Anne-Riikka Rautio

ON THE STABILITY OF CARBON NANOTUBE AND TITANIA NANOWIRE BASED CATALYST MATERIALS

FROM SYNTHESIS TO APPLICATIONS
Degradation of the support and sintering of catalyst nanoparticles inherently leads to a loss of functionality of catalyst materials in converters and sensors. Malfunction in such devices may lead to serious economic and environmental damage. The quest for novel and sustainable catalyst materials with better durability is thus ongoing. In this thesis, one-dimensional nanomaterials such as carbon nanotubes and titanium dioxide nanowires are studied and compared to their conventional zero-dimensional counterparts in regard to their structural and functional stability. With the combination of several catalyst nanomaterials and supporting surfaces, aging properties of more than 70 different materials are assessed by the means of X-ray diffraction, transmission electron microscopy and energy-dispersive X-ray analyses. Although CNTs were shown to be thermally the most stable carbonaceous supports for metal nanoparticles, they are, similar to other carbon supports, more sensitive to high temperatures than metal oxide supports and can suffer deactivation by catalytic oxidation and gasification even at moderate temperatures. In addition, the irradiation of the samples with e-beams caused the most dramatic changes in CNT based materials, where nanosized deformities (voids, channels) were formed when either nanoparticles or defects were present. The prepared nanocompositions have been utilized successfully in three different applications including (i) synthesis of hydrogen from ethanol via a steam reforming reaction, (ii) hydrogenation of citral to form value added chemicals and (iii) the application of advanced electrode materials in electric double-layer capacitors. Both CNT and TiO$_2$ nanowire based nanomaterials were shown to outperform their conventional nano- and microparticle based counterparts in the studied catalytic reactions, i.e. in citral hydrogenation and steam reforming of ethanol, respectively. Furthermore, nanostructured CNTs obtained by catalytic partial oxidation of the material showed an increased specific surface area, which could be exploited in supercapacitor electrodes with enhanced specific capacitance.

Keywords: capacitor, carbon nanotube, catalyst, citral hydrogenation, CNT, ethanol reforming, nanoparticle, nanowire, stability, titanium dioxide nanowire
Rautio, Anne-Riikka, Hiilinanoputki- ja titaanidioksidinanojohdinpohjaisten katalyyttien stabiilius. Synteesistä sovelluksiin
Oulun yliopiston tutkijakoulu; Oulun yliopisto, Tieto- ja sähköteknikian tiedekunta
Oulun yliopisto, PL 8000, 90014 Oulun yliopisto

Tiivistelmä
Katalyyttitukimateriaalin pilaantu minen ja katalyyttinanopartikkelien sinrautuminen johtavat siihen, että muuntajissa ja sensoreissa käytettävät katalyytiset materiaalit eivät enää toimi, mikä voi aiheuttaa sekä vakavia taloudellisia haittoja että ympäristöhaittoja. Tämän vuoksi kehitetään uusia kestävämpiä katalyyttimateriaaleja. Tässä väitöskirjassa tutkittiin yksiulotteisia nanomateriaaleja, kuten hiilinanoputkia sekä titaanidioksideinanojohvimia ja verrattiin niiden rakenteellista ja toiminnallista stabiiliutta perinteisiin nollaulotteisiin vastineisiin. Erilaisten katalyyttinonanomat erilaisten ja tukimateriaalien yhdistelmien ikääntymistä arvioitiin röntgendiffraktion, läpäisylekelektronimikroskopian ja energiadispersiivisen röntgenanalyysin avulla yli 70 erilaisesta näytteestä.

Vaikka hiilinanoputket osoittuivat termisesti stabiileimmaksi hiilipohjaiseksi tukimateriaali-liksi metallinonapartikkeleille, ne ovat kuten kaikki hiilimateriaalit, metallioksiditukimateriaaleja ja herkempiä korkeille lämpötiloille. Hiilinanoputkipohjaiset katalyytit voivat deaktivoitua katalyyttisen hapettumisen tai kaasuuntumisen vuoksi jo kohtalaisissa lämpötiloissa. Lisäksi elektrotoimisateellä säteilytetty nanopartikkelit tai pintavirheitä sisältävät hiilinanoputkipohjaiset katalyytit olivat tutkituista nanomateriaaleista herkimpikin muodostumaan nanorakenteita (koloja, kanavia).


Asiasanat: CNT, etanolin reformointi, hiilinanoputki, katalyytti, kondensaattorit, nanojohdin, nanopartikkelit, sitraalin hydraus, stabiilius, TiO2, titaanidioksidinanojohdin
“Do what I do. Hold tight and pretend it’s a plan.”

The Doctor
Acknowledgements

I am deeply grateful to my supervisor professor Krisztian Kordas for his guidance, patience and especially his trust throughout this work. I have learned a lot from you! I would also like to thank Dr. Päivi Mäki-Arvela and Dr. Melinda Mohl for their knowledge and help in the laboratory. I am grateful to Dr. Gabriela S. Lorite and docent Antti Uusimäki for their “fresh eyes” and advice in the final steps of this work.

I would like to thank my colleagues in the Microelectronics and Materials Physics Laboratories for interesting (and sometimes a little bit disturbing) conversations in the coffee room and the employees in the Centre for Microscopy and Nanotechnology, who have again and again helped me to align the TEM. I would like to acknowledge the work made by my co-authors in the University of Oulu (Dr. Prem Kumar Seelam, Dr. Mika Huhtanen), Åbo Akademi University (Dr. Kari Eränen, Dr. Atte Aho) and Umeå University (Prof. Jyri-Pekka Mikkola, Dr. Andrey Shchukarev, Dr. Ajaikumar Samikannu). To my present and former team members Aron Dombovari, Jani Mäklin, Jarmo Kukkola, Jhih-Fong Lin, Niina Halonen, Olli Pitkänen and Topias Järvinen: without your knowledge and support things would have been difficult and less fun.

This work has been financially supported by Tauno Tönnling Foundation, Emil Aaltonen Foundation, Riitta and Jorma J. Takanen Foundation as well as the Graduate School in Electronics, Telecommunications and Automation, GETA, in the form of a graduate school position.

Special thanks go to my friends and family for their support and love. Finally, my deepest gratitude belongs to my loving husband Aatto and my precious son Akseli. Without you this process would have been faster but pointless.

Oulu, December 2015

Anne-Riikka Rautio
## List of abbreviations and symbols

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<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>Sticking coefficient</td>
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<tr>
<td>$\gamma$</td>
<td>Surface energy</td>
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<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Surface charge density</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Time constant</td>
</tr>
<tr>
<td>$\Delta U$</td>
<td>Voltage difference</td>
</tr>
<tr>
<td>(acac)$_x$</td>
<td>Acetylacetonate</td>
</tr>
<tr>
<td>$A$</td>
<td>Arrhenius pre-exponential factor</td>
</tr>
<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Aluminium oxide</td>
</tr>
<tr>
<td>at.%</td>
<td>Atomic percent</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller theory</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett, Joyner, and Halenda method</td>
</tr>
<tr>
<td>C</td>
<td>Specific capacitance</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Methane</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>C-V curve</td>
<td>Capacitance–voltage curve</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electric double-layer capacitor</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusivity</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Diffusion coefficient at infinite time</td>
</tr>
<tr>
<td>$dr/dt$</td>
<td>Evaporation rate</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EFTEM</td>
<td>Energy-filtered transmission electron microscopy</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>Graphite</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography–mass spectrometry</td>
</tr>
<tr>
<td>H$_2$</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>Sulphuric acid</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
</tbody>
</table>
HNO₃  Nitric acid
I     Current
I₀    Initial current
IL    Ionic liquid
KOH   Potassium hydroxide
m     Mass
M     Molar mass
m₀    Initial mass
mₜ    Final mass at time t
MWCNT Multi-walled carbon nanotube
N₂    Nitrogen
N₄    Avogadro’s constant
NP    Nanoparticle
NW    Nanowire
P     Pressure
PTFE  Polytetrafluoroethylene
q     Heating rate
r     Radius
R     Gas constant
Rc    Resistance of device
RF-sputter Radio frequency sputtering
S₁₁₂  Hydrogen selectivity
SiO₂  Silicon dioxide
SnCl₂ Tin chloride
SRE   Steam reforming of ethanol
SWCNT Single-wall carbon nanotube
t     Time
T     Temperature
Tₛ    Inflection temperature
TG    Thermogravimetric
TGA   Thermogravimetric analysis
TEM   Transmission electron microscopy
TES-TFSI Triethylsulphonium bis(trifluoromethylsulphonyl)imide
TiO₂  Titanium dioxide, titania
TOF   Turnover frequency
TPD   Temperature programmed desorption
TPR   Temperature programmed reduction

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U$</td>
<td>Voltage</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet visible</td>
</tr>
<tr>
<td>vol.%</td>
<td>Volume percent</td>
</tr>
<tr>
<td>wt.%</td>
<td>Weight percent</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>$Z_W$</td>
<td>Collision flux</td>
</tr>
</tbody>
</table>
List of original papers

This thesis is based on the following publications, which are referred throughout the text by their Roman numerals:


The experiments were designed by Rautio A-R, Kordas K, Mäki Arvela P and Seelam PK. All of the materials were prepared and analyzed (TEM, XRD and SEM-EDX) by Rautio A-R. TGA (Paper I) was carried out by Kokkonen T (University of Oulu). XPS measurements were performed by Shchukarev A (Umeå University) (Paper I) and Aho A (Åbo Akademi University) (Paper IV). HRTEM imaging was made by Ge L (Rice University) (Paper II). Kordas K, Kukkola J and Pitkänen O assisted with the calculations (Paper I-V). Experiments on the hydrogenation of citral (Paper IV), as well as temperature programmed reduction and desorption measurements of catalyst samples were done in cooperation with Mäki-Arvela P (Åbo Akademi University) (Papers I, III-IV). Experiments on steam reforming of ethanol were carried out by Seelam PK (Paper III). Electrical measurements and the preparation of electrode thin films were carried out with the help of Pitkänen O and Järvinen T (University of Oulu) (Paper V). The results have been discussed and concluded together with each co-author. Each original publication was written by Rautio A-R together with the kind help of the co-authors.
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1 Introduction

1.1 Background of catalyst

A catalyst is generally defined as “a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change”.\[1\] The catalyst takes part in the reaction and provides an alternative route with lower activation energy for the reaction to proceed. Catalysts are generally categorized on the basis of whether they are in the same phase as the reactants (homogeneous catalyst) or not (heterogeneous catalysts). While homogeneous catalysts are generally gaseous or liquid (e.g. enzymes in biochemical reactions or transition-metal complexes in liquid phase organic reactions), typical heterogeneous catalysts are solid materials (metals, alloys, metal oxides, sulphides, halides and their combinations) and therefore the reaction occurs on the interface of liquid/solid and gas/solid. Nowadays, catalysis plays a key role in industry and economy since ~90% of material synthesis and refinement is carried out by catalytic processes. \[2\]

In spite of its definition, at some point during the reaction a catalyst may undergo temporary and/or permanent physical changes that lead to deterioration or even complete loss of activity. This phenomenon is called deactivation since the changes, either on the support or on the catalyst nanoparticles, cause a decrease in the activity of the catalyst. There are several different types of deactivation process, however, the main causes of deactivation are the loss of active area generated by undesirable physical changes (evaporation, recrystallization, surface diffusion/migration, agglomeration, fouling and sintering) or chemical reactions (poisoning, change in oxidation state) (Fig. 1). \[3, 4\]

Nanomaterials are defined as materials having at least one dimension with a size of 100 nm or less. Such a definition is rather vague because materials having sizes below 100 nm do not necessarily differ from their bulk counterparts with regard to their physical and chemical properties. Accordingly, the prefix “nano” is more apt when the surface of particles starts to play an important role in the overall electronic properties, which consequently influences the electrical, optical, thermal, mechanical as well as chemical attributes of such kinds of material. Although catalyst metals typically have high melting points and therefore should be resilient against physical changes, when dealing with nanoparticles with a size of a few nanometres, melting-point depression as well as size dependent sublimation rate and enhanced nanoparticle/cluster diffusivities on supporting surfaces could contribute to physical transformations. The
properties (such as phase transition temperatures, absorption, fluorescence, as well as catalytic activity and selectivity) of nanomaterials are size dependent mainly due to two reasons: [5] i) Surface effects, because the ratio of surface atoms to the total number of atoms increases as the particle size decreases. Moreover the surface atoms are less stabilized and have lower average binding energy per atom compared to larger crystals. ii) Quantum size effects caused by the electron wavelength being comparable with the particle size. A good example of such size dependency is gold that used to be considered as a poor catalyst. However, as the size of gold particles is decreased to nanoscale the catalytic activity is increased significantly with the result that nowadays gold is used as a catalyst in various different organic reactions such as oxidation [6-8], rearrangement [9] and hydrogenation [10, 11].

