 2002, **8**, 1151.

12 (*a*) S. D. Jackson, G. J. Kelly, S. R. Watson and R. Gulickx, *Appl. Catal., A*, 1999, **187**, 161; (*b*) L. B. Okhlopkova, A. S. Lisitsyn, V. A. Likholobov, M. Gurrath and H. P. Boehm, *Appl. Catal., A*, 2003, **204**, 229.