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*Suzuki-Miyaura cross-coupling and Heck reactions
catalysed by Pd on carbon nanofibres*

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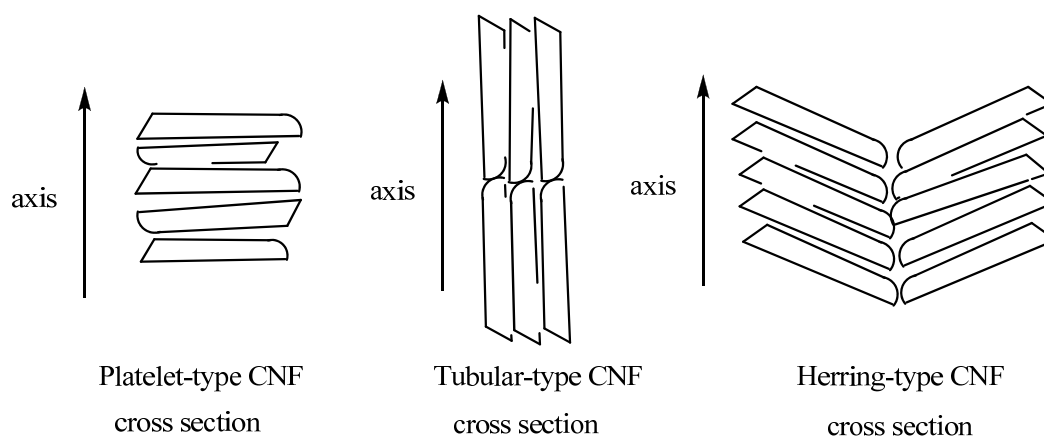
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Abstract: Platelet, tubular and herring-bone carbon nanofibres were doped with Pd under various conditions. The catalysts were analysed as to the Pd-content and as to the size distribution of the Pd particles. The Pd-doped carbon nanofibres were screened for their catalytic activity in the Suzuki-Miyaura cross coupling and in the Heck reaction.

Keywords: Carbon nanofibres, Heck reaction, Suzuki-Miyaura cross coupling, ultrasonication, catalysis

1. Introduction

Both the Suzuki-¹ and Heck-Mizoroki² reactions have become part of the standard repertoire in organic synthetic chemistry. Starting with the seminal work of Jeffery³ on the use of 'ligandless' palladium as catalysts for these reactions, a large amount of research work has been devoted to the development of catalytic systems using palladium 'immobilized' on solid surfaces.⁴ Within this context, palladium on carbon (Pd/C) has been used extensively.⁵ More recently, defined carbon structures such as carbon nanotubes,⁶ have been investigated as supporting surfaces for palladium (Pd) and other catalytic metals. In the following, the authors describe a study of using carbon nanofibres (CNFs) as support for Pd.



Schematic representation (adopted) of the three basic types of carbon nanofibers used in this study

2. Results and Discussion

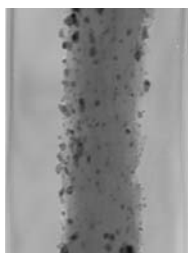
The structure of CNF has been recognized as nano – sized monocrystals of graphite. CNFs are commonly classified into 3 types, depending on how the graphene sheets line up to the fiber axis: *platelet type* CNFs have the graphene sheets lined up vertically to the fiber axis, while in the *tubular type* CNFs graphene sheets are parallel to the axis. In the *herringbone type* CNFs, the graphene sheets show an inclination to the fiber axis. The platelet type CNFs have dense lamination and largely characteristics of a crystal. Tubular type CNFs possess an inside cavity. In herringbone type CNFs, the surface area is large, and surface edges are mainly exposed. Usually, the CNFs have a diameter in the nm scale and a length in the $\mu\text{m} \sim \text{nm}$ scale. For the most part, CNFs are structurally strong and chemically stable.⁷

Herringbone type CNF has been thought to be suitable as a catalyst support medium and has been reported to be a good absorbant of hydrogen.^{7e,8} Endo and co-workers^{8a} have shown that it is possible to dope certain CNF materials with metals selectively along the edges. There have been reports of better reactivity and selectivity in certain cases in hydrogenation reactions with Ni, Pd, Pt or Ru supported on CNF when compared to these metals supported on silica or alumina.⁹ Nevertheless, very little had been done on studying the use of metal doped CNFs as catalysts in C-C coupling reactions when the present work was started.