Fig. 1. Schematic drawing of catalyst deactivation mechanisms, (a) atomic and crystallite migration, resulting in particle size growth, (b) sintering of the support, (c) poisoning, and (d) coke formation.
1.2 Background of carbon nanotubes and titanate nanowires

The properties of the large variety of carbon allotropes (such as diamond, graphite, amorphous carbon, fullerenes and carbon nanotubes) are mainly determined by the manner in which the atoms are arranged and bond to each other. Carbon in different forms has played an important role in the history of humankind as it is not only a building block of all living creatures on Earth but it has provided heat and electricity by burning charcoal and coal. Although charcoal has been employed throughout the ages, during the industrial revolution the use of coal multiplied in order to supply the growing demand for fuel for steam engines. In the last decades, the use of carbon has no longer been limited to energy release by combustion. By exploiting its electrical conductivity, chemical purity and inertness as well as its mechanical softness, carbons are used for steel production, battery electrodes, structural reinforcement and for solid lubricants. The excellent adsorption property of activated carbon is exploited in water and air purification, in medicine and the food industry as well as in heterogeneous catalysis.

The renaissance of carbon started when its novel allotropes such as fullerenes, carbon nanotubes and graphene were found and explored in the past three decades. Although S. Iijima [12] is often referred to as the discoverer of carbon nanotubes, evidence of the existence of CNTs can be found in literature [13] as early as 1946 and the excellent mechanical properties of CNTs were utilized (unknowingly) already in ancient Damascus blades [14]. CNTs are considered to consist of \(sp^2\) hybridized carbon atoms that are arranged in a form of a honeycomb lattice rolled into a cylinder. Depending on the number of cylinders inside each other the nanotubes are called single-wall carbon nanotubes (SWCNT) or multi-walled carbon nanotubes (MWCNT).

CNTs (Fig. 2 a) have been studied and used widely in several different applications, which is not surprising considering their outstanding properties. CNTs are at the same time chemically inert, mechanically strong and flexible, have large specific surface area, low mass density, and have good thermal and electrical conductivity. In addition, CNTs can be integrated with various materials to form macroscopic but nanostructured composites, hierarchical assemblies as well as template-based structures. [15-17] The addition of even a small amount of carbon nanotubes to composites can substantially enhance the mechanical and electrical properties of the material. [18,19] CNT nanocomposites have been demonstrated to catalyze a number of different reactions such as reforming (ethanol [20] and methane [21]), hydrogenation/dehydrogenation of hydrocarbons [16, 22, 23] and Fischer-Tropsch synthesis [24-27]. Further utilization such as in energy applications (batteries, fuel and solar cells and supercapacitors), [28-
actuators, [33] (gas, mechanical and bio) sensors [33, 34, 35], biomedical applications [36] and electrical contacts [37] as well as gecko tape [38] and self-cleaning adhesive [39] also demonstrate the versatility of CNTs.

However, the property that made carbon so popular during the industrial revolution could be its Achilles heel at least in the field of catalysis. Although CNTs have several beneficial properties as catalyst supports i.e. relatively high specific surface area, large porosity, good inertness to chemicals and the possibility to be grown on templates in order to form scaffolds and hierarchical structures, [16, 20, 40] their disadvantage is the same as other carbonaceous materials: i.e. a sensitivity for oxidation (in oxidizing atmospheres) and for gasification (in the presence of H₂ or H₂O) at elevated temperatures. Oxidation as well as gasification of the carbon support creates a risk of catalyst sintering and deactivation as the gradually collapsing and disappearing support surface can no longer fulfil its function and the catalyst nanoparticles end up in contact with each other, thus undergoing coalescence.

Fig. 2. High resolution TEM images of (a) carbon nanotubes and (b) TiO₂ nanowires [41]. The inset shows the electron diffraction of titania nanowire.

Titanium dioxide (TiO₂) has been commercially prepared since the early 20th century and due to its stability, nontoxic nature and affordable price it is commonly used in many household products such as paints and pigments, sunscreens, medication pellets, toothpastes, paper products and even in certain alcoholic drinks. Soon after photoelectrochemical water splitting on TiO₂ was first reported [42] an
enormous research effort on the development of TiO$_2$ based energy, photovoltaic and environmental applications has begun. [43] In nature, titanium dioxide has three different crystal structures; rutile, anatase and brookite, in which the first one is the most stable phase whereas anatase and brookite are metastable (the latter being difficult to prepare and therefore not examined as much as the other two phases). Anatase, having a larger band gap than rutile (~3.2 eV and ~3.0 eV, respectively), has always been the most popular phase in photocatalyst research, although it has been shown that the mixture of the two phases is even more active. [44] TiO$_2$ itself has good photocatalytic properties yet it is often used simply as a support for catalyst metals.

TiO$_2$ nanostructures, such as nanoparticles, nanorods, nanowires and nanotubes, have a slightly higher band gap than that of bulk TiO$_2$. [45, 46] Nanowires of TiO$_2$ (Fig. 2 b) are relatively new materials, having been first reported at the beginning of this century. Similarly to CNTs, TiO$_2$ NWs are one-dimensional nanostructures having several practical advantages compared to their 0-dimensional counterparts (e.g. easier filtration, preparation of films and porous composites). Although, the material is well studied in the field of photocatalysis, [47-49] its use in other reactions [50] or applications (such as batteries [51], supercapacitors [52, 53] and gas sensors [54]) is still in its infancy. Nevertheless, TiO$_2$ NWs have potential industrial applications in several fields such as electronics, energy storage, pharmaceutics, and paints. [45]

1.3 Objective and outline of thesis

The objective of this thesis was to prepare metal/metal oxide decorated nanomaterials and study the influence of different atmospheres and temperatures on the materials in nanoscale. The activity of anchored nanoparticles in catalytic oxidation and hydrogenation of carbonaceous supports is highlighted. This work also shows that the prepared nanomaterials supported on CNTs and TiO$_2$ NWs are not only functional in applications such as catalysis in chemical synthesis and electrodes in supercapacitors but also outperform their conventional nanoparticle based counterparts.

In Chapter 2 Materials and methods, the preparation and general characterization of the nanomaterials is presented. Also the properties of the materials and the problems related to analysis of nanomaterials are discussed. Chapter 3 focuses firstly on the thermal stability of CNTs decorated with nanoparticles, and secondly on the thermal stability of nanoparticles supported on
carbonaceous and TiO\textsubscript{2} supports in different atmospheres (Papers I-II). In Chapter 4, the nanostructuring of carbonaceous supports with the help of anchored nanoparticles is discussed (Papers II and V). Chapter 5 focuses on a few selected applications revealing the feasibility of the materials in catalytic reactions (Papers III-IV) as well as in electrical devices (Paper V). Lastly, in Chapter 6 Summary and conclusions, the most important results are summarized and the final conclusions are drawn.
2 Materials and methods

2.1 Preparation of nanomaterials

2.1.1 Support pre-treatment

Typically, carbon nanotubes are pre-treated in order to decrease the amount of other carbonaceous materials (amorphous carbon) and catalyst residuals (from the CNT synthesis, in our case from catalytic chemical vapour deposition) on its surface. In papers I-III pre-treatment was performed in the following way: multi-walled carbon nanotubes (MWCNTs, 677248, Aldrich) were sonicated for 1 h and then refluxed for 8 h in concentrated HNO₃ followed by washing with deionized water and drying. In paper V, MWCNTs (724769, Aldrich) were treated with a concentrated HNO₃:H₂SO₄ mixture (1:3). All the other carbon support materials (e.g. activated carbon (AC, 05120, FLUKA), graphite (GC, 282863, Aldrich)) were used as received.

The TiO₂ nanowires (TiO₂ NW) were synthesized from hydrothermally grown titanate nanowires by annealing in air at 600 °C for 12 h [49, 55], whereas the TiO₂ nano and microparticles (<25 nm (637254, Aldrich) and mesh 325 (036199, Alfa Aesar)) were used as received.

2.1.2 Catalyst preparation

The catalysts (Paper I-IV) were prepared with a simple wet impregnation method: First, the support was dispersed in the solvent by ultrasonication, then pre-defined amounts of metal acetylacetonates (Pt(acac)₂, Pd(acac)₂, Ni(acac)₂, Co(acac)₃ corresponding to ~2 wt.% metal in the final product) were added, followed by stirring at room temperature overnight and drying. The typical solvents used were toluene in the case of carbon supports and a mixture of water and acetone (1:1) in the case of TiO₂ based catalysts. The bimetallic catalysts (Paper IV) were prepared from reduced Pt/TiO₂ NW samples by stirring in 1 M HCl with SnCl₂ for 3 h at room temperature. The applied calcination and reduction conditions are summarized in Table 1.
Table 1. Calcination and reduction parameters for different catalysts. Typical heating rate of 10 °C/min was used.

<table>
<thead>
<tr>
<th>Catalyst metal</th>
<th>Calcination in air</th>
<th>Reduction in 15% H₂/Ar</th>
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</thead>
<tbody>
<tr>
<td>Pt</td>
<td>300 °C for 1 h</td>
<td>500 °C for 5 min</td>
</tr>
<tr>
<td>Pd</td>
<td>300 °C for 1 h</td>
<td>500 °C for 5 min</td>
</tr>
<tr>
<td>Ni</td>
<td>185 °C for 2 h; 380 °C for 1 h</td>
<td>250 °C for 15 min</td>
</tr>
<tr>
<td>Co</td>
<td>105 °C for 45 min; 200 °C for 45 min</td>
<td>-</td>
</tr>
<tr>
<td>Sn-Pt</td>
<td>500 °C for 3 h</td>
<td>500 °C for 3 h</td>
</tr>
</tbody>
</table>

2.1.3 Aging and nanostructuring of nanomaterials

Aging treatments of Pt and Pd supported on carbon supports (i.e. CNTs, graphite and activated carbon) and TiO₂ nano and microparticles were conducted by exposing the samples to oxidizing (air) or reducing (15% H₂/Ar) atmospheres at 300 °C for 3 h, 12 h, and 48 h.

Furthermore, nanostructuring of nanotubes was carried out by two different methods (Paper V). In the first, acid-treated carbon nanotubes (labelled as CNT-COOH) were subjected to a partial localized oxidation step with the help of cobalt oxide nanoparticles anchored on the surface. In the process, Co(acac)₃, impregnated on the surface of CNTs (nominal metal loading of 5 wt.%) was decomposed in air at 330 °C for 5 min (with a heating rate of 5 °C/min), which resulted in the formation of non-stoichiometric CoOₓ nanoparticles on the nanotubes (CNT-CoOₓ) and simultaneously caused a low-temperature catalytic oxidation of the carbon support leaving behind highly nanostructured CNT walls caused by the CoOₓ nanoparticles. The cobalt nanoparticles were removed from the nanotubes with a simple acid treatment. The metal decorated CNTs were sonicated in 4 M HCl for 15 min followed by refluxing at 70 °C for 1 h, followed by filtration and washing with deionized water (CNT-CoOₓ/acid). In the other method, the surface area of pristine CNTs was increased with CO₂ activation either at 750 °C or 800 °C (CNT/Act.750°C and CNT/Act.800°C). The activation was done as described in reference [56] except for using a flow rate of 30 mL/min. First the sample was heated to the desired temperature under N₂ flow followed by the introduction of CO₂ gas. The temperature was kept constant for 5 h, after which the gas was changed back to N₂ and the sample was cooled to room temperature.
2.2 Preparation of electric double-layer capacitor

Buckypaper-type CNT electrodes were prepared by sonicating powder samples (as prepared in Chapter 2.1.3, Nanostructuring) in DMF and filtering the dispersed CNTs through PTFE membranes, followed by drying at room temperature and cutting with a scalpel into small pieces with an area of \(\sim 0.6-0.8\ \text{cm}^2\). The area normalized mass of the resulting films was \(\sim 1.5\ \text{mg/cm}^2\). The capacitors (Fig. 3) were assembled from CNT thin films (each supported on the PTFE filters), a filter paper working as a separator between electrode pairs, and evaporated Ti (50 nm) and RF-sputtered Au (450 nm) surface coatings as electrical contacts.

