

1 Title of the project

Characterization and catalytic properties of systems of Pt particles supported on multi-wall carbon nanotubes for the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol.

2 Applicants

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5 Abstract:

The importance of catalysis and catalytic systems in contemporary industry cannot be overestimated. Innovation in this so well established field arises from a desire for higher selectivity and efficiency, lower costs, as well as modern legislation which pushes for environmentally friendly processes. Carbon supported precious metal catalysts are currently frequently employed as they present a number of advantages. In accordance with this paradigm the proposed research will attempt to characterize the catalytic activity of model systems of platinum nanoparticles supported on multi-wall carbon nanotube (MWCNT) supports. The actual catalytic efficiency will be measured against the hydrogenation of α,β -unsaturated aldehydes to the corresponding unsaturated alcohol (specifically cinnamaldehyde to cinnamyl alcohol) in terms of activity and selectivity. These systems will be created using novel nanoscience techniques, both physical and chemical in nature, that allow for maximum precision, control and reproducibility facilitating the detailed study of all the properties pertinent to catalysis. Our aim is to correlate the techniques used to the morphology of support and active phase and, ultimately, to the catalytic activity these present, by a rigorous characterization of these systems in every step of the synthetic procedures.

6 Duration of the project

4 years starting January 2008

7 Personnel

7.1 Senior scientist

Name	Main Task	Time
Prof. Dr. P. Rudolf	Supervision and management	10%

7.2 Junior scientist and technician

Name	Main Task	Time
A. Ampoumogli	Experiments	90%

8 Cost estimates

8.1 Personnel positions

One PhD position for 4 years.

8.2 Running budget

The running budget will be 15k€ per year.

8.3 Equipment

8.3.1 Available equipment

- XPS (X-ray Photoemission Spectroscopy).
- STM (Scanning Tunneling Microscope).

8.3.2 Not currently available equipment

- TEM (Transmission Electron Microscope). This will be available through a collaboration with the group of Prof. Dr. J.Th.M. De Hosson.
- N₂ BET (Brunauer, Emmett and Teller) porosimetry. This will be available through a collaboration with the group of Prof. Dr. Ben L. Feringa.
- Evaporation chamber for the loading of the Pt metal on the support. This will be available through a collaboration with the group of Prof. Dr. Paul Blom.
- Setup for the catalytic tests. This will be available through a collaboration with the group of Prof. Dr. Ben L. Feringa.

- Chemical Fluid Deposition (CFD) setup. Will be assembled.
- Plasma treatment chamber. This will be available through a collaboration with the group of Dr. Carla Bittencourt at the university of Mons-Hainaut, Mons, Belgium.

8.4 Other support

The project will be supported by the Zernike Institute for Advanced Materials and the Rijksuniversiteit Groningen which also contributes the senior scientist and the technician.

8.5 Budget summary (in k€)

Personnel	2008	2009	2010	2011	Total
PhD students					
Postdocs					
Technicians					
Visitors					
Personnel Costs	43	43	43	52	172
Running Budget	15	15	15	15	60
Equipment					
Total					

9 Research program

1. Introduction
2. Motivation
3. Goals
4. Description of the research
5. Plan of work

9.1 Introduction

Catalysts in the form of metal nanoparticles dispersed on a carbonaceous support are at the heart of many chemical processes in the industry (in liquid phase hydrogenation, dehydrogenation or oxidation reactions [1]) as well as being the functional part of many everyday systems such as sensors, filters and detectors [2]. Supported catalysts finely disperse and stabilize the metallic particles allowing more catalytically active atoms to be reachable than even when the metal is ground to a fine powder. Carbon is employed as a support because it can be made very porous, it is resistant to acidic and basic media (which is not true for alumina or silica which are other traditionally used supports, valued

for their porosity) and the precious (or toxic) metal can easily be recovered i.e. the carbon support is simply burned away. Currently used carbon supports are activated carbon, carbon black, graphite and graphitized material. The relevant chemical properties arise from the incorporation of oxygen in the form of surface oxides (e.g. carboxylic groups, phenolic groups, etc) onto the carbon surface during manufacture of the support (activation of carbon).

Carbon nanotubes (CNTs), regarded as a mesoporous material, have been studied for their potential role as supports for nano-sized catalytic metal particles, in accordance with the current practice of using carbon supports, so far with encouraging results [2, 3]. The essential features of carbon support are all already to be found in nanotubes. The foreseeable advantages and potential innovations stem from the possibility of precisely tailoring features essential to catalysis (e.g. porosity and morphology of the support, size, density and dispersion of the active phase) by using newly available CNT chemistry and techniques to engineer the structure and morphology of the support and the active phase, at the nanoscale, in novel ways.