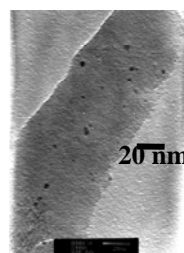
Doping Experiments of CNFs with Palladium

In the experiments detailed below, the following CNFs were used: platelet CNFs, synthesized from carbon monoxide (in a mixture with hydrogen) over an iron catalyst at 600 °C, tubular CNFs from ethylene (in a mixture of hydrogen) over an Fe-Ni (6 : 4) alloy catalyst at 630 °C, and herringbone CNF synthesized over a Cu-Ni (2 : 8) alloy catalyst at 580 °C.¹⁰ Two main methods of doping were adopted: a) doping by permeation at rt; b) doping in ethylene glycol under microwave irradiation.^{11,12} Specifically, the following doping procedures were employed: 1.) doping with PdCl₂ / 1.5N HCl under silent conditions at rt and subsequent reduction with either NaBH₄, sodium formate or hydrazine [abbreviated below as permeation]; 2.) doping with PdCl₂ / 1.5N HCl in the presence of polyvinylpyrrolidone K-30 (PVP) in ethanol under silent conditions at rt and subsequent reduction with NaBH₄ [abbrev. permeation/PVP]; 3.) doping by

the microwave-polyol method¹¹ in absence [abbrev. microwave]; and 4) in presence of PVP [abbrev. microwave/PVP]. The prepared materials were analysed by TEM, ICP-mass, elemental analysis and wet-chemical analysis to determine the Pd-content, and the Pd particle size distribution.



Herringbone type CNF doped
with the microwave-polyol method



Platelet type CNF doped
with the permeation method

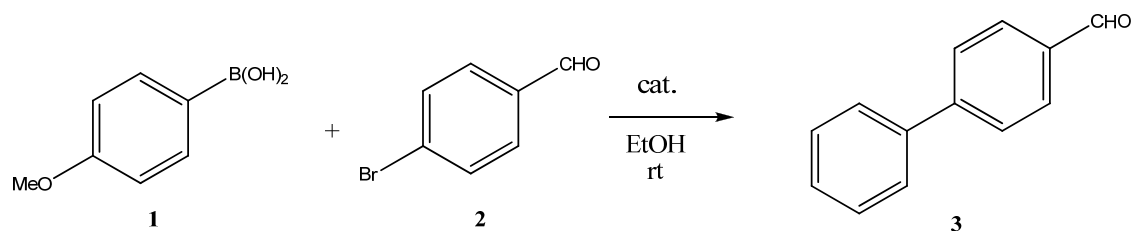
Overall, it was noted that when the carbon material was doped using the permeation method (PdCl_2/HCl resulting in $0.1\text{M H}_2\text{PdCl}_4$) at rt, followed by reduction with NaBH_4 , 0.9 w% – 2.7 w% Pd with a size distribution of 2-5 nm could be found on the *platelet type* CNF, and 2.4 w% – 4.8 w% Pd with a size distribution of 5-15 nm on the *tubular-type* CNF. The lower values of 0.9/2.4 w% Pd could be found in the presence of PVP during the permeation, the higher values of 2.7/4.8 w% Pd in the absence of PVP during the permeation. Using the microwave-polyol method in the absence of PVP, the *platelet type* CNF could be doped with 4.5w% to 4.7w% Pd of 15-25 nm particle size. In the presence of PVP 1.6 w% to 1.9 w% Pd could be found on the *platelet type* CNF with a particle size of 15-25 nm. Under the same conditions (no PVP), the *tubular* CNF was doped with 3.2 w% to 3.8 w% Pd with a particle size distribution of 5-20 nm. Here, no significant doping could be achieved when using the microwave-polyol method in the presence of PVP. Herring-bone CNF could be doped with 3.2 w% to 3.7 w% Pd (particle size 15-25 nm) using the microwave polyol method in the presence of PVP, and with 1.8 w% to 2.0 w% in absence of PVP. Similarly, activated carbon (Darco KB, 100 mesh, wet powder) was doped with Pd.