The capacitors were wetted either with a (4:1) mixture of aqueous KOH (6 mol/L) and isopropanol or with a mixture of triethylsulphonium bis-(trifluoromethylsulphonyl)imide (TES-TFSI) and ethanol acting as electrolytes. The role of the alcohols was to enhance the wetting of the CNT electrodes. The ionic liquid (IL) TES-TFSI was selected due to its broad electrochemical window (\(-2.4-3.1\ \text{V}\)) and good conductivity (5.5 mS/cm).

![Fig. 3. Schematic of the thin film double layer capacitor.](image)

2.3 Characterization of the prepared nanomaterials

In order to understand how the nanomaterials eventually work and act in a particular process, it is important to know their textural and chemical properties such as size and its distribution, porosity, microstructure, crystal structure, surface chemistry etc. For example, in the case of catalysts the high specific surface area is
essential to have high catalytic activity, which correlates with a high proportion of surface atoms with surface energy and electron density differing from those in the bulk.

Accordingly, several different analytical methods have been used in order to determine the structural and chemical properties of the prepared materials (Table 2).

Table 2. Typical analytical methods used in nanomaterial characterization.

<table>
<thead>
<tr>
<th>Analyzing method</th>
<th>Apparatus and parameters</th>
<th>Material properties</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy-filtered transmission electron microscopy, TEM</td>
<td>Leo 912 Omega, 120 kV</td>
<td>Particle size and homogeneity</td>
<td>I-V</td>
</tr>
<tr>
<td>Field emission scanning electron microscopy, FESEM</td>
<td>Zeiss Ultra plus equipped with an energy-dispersive X-ray spectroscopy analyser, EDX</td>
<td>Microstructure, elemental concentration, particle homogeneity</td>
<td>I-V</td>
</tr>
<tr>
<td>Nitrogen physisorption</td>
<td>Micromeritics ASAP 2020 Surface Analyzer,-196 °C,</td>
<td>Specific surface area (BET)</td>
<td>IV-V</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td>Horiba Jobin-Yvon Labram HR800, 488 nm excitation</td>
<td>Pore size and volume (BJH)</td>
<td>V</td>
</tr>
<tr>
<td>Temperature programmed desorption/reduction of H₂, CO₂</td>
<td>Micrometrics Autochem 2910.</td>
<td>Crystal structure</td>
<td>I, III-IV</td>
</tr>
<tr>
<td>X-ray diffraction, XRD</td>
<td>a) Siemens D5000</td>
<td>Crystal phase and volume averaged size</td>
<td>a) III</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy, XPS</td>
<td>b) Bruker D8 Discover, Cu Kα radiation</td>
<td></td>
<td>b) I, IV-V</td>
</tr>
<tr>
<td></td>
<td>a) Perkin-Elmer PHI 5400 spectrometer, 300 W</td>
<td>Oxidation state, and elemental concentrations</td>
<td>a) IV</td>
</tr>
<tr>
<td></td>
<td>b) Kratos Axis Ultra DLD electron spectrometer, 150 W, monochromatized Al Kα-radiation</td>
<td></td>
<td>b) I, V</td>
</tr>
</tbody>
</table>

2.4 Properties of the catalytic nanocompositions

2.4.1 Catalyst support

The materials selected for supports were either carbon (i.e. CNTs, graphite and activated carbon) or titanium dioxide based. The activated carbon is mostly amorphous and does not have a well defined crystalline structure, whereas CNTs and graphite are basically the same $sp^2$ hybridized carbon crystal except that the
former has curved while the latter one has a planar structure of the hexagonal lattice. Also, the specific surface area is significantly different for different supports: AC has the highest (~900 m²/g), followed by CNTs (250-290 m²/g) and graphite (~10 m²/g). In the case of TiO₂ materials the major difference is in their size, since all of the materials have the crystal structure of anatase. The specific surface areas measured for the smallest TiO₂ particles (size less than 25 nm) and for the TiO₂ NWs were similar, (~50 m²/g) which is due to the porous surface of the NWs (voids with a diameter 7-10 nm according to BJH measurement and TEM observations, respectively. Paper IV).

Although the CNTs had been acid treated in order to remove the impurities, the pre-treatment generates polar surface groups (carbonyl, carboxyl and hydroxyl) and defects, which favour the nucleation and growth of smaller metal nanoparticles as compared to pristine untreated carbon surfaces. [57] However, it is worth emphasizing that the acidity of acid-treated CNTs is lost subsequently during the decomposition and reduction of nanoparticles. [58] Contrary to the case of carbon supports, TiO₂ supports are alkaline, though there are differences regarding the nature of the alkalinity between the various TiO₂ materials. While the surface of the TiO₂ NW is basic (Brønsted base sites) due to the considerable Na⁺ content (4-5 wt.%) from the preparation method [41, 55], the pH of TiO₂ NPs is neutral. However, according to the CO₂-TPD, the total density of (Lewis and Brønsted) basic sites of NP and NW were similar but had a difference in strength; weak Lewis acid CO₂ bonds weakly on NW (<400 °C, Fig. 4 red line, second TEM image) while in the case of NP the basic sites were medium strong (desorption between 400 °C and 600 °C, Fig. 4, black line, first TEM image).

Fig. 4. Temperature programmed CO₂ desorption of TiO₂ NWs (red) and NPs (black). (Reprinted from Paper IV, Copyright 2014, with permission from Elsevier.)
2.4.2 Catalyst nanoparticles

Typically, after impregnating the support surfaces with metal acetylacetonates, the formed nanoparticles detected with TEM were small for each support and metal precursor (<1.5 nm for CNT and TiO$_2$; <2.5 nm for GC and AC, Table 3). The average particle size tended to increase slightly during thermal decomposition in air and/or hydrogen while the metal/metal oxide particles were forming. Cobalt oxide decorated CNTs were the exception, since the metal oxide particles seemed to be somewhat smaller than the precursor salt particles. This may be explained by the surface diffusion and growth of previously undetected Co(acac)$_3$ particles (that in turn decompose to oxide). In general, the average size of palladium particles was found to be larger than that of platinum over each support. This can be explained by the better adsorption and higher activation energy of diffusion of platinum compared to palladium. Addition of co-catalyst Sn to Pt on TiO$_2$ NWs caused a small increase in the average particle size, mainly because of the fusion of platinum and tin nanoparticles into an alloy, according to XRD (Paper IV). [59]

TEM can be considered to be the most accurate method to analyze the physical size of nanoparticles. However, the resolution of the microscope and also the analysis method to estimate the particle size (manually in this case) can slightly misrepresent the results. In addition, the results may differ significantly from the results gained with other analyzing methods. As an example, CO chemisorption provides information related to the chemical surface area (CO binding to active sites), which is only indirectly related to the actual particle size (Table 3, TiO$_2$ supported samples). Although it is possible to determine the volume averaged crystal size from the broadening of reflections in XRD patterns, very often the low concentration and extremely small size of the nanocrystals make the detection difficult and inaccurate. Furthermore, the possible amorphous nature of nanoparticles and the existence of a few extraordinarily large crystals (having sharp reflection superposing on the broad one for the majority of crystals) can make XRD assessment an unreliable method in crystal size determination.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (nm)</th>
<th>Oxidation state and crystal size (nm)</th>
<th>Elemental conc. (wt. %)</th>
<th>Oxidation state and binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(acac)_2/CNT</td>
<td>1.3 ± 0.3</td>
<td>n.m.</td>
<td>Pt 0.9 ± 0.4; C 87.6 ± 1.1; Fe 0.9 ± 0.4; Al 1.1 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>PtO_x/CNT</td>
<td>1.9 ± 1.3</td>
<td>Pt ~7.0</td>
<td>Pt 2.9 ± 0.8; C 87.6 ± 1.9; Fe 0.4 ± 0.3; Al 0.1 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Pt/CNT</td>
<td>1.9 ± 0.7</td>
<td></td>
<td>Pt 2.3 ± 0.7; C 86.9 ± 0.9; Al 1.3 ± 0.3; Fe 0.8 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Pd(acac)_2/CNT</td>
<td>1.4 ± 0.3</td>
<td>n.m.</td>
<td>Pd 1.6 ± 0.5; C 86.0 ± 0.2; Fe 0.8 ± 0.3; Al 1.1 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>PdO_x/CNT</td>
<td>1.6 ± 0.5</td>
<td>PdO ~5.0</td>
<td>Pd 1.7 ± 1.0; C 84.8 ± 1.7; Fe 0.4 ± 0.2; Al 0.1 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Pd/CNT</td>
<td>2.7 ± 2.1</td>
<td></td>
<td>Pd 3.6 ± 2.3; C 83.0 ± 1.9; O 11.3 ± 3.5; Al 1.1 ± 0.04; Fe 1.0 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>Ni(acac)_2/CNT</td>
<td>1.3 ± 0.3</td>
<td>n.m.</td>
<td>Ni 1.9 ± 0.6; C 87.6 ± 1.8; Fe 0.9 ± 0.4; Al 1.5 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>NiO_x/CNT</td>
<td>1.9 ± 0.8</td>
<td>n.d.</td>
<td>Ni 14.8 ± 13.0; C 72.8 ± 16.7; O 10.2 ± 2.3; Fe 2.2 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>Ni/CNT [60]</td>
<td>2.0 ± 0.8</td>
<td></td>
<td>Ni 1.4 ± 0.4; C 84.1 ± 1.2; O 12.9 ± 1.9; Al 0.9 ± 0.2; Fe 0.8 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Co(acac)_3/CNT</td>
<td>1.5 ± 0.4</td>
<td>n.m.</td>
<td>Co 1.3 ± 0.4; C 89.9 ± 1.5; Fe 0.9 ± 0.4; Al 1.9 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>CoO_x/CNT</td>
<td>1.4 ± 0.4</td>
<td>n.d.</td>
<td>Co 3.8 ± 3.2; C 83.5 ± 5.0; O 11.8 ± 4.1; Fe 0.8 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>Pt/GC</td>
<td>3.9 ± 2.4</td>
<td></td>
<td>Pt 1.7 ± 0.9; C 86.5 ± 2.1; O 11.9 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>Pd/GC</td>
<td>9.8 ± 4.7</td>
<td></td>
<td>Pd 2.6 ± 1.8; C 86.7 ± 0.9; O 10.6 ± 1.8</td>
<td></td>
</tr>
<tr>
<td>Ni/GC [60]</td>
<td>3.3 ± 1.4</td>
<td></td>
<td>Ni 2.0 ± 0.6; C 88.8 ± 1.6; O 9.2 ± 1.3</td>
<td></td>
</tr>
</tbody>
</table>
According to XRD measurements the catalyst nanoparticles in both the calcined and reduced Pt/CNTs were in metallic form, whereas in the case of palladium, reflections for PdO in addition of those of Pd were visible after calcination and reduction. For Ni/CNT no reflections from the catalyst were visible after the decomposition of the precursor indicating a very small crystal size and/or the amorphous nature of the particles. The 2 wt.% CoOx/CNT did not show any reflections in XRD, whereas the CNTs containing ~15 wt.% of Co (after annealing in air, Paper V) suggest the existence of cobalt oxide in such samples.