9.2 Motivation

9.2.1 Nanotubes

The field of materials science supplies the researcher with a novel and impressive arsenal of techniques, instrumentation and methodologies that bring unprecedented control over the nano-world in terms of assembly and characterization. In this context, nano-structured materials such as CNT's present a very interesting starting point in the aim for innovation. Carbon nanotubes present high thermal and electrical conductivity and superbly high mechanical strength coupled to a unique morphology. This last feature is key to many envisioned catalytic applications where the support (the CNT's) constitutes an improved mass/heat/charge transfer network with features that meet or exceed the relevant properties of activated carbon (carbon black, graphite). The combination of the small size, i.e. high external surface area, and of the tube structure (confinement or aggregate effect) allowed a significant improvement of the catalytic performance when compared to that obtained on traditional grain shaped catalysts. Additionally, nanotubes have no ash content which poisons wood-based carbon catalysts. CNT-supported metal-particle catalysts are being increasingly studied as the functional part of catalytic systems, sensors and detectors [2], predominantly focused on transition metals (Pt, Pd, Ag, Au, Ru). Results show that there is indeed potential in these materials: Researchers have demonstrated increased catalytic efficiency and/or selectivity, often at reduced metal loadings, [3, and references 62,91,95 therein], [2, and references 32,47,52-54 therein], hydrogenation reactions included. Experiments have shown that metals form crystalline nanoparticles with remarkably uniform size distributions on surfaces of carbon nanotubes [4, and references 1-12 therein]. The selectivity towards hydrogenation reactions is expected to be enhanced when the support forces a higher electron density on the metal particles (through charge transfer

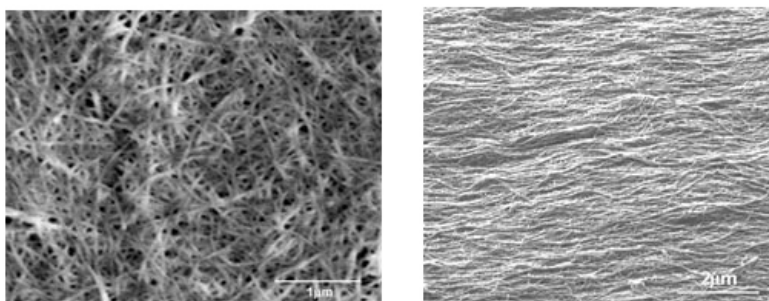


Figure 1: Buckypaper film morphology: SWNT's in random (left) and aligned (right) arrangements.

from the support to the particles) [5], which we expect will also be the case in our system, taking into account that CNT's are more electropositive than Pt.

Additionally, traditional carbon is by default microporous and it has been identified that this is in fact not ideal for a number of catalytic cases [3, ref. 62 pg. 353],[6], (and for our reaction specifically[7]) where a mesoporous network would increase the transfer processes.

Due to their chemical inertness CNT's have to be functionalized (or activated), i.e. proper moieties have to be introduced on the tube sidewalls or ends that will act as anchor points for the nucleation of the metal crystallites. The processes to do this will be described in section 9.4.

The nanotubes will be arranged in a film to serve as the substrate material. A readily available freestanding form is Buckypaper, a film with the consistency of paper (typical thickness is about 100nm) that consists almost entirely of nanotubes. The typical appearance of this material is as in Fig.1. Using this support morphology is convenient for a number of reasons: Firstly, it is a support of consistent quality, which will assist with the reproducibility of the experiments. Secondly, it is already well characterized in terms of porosity, density, weight and the features of the nanotubes it consists of. Finally, this form facilitates the application of various techniques (XPS, BET).

9.2.2 Impregnation and functionalization processes

Impregnation (loading) processes fall in general in two categories, physical and chemical. Chemical impregnation processes use wet chemistry approaches in which the metal particles are deposited from metal salt solutions and later reduced to the pure metal. Physical processes use evaporation techniques. A similar division applies to functionalization processes. The procedures and methods that are proposed allow for very pure and precisely controlled modification and deposition thus leading to the well defined and fully reproducible systems that are needed for the scrutiny of the multi-faceted phenomenon of catalysis. An example of a physical functionalization process is using a plasma chamber to force the introduction of a variety of otherwise unreactive species on the tubes.