Reactivity of the Pd doped CNFs towards the Suzuki-Miyaura- and the Heck-Mizoroki cross coupling reactions

The Pd doped CNFs produced above were utilized in Suzuki-Miyaura cross coupling reaction of 4-bromobenzaldehyde with arylboronic acids under different conditions. The relative turn-over frequencies of the prepared catalysts were compared with palladium salts, palladium complexes and commercially available Pd on carbon (10w% Pd on C, Kishida). Initially, the Suzuki reaction of 4-bromobenzaldehyde with phenylboronic acid was studied in acetone, a solvent which is not very conducive to this reaction. Here, it was found that *Pd doped herringbone type* CNF prepared by the *microwave/polyol method in the presence of PVP* with subsequent washing of the catalyst with ethanol to remove excess PVP from the catalyst's surface produced the

highest turn-over frequency (TOF) under these conditions. The TOF was found to be higher than for PdO, PdCl₂, Pd(OAc)₂, Pd(PPh₃)₂Cl₂, Pd(PPh₃)₄, commercial Pd/C, and Pd on activated carbon, produced by the authors in the same manner as described above for the CNFs.

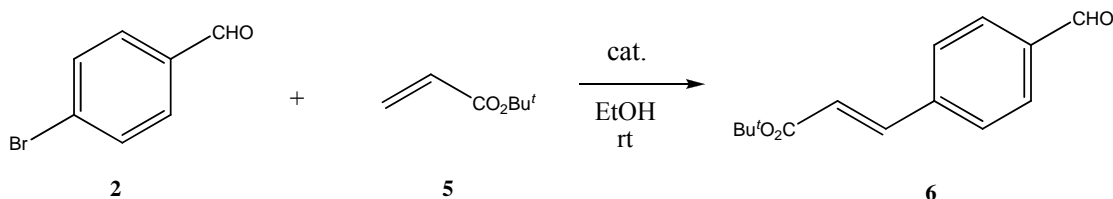
Next, the reaction was studied in ethanol as solvent. Here, again the Pd doped herringbone type CNF prepared by the microwave/polyol method in the presence of PVP gave the best TOF among the Pd on C studied, which included commercially available Pd on C and Pd on C prepared under the conditions described above for the CNFs. However, the TOF could not compare with the TOF found for PdCl₂ and for Pd(OAc)₂ under these conditions. A typical reaction is found below.



microwave: microwave-polyol method
H: herringbone structure
PVP: doping occurred in the presence of PVP

for Pd(PVP)/CNF(H) (Microwave): TOF = 21.0 h⁻¹

Lastly, the Heck reaction of 4-bromobenzaldehyde with *tert*-butylacrylate was studied in DMF at 100 C. Here, the best TOF was found for Pd doped tubular type CNF produced by the permeation method in presence of PVP. Slightly lower was the TOF of Pd doped activated carbon produced by the permeation method in absence of PVP. Notable but lower TOF numbers were found for Pd(OAc)₂ and Pd(PPh₃)₂Cl₂ under these conditions. Other Pd on CNF catalysts and commercial Pd on C gave appreciably lower TOFs.



T: tubular structure
PVP: doping occurred in the presence of PVP

for Pd(PVP)/CNF(T) (Permeation): TOF = 44.6 h⁻¹

In conclusion, selected Pd on CNF catalysts showed a good catalytic reactivity in Suzuki- and Heck reactions. Specifically, Pd on herringbone CNF produced by the microwave/polyol method in presence of PVP was found to be a good catalyst in the Suzuki reaction, while Pd on tubular CNF produced by the permeation method in presence of PVP was found to be a good catalyst in the Heck reaction.

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