Although, SEM-EDX is widely used analyzing method when the elemental content of materials is examined, one should be careful when interpreting the results obtained for heterogeneous nanomaterials. EDX analysis was performed typically on >100 µm² area from at least five different sample locations. The elemental concentrations based on the SEM-EDX showed results close to the nominal metal concentrations. However, for nickel decorated CNTs the calcined sample showed a high metal content (14.8 ± 13.0 wt.%) whereas for the same sample after the reduction the amount of nickel was similar to that of the non-treated metal salt CNTs. This, and the large nickel concentration deviation in the case of NiOx/CNT, indicates that the sample was remarkably inhomogeneous, having some locations with abundant nanoparticles while others had only limited amounts of nickel. While EDX shows elemental concentrations for a typical sample depth of a few micrometres, XPS can trace the surface only up to a few nanometres, in effect representing the surface composition. In addition, XPS also provides information about the oxidation states of elements making it extremely useful in
identifying not only the elemental composition but the true chemistry. In the case of calcined CNT supported samples (Paper I), XPS showed traces of Ni and Pd acetonates revealing that the precursors had not undergone complete transformation to metal or metal oxide during the calcination step. In the case of the 15% Co/CNT (Paper V) the catalyst nanoparticles were shown to be cobalt oxyhydroxide, contrary to the results from XRD.

2.5 Catalytic activity measurements

The activity of the prepared nanomaterials was studied in two different catalytic reactions that are timely and have practical importance. Low temperature steam reforming of ethanol (SRE) to produce H$_2$ was selected for the CNT and graphite supported catalysts (Paper III), whereas the TiO$_2$ supported catalysts were used in hydrogenation of citral to synthesize value added products important for the pharmaceutical, food and fragrance industries (Paper IV).

2.5.1 Steam reforming of ethanol

The activity of Pt, Pd and Ni nanoparticles supported on CNTs and graphite was tested in low temperature SRE. First, the catalysts (100 mg) were activated by reduction in 20% H$_2$/N$_2$ at 350 °C for 30 min (followed by cooling down in the reductive atmosphere). The catalytic activity was tested in the temperature range of 150 °C – 450 °C by analyzing the outlet gas flow using an FTIR spectrometer to detect infra active species and a thermal conductivity analyzer for H$_2$ (XMTC H$_2$ analyzer). The reactant mixture with a steam to ethanol molar ratio of 3:1 was evaporated and passed through the catalyst bed with N$_2$ carrier gas (20 vol. % of reactants and 80 vol. % of N$_2$). The selectivity towards hydrogen, $S_{H_2}$, was calculated by using equation (1):

$$S_{H_2} = \frac{H_{2,product}}{[3(C_2H_5OH_{in} - C_2H_5OH_{out}) + (H_2O_{in} - H_2O_{out})]} * 100\%$$

(1)

2.5.2 Hydrogenation of citral

In a typical reaction, 100 mg of Pt/TiO$_2$ catalyst was reduced in pure H$_2$ for 1 h at 250 °C in a Parr reactor (300 mL). A mixture of citral in either toluene or 2-pentanol with an initial concentration of 0.013 M was first deoxygenated and then introduced onto the catalyst. The reaction was carried out at 70 °C in H$_2$ under a total pressure
of 10 bar for 180 min. Small volumes of the liquid from the reaction vessel were collected, filtered and diluted with the solvent before analyzing. The liquid phase components were analyzed with gas chromatography equipped with a capillary column (HP-Wax, 30 m, 250 m, 0.25 m) flame ionization detector while the unknown peaks were identified with GC–MS (Agilent Technologies 6890N).

2.6 Electrochemical measurements

The capacitance of the electrode materials made of various kinds of CNT bucky paper was determined by cyclic voltammetry with sweep rates of 0.05, 0.1, 0.25, 0.5, and 1.0 V/s, respectively using a potentiostat (Princeton Applied Research VersaSTAT 3). The specific capacitance values from the averages of the integrated current–time hysteresis curves (after transforming the variable $V$ to $t$) were normalized by the electrode mass using equation (2).

$$C = \frac{\int_{t_2}^{t_1} I(t) \, dt}{\Delta U \cdot m},$$  \hspace{1cm} (2)

where $I(t)$ is the charging current averaged for 5 cycles, $\Delta U$ is the voltage difference between $t_2$ and $t_1$ moments upon charging/discharging, and $m$ is the mass of carbon in the electrode. In transient current measurements the capacitor was first connected in series with a 3.3 $\Omega$ resistor and then the circuit was powered by using a signal generator ($U = \pm 500$ mV at 0.5 Hz, Agilent 33120A). The current in the circuit was calculated from the potential drop on the resistor (measured with an oscilloscope, Tektronix TPS 2024B) by using Ohm’s law. The electrical measurements of devices with aqueous electrolytes were carried out in air, while those with an IL electrolyte were tested in an inert nitrogen atmosphere.
3 Thermal stability of nanomaterials

3.1 Thermal stability of CNTs

The thermal stability of CNTs decorated with metal acetylacetonates and the corresponding metal oxides (Fig. 5) were studied in air by thermogravimetric analysis (Paper I). Similarly to that reported earlier, [24, 61, 62] the oxidation of non-decorated CNTs (Fig. 6, black line) began after reaching 400 °C with a complete weight loss achieved at 600 °C. The small variations in oxidation temperature ranges are thought to be caused by the differences in the structure of the studied CNTs i.e. degree of graphitization, diameter of nanotubes, amount of surface defects and catalyst residuals.

![TEM images of metal precursor and oxide decorated samples.](image)

The thermal oxidation of pure metal acetylacetonates was studied in order to distinguish the decomposition temperatures of the precursors (Fig. 6, green lines). Contrary to the cases of platinum and palladium precursors that first decomposed to their corresponding metals before forming oxides, Ni(acac)₂ and Co(acac)₃ decomposed directly to oxides. This is due to the relatively low standard reduction potential of nickel and cobalt. [63, 64] Interestingly, when supported on CNTs the decomposition temperature of Pd(acac)₂ and Ni(acac)₂ was slightly higher than for the pure salts indicating that the decomposition of precursors somewhat depends on whether the acetylacetonates are supported or not. Such a stabilization effect of the surface partly
explains the presence of residual acetylacetonates for the PdO/CNT and NiO/CNT samples (Table 3, Chapter 2.4.2) detected with XPS. On the other hand, impregnation of CNTs with metal acetylacetonates decreased the oxidation temperature of CNTs to 380 °C for Pd(acac)₂/CNT and to 330 °C and 230 °C for Ni(acac)₂ and Co(acac)₃ decorated CNTs, respectively. When impregnated with platinum precursor, no changes were observed in the oxidation of CNTs or in the decomposition of the precursor. However, when decorated with Pt and PtOₓ nanoparticles, CNT oxidation started at a lower temperature than that of the non-decorated CNTs, similarly to other oxide decorated samples (Fig. 6, red lines). Typically, the metal precursor decorated samples initiated oxidation of CNTs at higher temperatures than the corresponding metal/metal oxide samples. However, Ni(acac)₂/CNT were an exception, displaying a lower oxidation temperature than for a NiO decorated sample. The reason for this could be the better thermal stability and different decomposition mechanism of nickel precursor compared to other studied metal acetylacetonates. [65, 66]

Fig. 6. Results of thermogravimetric analysis made on CNTs decorated with a) Pt, b) Pd, c) Ni and d) Co acetylacetonates and corresponding metal oxides. (Adapted from Paper I, Copyright 2013, with permission from Elsevier.)

The impregnation and decomposition of metal precursors caused defects on the walls of CNTs. To study whether the defects on the surface of CNTs themselves may lower the oxidation temperature, the NiO catalyst nanoparticles were removed from
the nanostructured surface with a simple acidic treatment (refluxing in 3 M HCl at 70 °C for 39 h, followed by washing with deionized water). The resulting nickel free (Ni content below XPS detection limit, i.e., <0.05 at.%) CNTs had a composition similar to that of the original pre-treated CNTs but with more defects introduced to the walls. Interestingly, the measured TG curves of the flawed CNTs (Fig. 6, grey line) is very similar to that recorded for the pre-treated non-decorated CNTs (Fig. 6, black line) refuting the general belief that defects would play a significant role in the thermal oxidation of carbon nanotubes. Additionally, the results indicate that the reason for the accelerated decomposition of the CNTs is due to the metal/metal oxide nanoparticles being in contact with the surface.

The activation energies of the oxidation processes for different samples were determined by using equation (3) based on the Horowitz–Metzger method [67]:

$$\ln \ln \frac{m_0 - m_t}{m_0 - m_f} = \frac{E_a \theta}{RT^2},$$  

where $m_0$, $m$ and $m_f$ are the initial mass, mass at the time $t$ and final mass obtained from the TG data and $E_a$ and $R$ are the activation energy and gas constant, respectively. Parameter $T_s$ denotes the inflection point in the TG curves and $\theta = T - T_s$. The activation energies were determined by fitting equation (3) in the mass range of 94-78%. The mass range was selected so that the mass losses caused by the moisture and other volatile impurities were ignored (first mass losses) and the reaction could be treated as a first-order reaction (excess carbon). In the cases of cobalt oxide and precursor decorated CNTs, two different slopes were fitted because two different steps were visible. The Arrhenius pre-exponential factor is determined by using the heating rate $q$ and the equation (4):

$$A = \frac{q E_a}{R T_s^2 e^{-\frac{E_a}{RT_s}}}.$$  

The activation energy for the pre-treated CNTs was in line with the values reported in literature [68]. As expected, the addition of a metal precursor decreased the activation energy of the CNTs’ oxidation [69] (Table 4). However, for each precursor decorated sample, the $E_a$ was found to be lower than for the corresponding metal oxide samples. There can be several reasons for this but it indicates that the oxidation mechanisms of carbon are influenced by the metal precursor salts and metal oxide nanoparticles being in contact with the support surface. On the one hand, the decomposition of the precursor is an exothermic process and can therefore form local hot spots and promote the oxidation near the nanoparticles. In addition,
the oxygen atoms of metal oxides being in contact with the support can directly react with the carbon atoms. The as-formed oxygen vacancies in the nanoparticles are filled with the oxygen from the gas phase by surface adsorption and surface/bulk diffusion. It is also possible that the oxidation takes place at the catalyst-support boundary due to oxygen atoms that adsorb and diffuse on the surface. Furthermore, the exothermic nature of carbon oxidation can also contribute to the formation of local hot spots, which in turn can promote oxidation even further.