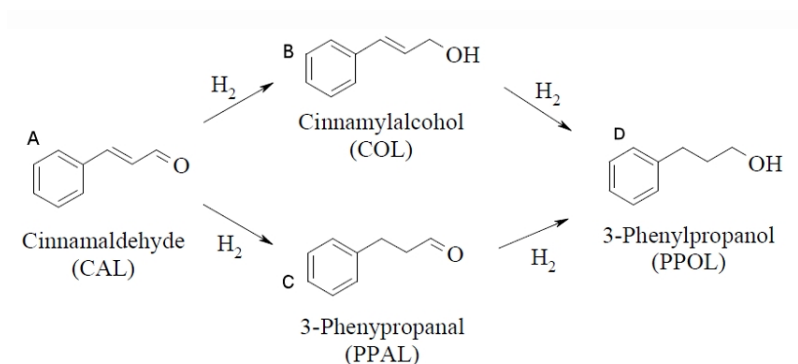


Figure 2: Reaction network of cinnamaldehyde hydrogenation [8]. α,β -unsaturated aldehyde (trans-cinnamaldehyde, A) conversion to the unsaturated alcohol (cinnamyl alcohol, B). Cinnamaldehyde is the chemical compound which gives cinnamon its smell. The undesired antagonistic reactions give the saturated aldehyde (C) and the saturated alcohol (D).

This technique is fast, precise and environmentally friendly. A chemical process is the ubiquitous acid treatment, which is an easy and inexpensive technique. This treatment creates organic groups (-COOH, -OH) on the tube walls and open edges.

For the loading procedures we have selected the most famous of the physical i.e direct evaporation of the metal on the suspended support and one of the most promising of the chemical methods, the Chemical Fluid Deposition (CFD). This technique employs the special properties of supercritical fluids to finely disperse the metal particles on the support, that is, low surface tension and viscosity and high diffusivity achieving high mass-transfer characteristics and high permeation in the pores and channels of the CNT.

9.2.3 Catalytic testing

The catalytic efficiency and activity of the systems will be measured against the hydrogenation reaction of α,β -unsaturated aldehydes to the corresponding unsaturated alcohol (reaction scheme fig.2). α,β -unsaturated carbonyl compounds are an important class of carbonyl compounds with the general structure $C_a=C_b-C=O$. In these compounds the carbonyl group is conjugated with an alkene.

This is one of the most valuable reactions in the fine chemicals industry. These compounds are used as intermediates in the fragrance, flavour and pharmaceutical industries. They are currently produced by selective hydrogenation of the corresponding α,β -unsaturated aldehydes using costly stoichiometric processes [9]. This hydrogenation procedure remains a challenging task [10, ref. 6] because heterogeneous catalysts based on supported transition metals exhibit low selectivity towards C=O group hydrogenation since C=C group hydrogenation

tion is favored [5, 9]. These reactions have been studied much in the past 20 years because they were chosen in the academic investigations as model reactions to establish relations between selectivity and catalyst structure [5].

9.3 Goals

The goals of this project are:

- Produce an active and selective catalyst for the specific hydrogenation reaction.
- Apply novel nanoscience techniques to precisely arrive at a catalyst that can be considered a model for examining the relations between structure and catalytic efficiency while examining the prospects of carbon nanotubes as a support for metal-crystallite-based catalysts.

9.4 Description of the work

The creation of a CNT-supported metal particle catalyst is a multi-step procedure: The CNT (the support) must be placed (or produced) in the desired arrangement (e.g. film, forest, random (bird's nest arrangement) etc). Before or after this, the CNT must be activated (functionalized). Finally, the active phase (the metal particles) has to be transferred and stabilized on the support. For each of the functionalization and loading procedures two processes are proposed, one physical and one chemical in nature. The following proposed techniques were selected, aiming at reproducibility, the ability to tailor many aspects to alter the results, innovation and also to test both chemical and physical processes in a kind of a comparative study.

9.4.1 Functionalization of the starting material

For this step, the first technique we propose is nitric acid treatment (refluxing with an acid for a few hours) [11, and other works]. This process opens the ends of the tubes and introduces acid sites (-COOH, -OH) on the ends and the sidewalls of the tubes [12, refs. 7,8]. This is an effective process, albeit a harsh one that introduces imperfections and gaps to the graphite sidewalls of the CNT. It is cheap and simple to implement and is the most commonly used functionalization process.

The second technique is oxygen plasma functionalization of the CNT. In this process the tubes are inserted in a plasma chamber. The gas that will provide the plasma may be as trivial as pure O₂ up to almost any organic substance. The very reactive plasma species will graft onto the CNT while the tubes largely retain their structural integrity [13]. This process happens at room temperature, does not use wet chemistry, is fast (times needed are of the order of a few minutes), generates very little chemical residue and since no acids are involved, it is environmentally friendly. Like the acid treatment, it can be scaled up to large quantities.