Table 4. Arrhenius parameters calculated at mass range of 94-78%. (Reprinted from Paper I, Copyright 2013, with permission from Elsevier.)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_a ) (kJ/mol)</th>
<th>( A ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-treated CNT</td>
<td>144</td>
<td>6.6 \times 10^7</td>
</tr>
<tr>
<td>Pt(acac)(_2)/CNT</td>
<td>83</td>
<td>4.5 \times 10^3</td>
</tr>
<tr>
<td>PtO(_x)/CNT</td>
<td>115</td>
<td>1.5 \times 10^6</td>
</tr>
<tr>
<td>Pd(acac)(_2)/CNT</td>
<td>91</td>
<td>2.8 \times 10^4</td>
</tr>
<tr>
<td>PdO(_x)/CNT</td>
<td>140</td>
<td>1.3 \times 10^6</td>
</tr>
<tr>
<td>Ni(acac)(_2)/CNT</td>
<td>55</td>
<td>1.8 \times 10^2</td>
</tr>
<tr>
<td>NiO(_x)/CNT</td>
<td>142</td>
<td>6.9 \times 10^5</td>
</tr>
<tr>
<td>Acid washed NiO(_x)/CNT</td>
<td>123</td>
<td>1.2 \times 10^6</td>
</tr>
<tr>
<td>Co(acac)(_3)/CNT (94-92 %)</td>
<td>72</td>
<td>6.0 \times 10^3</td>
</tr>
<tr>
<td>(92-78 %)</td>
<td>52</td>
<td>3.9 \times 10^2</td>
</tr>
<tr>
<td>CoO(_x)/CNT (94-92%)</td>
<td>22</td>
<td>1.9</td>
</tr>
<tr>
<td>(92-78 %)</td>
<td>90</td>
<td>1.8 \times 10^5</td>
</tr>
</tbody>
</table>

3.2 Thermal stability of nanoparticles

Although, the stability of the CNTs is a very important parameter, it is from the practical point of view equally essential to know the stability of the nanoparticles on the support. The thermal stability of reduced platinum and palladium nanoparticles on different supports (\textit{i.e.} CNTs, graphite, activated carbon and two different crystal sizes of TiO\(_2\)) were examined by exposing them to moderately elevated temperatures (300 °C) in both oxidizing and reducing atmospheres (Paper II). The particle size distribution of each aged catalyst (Figs. 7 and 8) was determined by evaluating transmission electron micrographs taken from the samples (Figs. 9-11).
Fig. 7. Particle size distribution curves for Pt (red) and Pd (blue) nanoparticles supported on (a, b) CNTs, (c, d) graphite and (e, f) activated carbon. The evolution of size distribution as a consequence of aging at 300 °C in air and 15% H₂/Ar environments is displayed in panels (a, c, e) and (b, d, f), respectively. (Paper II, published by permission of Springer.)
The particle size distributions of Pt increased with time when supported on graphite and activated carbon. However, when supported on CNTs and TiO₂, the particle size did not change (Figs. 7 and 8). Although the reduction of platinum oxide to metallic form is a highly exothermic reaction (~178 kJ/mol) and could cause a sintering and loss of surface area of Pt/PlO particles even below 200 °C, that cannot be the reason here because the Pt particles were pre-reduced. [70, 71] Therefore the size distribution shift towards larger particles could be associated with (i) Ostwald ripening caused by the faster evaporation of nanosized particles and/or (ii) surface diffusion of metal particles and atoms followed by agglomeration. The key factor in Ostwald ripening is the evaporation and re-condensation of the matter in question. The evaporation rates (the absolute value of the change of particle radius with time, \( dr/dt \))
estimated for 1 nm platinum and palladium particles at 300 °C by the modified Kelvin equation [72] were \( \sim 10^{-39} \text{ m/s} \) and \( 10^{-23} \text{ m/s} \), respectively. This is given by Equation 5.

\[
\frac{dr}{dt} = -\alpha \frac{M}{2nR\rho^2} \frac{\sqrt{\gamma}}{\sqrt{T}} \exp \left( \frac{-2M\gamma}{\rho RT} \right), \tag{5}
\]

where \( \alpha \) is the sticking coefficient (assumed to be 1), \( M \) is the molar mass of the element evaporating, \( R \) is the gas constant, \( \rho \) the density, \( P \) is the vapour pressure at \( T \) temperature, \( \gamma \) is the surface energy of the solid element and \( r \) is the particle radius. The extremely low evaporation rates and the excellent stability of Pt and Pd nanoparticles when supported on both TiO\(_2\) supports (Figs. 8 and 11) indicated that Ostwald ripening may be ruled out for these metals at such low temperatures. A more likely reason for the particle growth is surface diffusion where the particles and atoms would migrate on the surface, collide and agglomerate to form larger clusters. As the activation energy for sintering is typically lower than that for diffusion, this latter is therefore assumed to be the rate determining step. [73] In order to be able to estimate the diffusion length at the process temperatures applied in the experiments, the temperature dependent diffusivities, \( D \), were calculated from the corresponding activation energy values \( E_a \) required for diffusion [74,75] as:

\[
D = D_0 \exp \left( \frac{-E_a}{RT} \right), \tag{6}
\]

where \( D_0 \) is the diffusion coefficient at infinite temperature and \( R \) is the gas constant. The \( D \) values calculated for Pt nanoparticles on graphene, graphite and CNTs at 300 °C are in the range of \( 10^{-9} \) - \( 10^{-11} \text{ m}^2/\text{s} \) and the average distance \( \bar{x} \) that particles can diffuse in a given time period \( t \) are in the range of \( 10^{-4} \) - \( 10^{-2} \text{ m} \), according to the Einstein equation \( \bar{x} = \sqrt{2D\bar{t}} \). The large diffusion distance makes it possible for the Pt atoms and particles to collide and coalesce under the given conditions. In the case of Pd, the activation energy for diffusion is lower and the adsorption is weaker than for Pt, the surface mobility is higher and the sintering is more visible than for Pt. [76]
Pt particles seem to be more mobile when supported on graphite and activated carbon (increase in particle size distribution) than on CNTs (no change in size distribution). These results are supported by the molecular dynamic simulations [74] for the activation energies of diffusion and corresponding diffusion coefficients of Pt clusters supported on graphite and CNTs. The results also indicate that in the case of carbonaceous supports only on CNTs are the Pt nanoparticles stable when calcined in 15% H₂/Ar or in air for extended periods of time. On the other hand, the particle size distribution of Pd particles remains fairly constant on each carbon support aged in H₂ atmosphere but shows a slight increase and bimodal behaviour on graphite and activated carbon supported Pd when aged in air (Fig. 7).
The stability of Pd and Pt nanoparticles on TiO$_2$ based supports is remarkable especially when comparing it to their behaviour on carbonaceous supports (Figs. 9, 10 and 11). Similarly to other supports, the Pd particles were slightly larger than the Pt particles although prepared under identical conditions. The size distributions for both kinds of metal nanoparticles hardly changed at all during the aging experiments, even at higher temperatures (up to 500 °C, histograms not shown).
Fig. 11. TEM images of Pd and Pt decorated TiO$_2$ micro- and nanoparticles before (centre column) and after ageing 48 h in air (left column), in 15% H$_2$/Ar (right column) at 300 °C (first two rows) and at 500 °C under air (last row).

As mentioned earlier (Chapter 2.4.2) for bimetallic Sn-Pt/TiO$_2$ NW catalysts, the increase in average particle size was caused by the formation of an alloy since the conditions (high temperatures in both oxidizing and reductive atmosphere) used in preparation of the catalysts do not affect the particle size of platinum nanoparticles when supported on TiO$_2$. The reason for the significant difference between carbonaceous and TiO$_2$ supports could be explained by the adsorption energy of Pd to the surfaces, because for TiO$_2$ the adsorption energy of Pd atoms and clusters is high (1.7-2.7 eV) [73] while for graphene it is remarkably lower (1.1-1.4 eV) [76].
Also, the diffusion barrier for the catalyst particles on TiO₂ (0.9-1.4 eV) is greater than on graphene (0.2-0.4 eV) [76, 77], partly explaining the difference.

Not only the size but also the oxidation state of the nanoparticles has an effect on catalyst functionality. The literature data show large variations in the reduction temperature of different metal oxides [21, 22, 30, 78-81]. However, as detected with TG analysis, the support can significantly influence the decomposition of metal/metal oxides. In order to examine the effect of a CNT support on the reduction of metal oxide particles the temperature programmed reduction experiments were run in a reductive atmosphere (Fig. 12 a, Paper I). The TPR profile of the pre-treated CNTs (black line) shows two reduction peaks at 430 °C and at 560 °C that correspond to the reduction of iron residuals (Fe₂O₃ to FeO and to metallic Fe, respectively) [25]. The reduction temperatures of metal oxides supported on CNTs were coherent with the data reported in literature and increased in the following order: PtO < PdO < NiO < CoO. [25-27, 79-82] The reduction peaks of iron catalyst residuals were visible for each sample above 380 °C. However, it should be mentioned that in the case of Pt/CNT and Pd/CNT, the TPR profiles (blue and gray lines, Fig. 12 a) showed an increase in H₂ consumption [81, 82] that could be a sign of low temperature gasification i.e. catalytic hydrogenation of the support. [23, 83, 84]

The difference in reduction temperatures caused by the support could be seen when the TPR-H₂ was measured for reduced nickel nanoparticles supported on different carbon supports i.e. CNTs and graphite (Fig. 12 b, Paper III). The reduction of nickel occurred at a lower temperature when supported on GC than on CNTs and also the consumption of hydrogen was lower for the low surface area GC than for the higher specific surface area CNT. This indicates that not only the metal but also the support was being somewhat reduced during the measurement. Although, the nickel catalyst was already reduced, the measured TPR curve did not significantly differ from that for calcined NiO/CNT (Fig. 12 a, red line), indicating that the reduction conditions for nickel nanoparticles were not sufficient.
The TPR measurements (Paper IV) of Pt/TiO$_2$ NW and Sn-Pt/TiO$_2$ NW catalysts revealed the highest hydrogen consumption at $\sim$390 °C for monometallic and at $\sim$190 °C and $\sim$405 °C for bimetallic catalysts. The addition of Sn to Pt/TiO$_2$ NW slightly increased the measured reduction temperatures [85-87] (which is rather plausible since Sn has a considerably lower redox potential than Pt, -0.14 and 1.2 V, respectively) but also decreased the hydrogen uptake significantly (due to the poor hydrogen adsorption capacity of Sn).
4 Nanostructuring of carbonaceous materials

4.1 Background of nanostructuring

As a consequence of the temperature treatments nanoscopic channels and voids were formed in the lattice of the carbon supports, resembling the defects formed when “nanocutting” graphite and graphene by catalytic hydrogenation and oxidation. [16, 88-91] These defects were especially visible on CNTs decorated with palladium (Fig. 10, previous chapter). However, no changes in the carbon content of the aged samples could be observed in EDX measurements (Paper II), indicating that the consumption of carbon from the nanotube walls was minimal. Nevertheless the appearance of the defects also indicates that Pd and PdO are particularly active in catalytic hydrogenation and oxidation of CNTs. The TPR curves showed signs of catalytic hydrogenation of CNTs in the presence of Pt or Pd nanoparticles even at moderate temperatures (Fig. 12 a), whereas in the presence of Co or Ni, catalytic hydrogenation of graphite and graphene have been observed only at 600 °C and 700 °C. [92, 93] Catalytic oxidation of carbon can start at ~260 °C with CoOx, at ~280 °C with NiOx, and at ~400 °C with PtOx and with PdOx nanoparticles (Paper I, [16, 91]). Although, the temperatures reported for hydrogenation and oxidation are somewhat higher than those used in the aging experiments (Chapter 3.2, Thermal stability of nanoparticles), the reaction times were rather long compared to those reported in previous works.

Nanostructuring of CNTs is not necessarily disadvantageous in that it can increase the specific surface area, which is useful in certain applications. Nanostructuring has been exploited in supercapacitor electrodes, [94-97] in CNTs based gas sensors [98-100] and also in the fabrication of other nanodevices. [101, 102]

4.2 Chemical nanostructuring of CNTs

CNTs were modified chemically and thermally by acid treatments, catalytic oxidation with Co and by CO2 activation at high temperatures (Paper V). As a consequence of the higher specific surface area the specific capacitance is also expected to increase. The changes in physical appearance and surface properties of CNTs before and after nanostructuring are displayed in Fig. 13 and Table 5. The pre-treatment of CNTs did not change the appearance nor the specific surface area
significantly, whereas the addition of metal oxide nanoparticles and annealing in air resulted in broken nanotubes and increased specific surface area. The specific surface area was further increased by removing the metal oxide in an acid bath resulting in highly damaged CNTs with several hollow defects (voids in the lattice). CO$_2$ activation of CNTs made the nanotube powders extremely heterogeneous, in some locations CNTs had a corrugated surface, while in other locations, 2-dimensional structures and carbonaceous deposits (soot) could be observed. Formation of these carbon structures was most probably caused by the disproportionation of carbon monoxide (2CO $\rightarrow$ C + CO$_2$) formed during the etching step (C + CO$_2$ $\rightarrow$ 2CO) of the reversible Boudouard reaction. For CNTs activated at 800 °C, the specific surface area varied significantly within a single sample due to the heterogeneous nature of the sample (Table 5). The CNTs activated at 750 °C had a mass loss of $\sim$7% while the total mass loss of CNT activated at 800 °C was $\sim$28%.

Fig. 13. TEM images of (a) pristine CNT, (b) CNT-COOH, (c) CoO$_x$/CNT, (d) acid-washed CoO$_x$/CNT, (e) CNTs activated at 750 °C and (f)-(g) CNTs activated at 800 °C. (h) Raman spectra of capacitor materials. (Reprinted with permission from Paper V, Copyright 2015, American Chemical Society.)
Table 5. Surface properties of nanostructured capacitor materials measured with nitrogen physisorption. (Reprinted with permission from Paper V, Copyright 2015, American Chemical Society.)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²/g) BET</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs/pristine</td>
<td>255.4 ± 3.5</td>
<td>1.2±0.5</td>
<td>18.0±7.3</td>
</tr>
<tr>
<td>CNT-COOH</td>
<td>266.4 ± 14.6</td>
<td>0.9±0.3</td>
<td>13.0±3.7</td>
</tr>
<tr>
<td>CNT-CoOₓ</td>
<td>302.4 ± 10.2</td>
<td>0.9±0.3</td>
<td>11.2±4.0</td>
</tr>
<tr>
<td>CNT-CoOₓ/acid</td>
<td>354.7 ± 5.7</td>
<td>1.0±0.2</td>
<td>11.5±3.0</td>
</tr>
<tr>
<td>CNT/Act.750°C</td>
<td>324.2 ± 5.0</td>
<td>1.0±0.2</td>
<td>12.2±2.2</td>
</tr>
<tr>
<td>CNT/Act.800°C</td>
<td>416.3 ± 92.9</td>
<td>2.3±1.6</td>
<td>21.2±10.1</td>
</tr>
</tbody>
</table>

4.3 Nanostructuring with electron beam irradiation

Electron beam irradiation in TEM analysis is a convenient method to generate and study in situ material phase transition [103, 104], nanostructure growth [105] and nanostructuring of materials [91, 106, 107]. Although, e-beam induced growth or nanostructuring does have very limited practical significance for applications (e.g., catalytic reactions or electrical devices) due to the minute amount of the samples one can manipulate or produce by the method, studying the interaction of the beam and the matter can help us avoiding sometimes misleading interpretation related to the microstructure of samples caused by the analysis itself. This is particularly important for catalyst materials with carbonaceous support as various metals can induce defect formation in the support as seen earlier for nickel decorated CNTs [91, 107] and for silver on graphene. The difference in reduction temperatures caused by the support could be seen when the TPR-H₂ was measured for reduced nickel nanoparticles supported on different carbon supports i.e. CNTs and graphite (Fig. 12 b, Paper III). The reduction of nickel occurred at a lower temperature when supported on GC than on CNTs and also the consumption of hydrogen was lower for the low surface area GC than for the higher specific surface area CNT. This indicates that not only the metal but also the support was being somewhat reduced during the measurement. Although, the nickel catalyst was already reduced, the measured TPR curve did not significantly differ from that for calcined NiO/CNT (Fig. 12 a, red line), indicating that the reduction conditions for nickel nanoparticles were not sufficient.

In order to examine the effect of electron beam irradiation on Pt, Pd and Ni decorated supports (as-prepared, calcined and reduced), the samples were placed on a TEM grid and exposed to the e-beam in the high vacuum of the TEM column.
while taking images at different time intervals up to 20 min (Paper II). In the case of CNT supported samples, the first changes were already visible after ~3 min regardless of the oxidation states of the metals (i.e. before and after calcination and reduction of nanoparticles), whereas for other carbon supports changes were only visible after 5 min or longer. Movement of nanoparticles on the surface of CNTs and graphite was clearly visible, as were tiny voids in the structures formed as the nanoparticles drilled and cut the materials (Fig. 14, first two rows). For activated carbon supported samples the changes were not entirely clear due to the initially highly structured surface (Fig. 14, last row), while for TiO$_2$ no defects were observed even after 20 min of exposure (not shown).
Fig. 14. TEM images of nickel decorated carbon supports before and after exposing to electron beam radiation.
Although the TEM column was under a high-vacuum, the presence of oxygen traces should not be ignored, as the reason for nanocutting and carbon consumption may be due to the catalytic oxidation of carbon. With a highly overestimated amount of O\textsubscript{2} ($P=10^{-5}$ Pa as an upper estimate), the collision flux ($Z_w = \frac{PN_A}{\sqrt{2\pi RMRT}}$, where $N_A$ is Avogadro's constant, $M$ is the molar mass, $R$ the gas constant and $T$ the temperature) is $2.7\cdot10^{17}$ m\textsuperscript{2}s\textsuperscript{-1} which gives the collision rate to be $\sim3.4$ s\textsuperscript{-1} for nanoparticles of 2 nm diameter according to the kinetic collision theory of gas species with surfaces. By assuming that each collision results in an oxygen molecule being adsorbed then dissociated on the catalyst surface, and ready to oxidize the carbon atoms nearby, $\sim200$ carbon atoms corresponding to 5 nm\textsuperscript{2} area of graphene may be removed in such an ideal case in each minute. Although the area is reasonable, the model used is extremely simplified and the amount of O\textsubscript{2} taking part in the actual reaction is highly overestimated. The probability of surface oxide metal formation on the catalyst per collision is definitely less than one, and the chemisorbed oxygen requires a rather large energy ($E\sim0.9$ eV) to diffuse on the catalyst. [108]

Another possible reason for nanocutting is a direct atomic displacement of carbon caused by colliding electrons of sufficiently high kinetic energy. The threshold energy for knocking out carbon atoms from the lattice of graphene is $\sim80$ keV and from SWCNTs is $\sim86$ keV. Thus the e-beam of the used instrument (120 keV) could definitely sputter carbon atoms from the lattice. [109-111] However, it should be kept in mind that the doses of the electron flux are too small ($8.1\cdot10^4$ e$^-\text{nm}^2\text{s}^-1$) for a significant direct knock-on displacement of carbon atoms during the analyzing periods. [107] Nevertheless, we observe a very clear degradation of the carbon material when metal clusters are present on the surface. A recent experimental and molecular dynamics simulation study [107] proposed that direct atomic displacement is not the major reason for nanocutting. A dominant multistep mechanism for nanocutting of nickel decorated SWCNT with an 80 keV electron beam was suggested: i) First, polyyne carbon chains form from the CNTs, then ii) the chains dissociate to single or paired adatoms adsorbed on the metal, and finally iii) ejection of the adatoms takes place leading to a structured surface. This suggested mechanism requires a significantly lower energy than that of direct atomic displacement and would therefore be more favourable. In this mechanism, however, the metal plays a crucial role and it do not explain the cutting of non-decorated nanotubes.

Defects already existing on the surface (as a consequence of thermal treatments) grew rather rapidly upon irradiation (Fig. 15), while the intact surface showed
practically no noticeable damage. This is in good agreement with other experimental and modelling results obtained on graphene. [109] Since the lattice atoms have having lower coordination number (2 or 1) than in flawless structures (coordination is 3) or the bonds are under stress (e.g. in pentagons), the knock-on ejection occurs more easily than from a flawless hexagonal lattice. On the other hand, the impurities (metal nanoparticles or traces of metal precursors) can also nucleate the formation of carbon vacancies. [109] The mechanism is not entirely clear, but the better electron absorption by elements with nuclei heavier than carbon is expected to cause better energy transfer from the electrons to the solid material. This results in more pronounced local heating and consequently enhanced chemical reactivity as well as phonon-assisted sputtering of carbon atoms.
Fig. 15. TEM micrographs of individual CNTs exposed to the electron beam for prolonged periods of time. (a) Intact CNT showing structural stability after 5 and 8 minutes of irradiation in the TEM column. (b) CNT with defects undergoing severe damage after 2 and 5 minutes electron beam exposure. (c) Nickel decorated CNT suffers from considerable degradation after irradiation. The arrows are pointing to the forming defects. (Paper II, published by permission of Springer.)
5 Selected applications

5.1 Background of selected applications

A few simple but important applications were selected to study the performance of the prepared nanomaterials and to find out whether any exploitation of the results could be directly possible. Two very different catalytic reactions utilizing the prepared materials as catalysts (steam reforming of ethanol (Paper III) and selective hydrogenation of citral (Paper IV)) as well as an electrical application (supercapacitor electrodes (Paper V)) where nanostructured carbons are used as conductive porous media, were tested in more detail. All three applications are industrially relevant since today (i) steam reforming is the major route to produce hydrogen, (ii) the products of citral hydrogenation are in high demand as the expensive chemicals used in fragrances, pharmaceutical and fine chemical intermediates, and (iii) supercapacitors are the ultimate fast charge/recharge devices to store and deliver electrical energy.

5.1.1 Production and use of $H_2$

The demand for new and sustainable energy sources is growing as fossil fuels are starting to run out, are getting more and more expensive, and pose global environmental concerns related to global climate change. Hydrogen, which is often considered to be a “green” energy source, is becoming more important due to its versatile applications in fuel cells as well as for feedstock in the chemical (e.g. ammonia synthesis and desulphurization of crude oil) and food (e.g. hydrogenation of unsaturated fatty acids) industries. It should be kept in mind that, whether the $H_2$ is “green” or not depends on the environmental friendliness of the method and the feedstock from which it is synthesized. Although steam reforming is the most efficient method to produce hydrogen, with an efficiency of up to 85%, [112] the feedstock used is often fossil based and therefore the process does not offer a sustainable solution. On the other hand, the use of ethanol as a feedstock in SR has many advantages compared to fossil based hydrocarbons; it is less toxic and poses much less environmental damage during production and processing, it does not contain sulphur (that is a well-known catalyst poison), it can be bio-waste based and it can be reformed at significantly lower temperatures (<450 °C) than the hydrocarbons (>500 °C). [17, 113-116] The development of newer and more
effective catalyst materials to allow processes to be carried out at low temperatures is ongoing. However, deactivation of catalysts caused by the formation of solid carbon in various side reactions (e.g. decomposition of methane, polymerization of ethylene and the Boudouard reaction) is a major problem, which requires detailed studies before conventional catalytic materials (10-20% Ni on alumina, calcium aluminate, or magnesium aluminate) can be replaced [117].

5.1.2 Products from citral

In citral hydrogenation, it is not only the pleasant odour and important applications of the products makes the reaction important but also the fact that the ethylenic double bond is thermodynamically easier to hydrogenate than the carbonyl bond, i.e. the reaction favours the formation of citronellal instead of unsaturated alcohols [118]. As there are three different double bonds in the citral molecule there are three possible reaction routes (Fig. 16) from which two are the most favoured. Firstly, hydrogenation of carbonyl to unsaturated alcohols (nerol and geraniol), and secondly the hydrogenation of the conjugated double bond to citronellal. Both reaction paths lead to citronellol (which is still considered to be the desired product), whereas, the hydrogenation of the isolated carbon-carbon double bond of citral (and also citronellal or citronellol) leads to the formation of undesired products such as dimethyloctenal (not shown in Fig. 16), and dimethyloctanal and dimethyloctanol. As in every reaction, several parameters (such as the solvent, the nature of the catalyst and the support, the size of the catalyst etc.) [119-123] affect the route by which citral hydrogenation proceeds. Transition metals (such as Pt, Pd and Ni) are often selected as catalysts in citral hydrogenation because they typically show high reduction activity towards unsaturated bonds. [124] The selection of supporting material is not straightforward due to the surface properties and the metal-support interactions. Typical supports are metal oxides (SiO$_2$, Al$_2$O$_3$, TiO$_2$), zeolites or carbon [123, 125-127]. Although different supports have been widely studied (TiO$_2$ nanoparticles and CNTs among those) [128-131] there are no reports of the use of novel TiO$_2$ NW as a support in citral hydrogenation.
5.1.3 Electrodes for supercapacitors

The use of CNTs as electrode materials in supercapacitors has been widely studied. In order to find the best material for capacitors, SWCNTs and also MWCNTs have been grown as patterned or non-patterned films on different substrates, used either free-standing or supported, and as thin or thick films. [32, 132-135] Furthermore, different kinds of modification (chemical and thermal treatments) [94-97, 136] have been made to CNTs in order to improve their specific capacitance, electrical conductivity and processing capabilities. [137-143]

Supercapacitors can generally be divided in two sub-categories depending on whether electrochemical oxidation of the electrode material takes place (pseudocapacitors) or not (electric double-layer capacitors, EDLC). The operation of pseudocapacitors is based on faradaic processes that involve electrochemical reduction and oxidation of the electrodes and the capacitance is primarily affected by the chemistry and mass of the used materials. In contrast, in the case of EDLCs, the device operation is based on an accumulated surface charge which is stabilized.
by counter-ions of the electrolytes attracted by electrostatic forces. The capacitance is mainly affected by the surface area of the electrodes and the size of ions in the electrolyte. The charge density, and thus the Coulomb repulsion of charged species with the same sign, can be lowered by increasing the specific surface area of the capacitors without increasing the mass of the device. However, it should be kept in mind that the overall performance of the capacitors is affected by other parameters besides the specific capacitance, such as the conductivity of the electrodes and associated power losses.