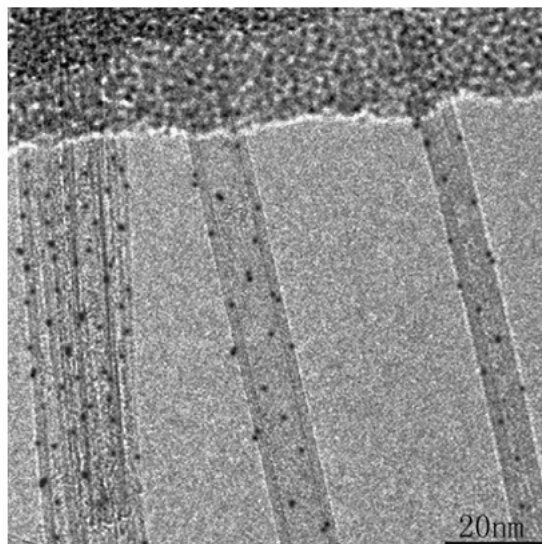


Figure 3: HRTEM of 3% loaded Pt on MWCNT [16]

9.4.2 Loading of metal crystallites

Group 8-10 (VIII) metal catalysts have been tested in cinnamaldehyde hydrogenation: Pd and Rh display high activity but poor selectivity, while Pt and Ru (the most commonly used metals, [10]) exhibit moderate selectivity [10, ref 6]. For several applications it is not very high dispersion that is needed but a controlled, narrow crystallite size distribution to optimize the exposed metal surface area. Nanotubes it has been shown allow for the growth of metal particles of narrow size distribution [4, refs 1-12].

The physical technique to be used is evaporation of the platinum metal directly to a film of the nanotubes. Atoms diffuse on the tube surface until they arrive at a point where they may bind (the functionalized points) and form a nucleus for the particle to grow. This technique is well established and is the norm in the loading of a support with metal particles without employing wet chemistry.

The second technique is Chemical Fluid Deposition (CFD) using supercritical CO_2 . The method has been successfully used to suspend most metals on CNT. A colloid suspension needs to be created first and then deposition takes place upon reduction of the metal precursor (usually under a H_2 flow). The density and viscosity of supercritical fluids (SCF's) are tunable by changing the pressure and temperature. Their low surface tension allows for better penetration and wetting of pores than liquid solvents [11],[14],[15]. Carbon dioxide is employed because it is inexpensive, non-flammable, non-toxic, environmentally benign and leaves no residue on the treated system.

The project will comprise four basic systems (four experiments):

	Deposition	
Activation	Evaporation	Chemical Fluid Deposition (CFD)
Acid oxidation	System I	System III
Plasma activation	System II	System IV

9.4.3 Outline of the procedures

- The first step is to characterize the starting buckypaper film in terms of the nanotube morphologies (TEM), the surface properties (i.e. measure the surface area and pore volume by N₂BET), and any possible catalytic activity without metal particles (a blank catalytic experiment).
- Next is to perform functionalization of the buckypaper film by concentrated acids or by oxygen plasma treatment. The aim is to introduce the functions on the nanotube sidewalls and also on any available open ends (open ends may be produced in situ by the acid functionalization). The extent of the functionalization can be determined by XPS, by measuring the oxygen content [17].
- Next step in the impregnation or loading of the metal catalyst. This will be done either with evaporation or with CFD. In either case the metal nanoparticles that are produced are very prone to oxidation and therefore before each catalytic test the catalyst will have to be reduced. This is easily achieved by treatment of the catalyst under H₂ flow usually at elevated temperatures for a few hours [10],[7]. The most ideal systems that are described in the literature are loaded to about 3% of the weight of the support and the particle sizes are in the range of 3-5 nm. These conditions are the starting point that we will be aiming at.
- The catalytic tests will be done within a setup of an autoclave coupled to a gas chromatograph (GC). To perform a measurement the system is left to react under a H₂ flow while tiny volumes of the reaction mixture are removed and analyzed with the GC.

10 Application perspectives in industry, other disciplines or society

Carbon nanotubes are being increasingly investigated in most fields of materials science. This project aims to investigate the quality of model catalysts based on carbon nanotubes by exploiting the capacities of novel nanoscience techniques. Direct application on an industrial scale is possible with some of the systems as the techniques allow for this. The new scientific knowledge that comes from this research could be applicable and relevant to contemporary research in the fields of industrial catalysis and catalyst manufacture.

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