Although the CNT based supercapacitors have shown promising results, the true potential of CNTs as electrode materials has not yet been truly exploited. The nanostructuring of CNTs is a relatively easy method to increase the specific surface area of electrodes and hence also increase the specific capacitance. However, it should be noted that the practical limit for surface area enhancement depends particularly on the electrode material since at some point highly structured materials tend to lose their electrical conductivity and also become sensitive to adverse effects such as oxidation and mechanical degradation.

5.2 Catalytic activity

5.2.1 Carbonaceous catalysts

The activity of Pt, Pd and Ni/NiO decorated CNTs and graphite was tested in the low temperature steam reforming of ethanol (Paper III). The results were similar to the reference data obtained under identical conditions from CNTs with higher catalyst loading (10 wt.%) [20]. From the ethanol conversion graph (Fig. 17 a) it is easy to observe that only three catalysts; Ni/CNT, Pt/CNT and Ni/GC showed significant reaction activity, whereas Pd on both supports and Pt/GC did not have any noticeable activity. The highest ethanol conversion (nearly 100%) with 42% selectivity towards H₂ was achieved with Ni/CNT at 450 °C while the second active catalyst Pt/CNT had 16% selectivity towards H₂ with ~70% conversion at 410 °C. In contrast, graphite supported Ni showed lower ethanol conversion, ~50% at 450 °C, but with a higher hydrogen selectivity of ~33%. When comparing the nickel catalysts the ethanol conversions indicate that CNTs are more useful than GC in the studied reaction temperature range. Although, the main product for each catalyst was H₂, considerable amounts of side-products such as CH₄, CO₂, CO and CH₃CHO (up to 2.5 vol. %, Fig. 17 b-d) were formed. The relatively high amount of methane (~2
vol. %) is understandable considering the high activity of nickel in the methanation reaction. [144] It is worth mentioning that the Pt/CNT catalyst was the only catalyst that showed a decrease in ethanol conversion at high temperatures (above 410 °C), while for all the other catalysts the maximum conversion was at the upper limit of the studied temperature range. However, in the reference data the 10% Ni/CNT [20] also had a clear decrease in ethanol conversion at 300 °C caused by the deactivation of the catalyst by coke formation.

Fig. 17. Comparison of (a) the activities of different carbon supported catalysts in steam reforming of ethanol and product gas compositions over (b) Ni/CNT, (c) Pt/CNT and (d) Ni/graphite catalysts. Ethanol conversion and hydrogen production over nickel catalysts adapted from [60]. (Adapted from Paper III with permission from the Royal Society of Chemistry, 2015.)
Closer examination of the side-products gives a hint of how the reaction might have proceeded. For Ni catalysts, first dehydrogenation of ethanol to acetaldehyde starts in the low temperature regime (150 – 325 °C). This is followed by the decomposition of acetaldehyde and the onset of the water-gas shift reaction above 350 °C, as the concentration of acetaldehyde starts to decrease while simultaneously that of methane, CO and CO₂ increases. In contrast with Ni, on a Pt/CNT catalyst, decomposition of ethanol to CH₄ and CO is more pronounced than dehydrogenation and the reforming of ethanol. It is worth mentioning that the existence of acetaldehyde in the product distribution substantiates the TPR results (Fig. 12, Chapter 3.2). According to the TPR measurements the nickel decorated carbon supports, especially CNTs, might already undergo reduction at the temperatures used in SRE. [145]

The type of metal used has a significant effect on the catalyst’s activity in SRE. Although each of the CNT supported catalysts has a nanoparticle size of ~2 nm, the activity varies from 10% (for Pd) to nearly 100% (for Ni) conversion. As suggested by Lin et al. [146], the reason for the better performance of nickel in SRE can be in the high d-character of the metal-metal bonding and the high Ni-C bonding stability that promotes the C-C and C-H scission.

Since there were clear signs of deactivation of the catalyst (decrease in ethanol conversion) for Pt/CNT, the spent catalysts were analyzed with TEM (Fig. 18) and SEM-EDX. In accordance with the results of thermal aging of different carbonaceous supports (Chapter 3.2, Fig. 7), CNTs provide a stable support for metal nanoparticles whereas the particle size of metals supported on GC increased due to surface diffusion. The elemental concentrations of the catalysts were measured after the reaction and compared to the fresh catalyst (Paper III, supplementary information). While the amount of oxygen decreased significantly (due to the reduction of the support either during the pre-treatment and/or the reaction), the amount of carbon increased, particularly on those samples that were active in SRE. The increased carbon content can easily be explained by some carbon depositing on the catalyst as a consequence of side reactions e.g. decomposition of methane, polymerization of ethylene and the Boudouard reaction. [20, 147, 148] TEM analysis of spent sample revealed that not only amorphous carbon but also some other carbon nanostructures such as carbon nanotubes and nanofibres, were formed on both nickel catalysts and also on Pd/GC. However, this is not surprising because alcohols are known to be excellent precursors for catalytic chemical vapour deposition of filamentous carbons on iron group nanoparticles even at moderate temperatures. [149-152] Due to the low solubility of carbon in noble metals, less filamentous carbon products
are observed on those than on the spent Ni catalysts (known to have high carbon solubility). [145, 153, 154]

Whether the formation of carbon structures on the catalysts caused any deactivation or not should be studied more in the future. However, probably the catalysts that had grown well-structured carbon nanofibres/tubes (as the side-products of the reforming reaction) are less deactivated than the catalysts that produced soot/coke (which eventually poisons the catalyst). This seems to be supported by the fact that Pt/CNT catalyst, the only catalyst that showed signs of deactivation (i.e. decrease in ethanol conversion and hydrogen production) was coated with amorphous carbon (Fig. 18 a).

![Fig. 18. TEM micrographs of CNTs (a-c) and graphite (d-f) decorated with Pt (first row), Pd (middle row) and Ni (last row). Image on the left hand side shows the fresh catalyst and on the right hand side the spent catalyst. (Adapted from Paper III with permission from the Royal Society of Chemistry, 2015.)](image)
5.2.2 TiO$_2$ supported catalysts

Chemoselective hydrogenation of citral was studied by using TiO$_2$ nanoparticles and nanowires as support materials for a platinum catalyst (Paper IV). The Pt/TiO$_2$ NW catalyst was found to be very active, achieving a 100% conversion after 30 min reaction whereas over the NP supported catalyst the conversion was 95% after 3 h (Fig. 19 a). Consequently, also the product distributions were also totally different; while on a TiO$_2$ NP support practically all possible products (citronellal, nerol and geraniol, citronellal and dimethyloctanal) were simultaneously produced, the TiO$_2$ NW supported platinum was more selective towards citronellal (Fig. 19 b). However, after the rapid formation of citronellal, the reaction continued and started to produce dimethyloctanal and citonellol, which in turn reacted further to dimethyloctanol. The difference in the catalytic behaviour of Pt/TiO$_2$ NP and Pt/TiO$_2$ NW must be associated with the support material because the Pt nanoparticles were of similar size distribution on both supports. Although both supports were the anatase phase of TiO$_2$, the major difference was the alkalinity of the materials as mentioned in Chapter 2.4.1. Apparently the weak basic sites of the NW support direct the reaction towards the hydrogenation of the ethylenic double bond, which is known to be the least energy demanding route, whereas the medium strong basic sites of an NP supported catalyst do not have a noticeable effect on the reaction. The promoting effect of alkalinity on the reduction of unsaturated ethylenic bonds has been reported earlier in the case of different organic compounds over various catalysts. [155-159]

The effect of the solvent on the reaction was also studied by changing the non-polar toluene to polar 2-pentanol in order to enhance the formation of alcohols (nerol and geraniol) (Fig. 19 b second row). Although the conversion rate in toluene was found to be slightly faster than in 2-pentanol, the product distributions and selectivities were rather similar in both solvents. However, the initial rates of different products were always higher for toluene than for 2-pentanol, possibly because of the adsorption of 2-pentoxy species on the metal surface.
Even though the change of solvent to polar 2-pentanol decreased the initial rates of reaction (Table 6), the selectivity towards unsaturated alcohols did not increase. Addition of tin to the Pt/TiO₂ NW further reduced the initial reaction rates making the values ~6 times lower than on the monometallic catalysts. TOF values obtained for monometallic catalyst were not as high as were expected, however the 1 wt.% Sn-2 wt.% Pt/TiO₂ NW catalyst seemed to outperform the monometallic one and the results in literature. [125, 160] The bimetallic catalyst with a higher tin loading did not show noticeable activity in the reaction, correlating with the CO chemisorption data that showed a decreasing dispersion of metal with increasing tin loading. The active sites of Pt are blocked by the tin but in the case of lower tin loadings there are still several active sites left. Nevertheless, the selectivity towards unsaturated alcohols was highest with the higher tin loading in the catalyst, as reported earlier. [161-164] Also, the product distributions were found to be very different after the addition of Sn to the monometallic catalyst [161, 162, 165]. While the monometallic catalyst promoted hydrogenation of the ethylenic double bond (and therefore formation of citronella), the bimetallic catalyst favoured the hydrogenation of the carbonyl bond (and therefore produced more nerol and geraniol). Although the measured selectivities toward unsaturated alcohols were somewhat lower than those reported in the literature [160, 166] this is
understandable since the alkaline nature of NWs promotes the reaction towards citronellal.

Table 6. Catalyst metals supported on TiO$_2$ nanoparticles (NPs) and nanowires (NWs), dispersion of metal by CO chemisorption, used solvents and the corresponding initial reaction rates and conversions. (Adapted from Paper IV, Copyright 2014, with permission from Elsevier.)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dispersion of metal (%)</th>
<th>Solvent</th>
<th>Initial rate ($\text{min}^{-1}\text{g}_\text{cat}^{-1}$)</th>
<th>TOF ($\text{s}^{-1}$)</th>
<th>Conversion at 180 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 wt.% Pt/NP</td>
<td>n.m.</td>
<td>Toluene</td>
<td>0.093</td>
<td>n.m.</td>
<td>95%</td>
</tr>
<tr>
<td>2 wt.% Pt/NW</td>
<td>19.3</td>
<td>Toluene</td>
<td>0.505</td>
<td>n.m.</td>
<td>100%*</td>
</tr>
<tr>
<td>2 wt.% Pt/NW</td>
<td>19.3</td>
<td>2-Pentanol</td>
<td>0.365</td>
<td>0.43</td>
<td>100%*</td>
</tr>
<tr>
<td>1 wt.% Sn-2 wt.% Pt/NW</td>
<td>4.3</td>
<td>2-Pentanol</td>
<td>0.059</td>
<td>0.59</td>
<td>95%</td>
</tr>
<tr>
<td>2 wt.% Sn-2 wt.% Pt/NW</td>
<td>2</td>
<td>2-Pentanol</td>
<td>0.005</td>
<td>0.08</td>
<td>13%</td>
</tr>
</tbody>
</table>

* after 30 min; * after 60 min.

5.3 Nanostructured supercapacitor electrodes of CNTs

Two different electrolytes were used in the measurements (Paper V) to test the buckypaper films made of different kinds of nanostructured carbon nanotubes. In aqueous KOH, the measured C-V curves followed the ideal rectangular shape for the hysteresis loop over a wide range of scan rates (Fig. 20 a-b). [133, 136] However, when using the TES-TFSI electrolyte, the curves were somewhat butterfly shaped which is believed to be caused by the different orientation of the nonspherical symmetric ions at different electrode bias values (Fig. 20 c). Even at the low surface charge densities ($\sigma$) used in the experiments (up to 0.5 e/nm$^2$ at 2 V) the nonspherical ions can orient parallel or perpendicular to the surface of the CNTs and influence the apparent thickness of the Helmholtz layer. [167]

Typically, the presence of surface functional groups and metal oxides in capacitor materials causes pseudocapacitance curves due to the redox reactions. [168] However, no evidence of that was observed in the case of the electrodes build of CNT-COOH and CoO$_x$/CNT. Although one would expect electrochemical reduction and oxidation (i.e., switching between oxidation states Co$^{2+}$ and Co$^{3+}$) [137, 169, 170] the concentration of metal oxide in CoO$_x$/CNT and carboxyl groups in CNT-COOH was not sufficiently high to have any influence on the shape of the C–V hysteresis curves. [140] Therefore the role of CoO$_x$ particles was limited to
the localized catalytic etching of CNTs during the synthesis phase, hence increasing the specific surface area and capacitance.

Fig. 20. a) Cyclic voltammetry curves of CNT capacitors in KOH electrolyte: CNT/pristine, CNT-COOH, CNT-CoO$_x$, CNT-CoO$_x$/acid, CNT/Act.750°C and CNT/Act.800°C. b) C–V curves of symmetric CoO$_x$/MWCNT electrodes measured at different charge/discharge rates in KOH electrolyte. c) C–V curves of symmetric CNT thin films in TES-TFSI ionic liquid electrolyte measured from −2 to 2 V. CNT/pristine, CNT-CoO$_x$/acid, CNT/Act.750°C and CNT/Act.800°C. d) Current versus time plot for the CoO$_x$/CNT supercapacitor. (Note: invalid data points caused by the acquisition software are masked.) (Reprinted with permission from Paper V, Copyright 2015, American Chemical Society.)

In order to determine the actual series resistance of the devices the capacitor was connected in series with a 3.3 Ω resistor and then powered by rectangular voltage
pulses \( (U = \pm 500 \text{ mV at } 0.5 \text{ Hz}, \text{ Fig. 20 d}) \). From the temporal change of the measured voltage drop across the series resistor, the current in the circuit could be calculated by Ohm’s law. The value of the measured initial current \( I_0 \) was then used to calculate the resistance, \( R_c \), of the device resulting in 41.5 \( \Omega \) and 39.8 \( \Omega \) for the capacitors made of pristine and CoOx decorated nanotubes, respectively. The obtained RC time constants \( (\tau = 0.51 \text{ s for pristine and } \tau = 1.00 \text{ s for CoOx/CNT, respectively}) \) were in reasonable agreement with those obtained from fitting the exponential decay curves on the experimental data \( (\tau_{\text{pristine}} = 0.74 \text{ s and } \tau_{\text{CoOxCNT}} = 1.48 \text{ s}) \).

The specific capacitance of the electrodes increased linearly with increasing specific surface area when using pristine CNTs and acid or catalytic oxidation nanostructured CNTs (CNT-COOH, CNT-CoOx, CNT-CoOx/acid). The capacitors based on the CNT-CoOx electrodes as well as those with the CNT-CoOx/acid showed \( \sim 2 \)-fold increase of the specific capacitance with reference to the pristine CNT and CNT-COOH based devices, respectively. Surprisingly, despite the significant increase of the specific surface area after the CO2 activation of CNTs (at 750 or 800 °C, respectively), the specific capacitance of the electrodes practically did not change. The reason for the low capacitance could be the carbonaceous deposit formed on the CO2 activated CNTs during the activation process causing electrically poor interfaces with the electrolytes.

Table 7. Specific capacitance and energy density of capacitors in KOH (at 0.5 V) and ionic liquid (at 2.0 V) electrolytes. (Reprinted with permission from Paper V, Copyright 2015, American Chemical Society.)

<table>
<thead>
<tr>
<th></th>
<th>Specific capacitance in KOH (F/g)</th>
<th>Energy density in KOH (Wh/kg)</th>
<th>Specific capacitance in IL (F/g)</th>
<th>Energy density in IL (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs/pristine</td>
<td>16.6</td>
<td>0.58</td>
<td>10.4</td>
<td>5.79</td>
</tr>
<tr>
<td>CNT-COOH</td>
<td>8.5</td>
<td>0.29</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>CNT-CoOx</td>
<td>24.9</td>
<td>0.86</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td>CNT-CoOx/acid</td>
<td>25.0</td>
<td>0.87</td>
<td>15.0</td>
<td>8.32</td>
</tr>
</tbody>
</table>

Although, the specific capacitance values were larger when using aqueous KOH compared to the ionic liquid, the electrochemical window is narrower causing the overall enabled energy and power densities to be approximately an order of magnitude lower (8.3 vs 0.9 Wh/kg as well as 10.3 and 1.3 kW/kg as evaluated for acid-washed CNT-CoOx electrodes) (Table 7). Consequently, the capacitors in the
IL electrolyte can compete with commercial and other CNT-based supercapacitor devices. [171-173]

The reliability of the capacitor structure was tested by measuring the C-V curves of the capacitor made from the acid-washed CNT-CoO$_x$ for more than 1500 cycles (Fig. 21). The open measurement system enabled the electrolyte to evaporate with the result that the charging current started to decrease after about 15 min of measurement. When the device was covered (nearly saturated vapour of the electrolyte) the C-V curves remained rather stable (for over 1000 cycles) indicating that devices integrated in hermetic packages would be functional for an extended number of charging/discharging cycles in practical applications.

Fig. 21. Envelope of the reliability measurement signals of acid-washed CNT-CoO$_x$ capacitor. One measurement consisted of 200 cycles (except the first where only 100 cycles were measured).
6 Summary and conclusions

The main objectives of this thesis were to study the thermal stability of CNT and TiO$_2$ nanowire supported nanomaterials and to show the applicability of the materials when compared to their conventional counterparts (i.e. graphite and TiO$_2$ nanoparticles). The prepared nanomaterials were exploited in different applications such as catalytic reactions and electric double-layer capacitors.

Pure well-structured CNTs are known to be stable in air up to 530 °C, however the addition of impurities (metal nanoparticles in this case) to the surface significantly decreased the ignition temperature and activation energy of oxidation. Also, under reductive conditions the CNTs decorated with palladium or platinum nanoparticles showed a relatively large hydrogen uptake indicating a tendency for low temperature gasification of the material.

The stability of palladium and platinum nanoparticles supported on three different types of carbonaceous support materials (CNT, graphite and activated carbon) and two different titanium dioxide (nano- and microparticles) supports were studied under moderate temperatures in reducing and oxidizing environments. Methods such as TEM imaging and simple mathematical simulations (Ostwald ripening and surface diffusion) were used to detect the particle size growth and explain the differences in behaviour of different metals and supports, respectively. The particle size distribution of Pd nanoparticles aged in H$_2$ was observed to be rather stable on each studied support, while under air the particle size distribution grew slightly. Surprisingly, only CNTs and TiO$_2$ supports provided stable support for Pt. The possible role of Ostwald ripening in particle size growth was ruled out since the evaporation rates of Pt and Pd were extremely low and also because (under identical conditions) particles supported on TiO$_2$ supports did not suffer from sintering. The large diffusion distances calculated for Pt and Pd supported on carbon make it possible that atoms can move on the surface to collide and coalesce explaining the increase in the particle size. The superior stability of the nanoparticles on TiO$_2$ surfaces with reference to carbonaceous supports was also a consequence of the excellent interaction of the metals with the surface.

The effect of the electron beam of a TEM on various carbon and TiO$_2$ supported catalysts was studied. While TiO$_2$ supports remained stable under the e-beam, the carbon based supports became partially damaged (formation of channels and voids) in a few minutes. The reasons for such nanocutting can be manifold. On the one hand, the presence of oxygen traces in the microscope column may result in catalytic oxidation in the proximity of the metal nanoparticles. However this cannot
be the only reason since the samples that did not contain any metal but only defects also underwent degradation. On the other hand, another possible reason for the nanocutting was concluded to be knock-on displacement of carbon atoms from the support by the scattering electrons. This would generate vacancies in the lattice and enlarge the defects in the structure.

The alkalinity and acidity of the novel TiO$_2$ NW and CNT support materials played an important role in the selected reactions, respectively. In the hydrogenation of citral over Pt catalyst supported on TiO$_2$ NP and NW the results showed that the alkaline nature of TiO$_2$ NW with weak basic sites promoted the formation of citronellal with higher activity and better selectivity than the catalyst based on the neutral TiO$_2$ nanoparticles. In the low temperature SRE the high activity of CNT supported catalysts could be explained not only by the high specific surface area and porous structure of CNTs but also by the acidic pre-treatment of CNTs which might promote the formation of smaller metal nanoparticles compared to the non-treated supports. The reasons for the better performance of Ni/NiO catalyst compared to other catalysts tested in SRE can be explained by the higher d-character of the metal-metal bonding and the promoting effect on the C-C and C-H scission. However, another possible reason could be the solubility of carbon in the metal, since the carbon forming as a side-product during the reaction can build-up on the catalyst, thus poisoning the surface. The metals with good carbon solubility can tolerate more carbon, hence the carbon can dissolve, diffuse and precipitate in the form of nanofibres/nanotubes and therefore coking (i.e. deactivation) is avoided.

The use of pristine and surface modified CNTs as electrodes in supercapacitors was studied in order to evaluate how an additional pore structure within the nanotube walls could affect the specific capacitance, energy, and power density in different electrolytes (i.e. aqueous KOH and ionic liquid). The specific surface area and the associated specific capacitance followed a linear correlation for CNTs modified via catalytic partial oxidation over CoO$_x$ nanoparticles. The electrodes composed of CO$_2$ activated CNTs demonstrated only a minor increase in their specific capacitance, despite the significant increase in specific surface area, revealing that a high surface area is not itself a guarantee of a high specific capacitance, since the soot formed during the activation process hinders the formation of good electric double layer at the solid–electrolyte interface. Among six different types of electrode materials tested, the CoO$_x$ decorated materials (metal oxide decorated as well as that decorated followed by acid washing) proved to have the highest specific capacitance, and give energy and power storage density
values comparable with commercial and other CNT based electric double-layer capacitor devices reported earlier.

In conclusion:

- The addition of impurities such as metal nanoparticles (as a precursor, metal or metal oxide) to CNTs decreases the temperature limit of oxidation and gasification of carbon. Such an effect is a disadvantage in catalyst applications. However, this could be beneficial in decoking processes by applying low cost and abundant cobalt and nickel oxide nanoparticles on surfaces such as exhaust pipes, catalytic converters and sensors.

- Surprisingly however, the defects formed on the surface of the CNTs by either partial oxidation or reduction or acid treatments do not have any significant influence on the enhancement of carbon removal from the structure.

- Aging experiments gave direct insight into the sintering of catalyst nanoparticles and highlighted issues related to stability/degradation of their support, important for designing catalytic reactions and converters. According to the results CNTs provide a more stable support for palladium and platinum nanoparticles than other carbonaceous supports under both reductive and oxidizing atmospheres.

- Studying the carbonaceous materials under an intense electron beam might lead to degradation of the material when metal impurities or defects are present.

- Although the Ni/CNT catalyst outperformed its counterparts in SRE in both ethanol conversion and hydrogen selectivity, the reasons for the superiority of CNTs should be examined more in the future, since the effect of acidic pre-treatment on the particle size and activity of the catalyst is still unknown.

- The catalyst deactivation caused by coke formation in SRE might be avoided by using metals with high carbon diffusion ability since the carbon precipitation could favour formation of fibrous instead of amorphous structures.

- TiO₂ nanowire based catalysts are suitable for liquid phase hydrogenation and – as a consequence of their basic character – may even outperform conventional TiO₂ based catalyst supports.

- Although it is possible to increase the specific capacitance of CNTs capacitors by nanostructuring the surface electrodes, the increase in specific surface area is not a guarantee of a large specific capacitance.
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ON THE STABILITY OF CARBON NANOTUBE AND TITANIA NANOWIRE BASED CATALYST MATERIALS

FROM SYNTHESIS TO APPLICATIONS