Modification of carbon materials for catalyst applications

Emma Sairanen

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Abstract

Sustainable methods to produce chemicals and energy are widely studied and the use of catalysts is notable as a means to make processes more efficient and selective. Carbon materials have many properties that can be utilized in catalyst applications. In this thesis, carbon was studied as a catalyst material and different carbon catalyst preparation methods were applied. The prepared catalysts were tested in xylose dehydration and alcohol electrochemical oxidation reactions. Cinnamaldehyde hydrogenation was used as a model reaction for characterization of part of the prepared catalysts.

Carbon materials can act as catalysts without any metals if the surface contains suitable heteroatoms. Functionalization of carbon surfaces by oxidation treatment was used to create these different type oxygen- and sulphur-containing acidic and basic sites on the surface. The carbon materials were used as catalyst supports and tested as catalysts for xylose dehydration using water as a solvent. Carbon was found to be a selective and stable catalyst towards furfural formation.

Three different methods for preparing carbon supported Pd, Pt, and PtCo metal catalysts were tested: the traditionally used dry and wet impregnation methods with liquid precursors and the less commonly used gas-phase deposition method based on atomic layer deposition (ALD). The ALD based preparation method was found to lead to catalysts with the highest metal dispersion and smallest metal particles with a narrow metal particle size distribution.

Mono- and bi-metallic catalysts were prepared by ALD and these catalysts were tested for electrochemical oxidation of alcohols. Mono-metallic ALD-prepared Pd catalysts gave higher current densities compared to similar commercial Pd fuel cell catalysts providing the possibility to lower fuel cell catalyst costs, as the same activity is obtained with lower metal loadings. With bi-metallic PtCo catalysts, the metal growth mode on the catalyst support was studied. Metal growth on the surface was found to follow mainly the island growth mode where metals attach on the surface more easily if there already are metals on the surface. The stability of the catalyst in alcohol electrochemical oxidation could be modified by adjusting the preparation parameters: with varying order of precursor cycles in ALD, the catalyst deactivation rate was lowered.

Tiivistelmä

Kemikaalien ja polttoaineiden tuottamista uusiutuvista luonnonvaroista tutkitaan laajasti. Katalyysillä on merkittävä rooli prosessien tehokkuuden ja selektiivisyyden parantamisessa. Hiilimateriaaleilla on monia ominaisuuksia, joita voidaan hyödyntää katalyysissä. Tässä työssä hiiltä tutkittiin katalyyttimateriaalina ja siitä valmistettiin katalyyttejä erilaisilla menetelmillä. Valmistettuja katalyyttejä testattiin ksyloosin dehydratoinnissa ja alkoholien sähkökemiallisessa hapetuksessa.

Hiilimateriaalit toimivat aktiivisina katalyytteinä ilman metalleja, jos hiilen pinnalla on sopivia hetero-atomeja sisältäviä ryhmiä. Hiilen pinnalle saadaan hapetuskäsittelyllä lisättyä erilaisia happamia ja emäksisiä happi- ja rikkiatomeja sisältäviä ryhmiä. Näitä hiiliä käytettiin katalyyttikantajina ja testattiin katalyytteinä ksyloosin dehydratoinnissa vesiliuottimessa. Hiilikatalyytin todettiin olevan selektiivinen ja kestävä katalyytti furfuraalin valmistamisessa.

Kolmea erilaista katalyytin valmistusmenetelmää testattiin Pd, Pt ja PtCo metallikatalyyttien valmistamisessa hiilikantajalle: yleisesti käytettyjä kuiva- ja märkäimpregnointia nestemäisillä metalliprekursoreilla ja katalyyttien valmistamisessa vähemmän käytettyä kaasufaasipinnoitusta, atomikerroskasvatustekniikkaa (ALD). Kaasufaasissa olevalla prekursorilla valmistetulla katalyytillä metallin dispersio katalyytin pinnalla oli suurin, metallipartikkelin koko pieni ja partikkelikokojakauma kapea.

Yksi- ja kaksimetallikatalyyttejä valmistettiin ALD-tekniikalla ja katalyyttejä testattiin alkoholin sähkökemiallisessa hapetuksessa. Yksimetallisilla ALD-tekniikalla valmistetuilla palladium-katalyyteillä saavutettiin suurempi virran tiheys katalyytin metallimäärää kohden kuin vastaavalla kaupallisella palladium-polttokennokatalyytillä. Tämä mahdollistaisi polttokennokatalyyttien kustannuksien pienentämisen, koska sama katalyytin aktiivisuus saavutetaan pienemmällä määrällä metallia. PtCo-kaksimetallikatalyyttien valmistuksessa tutkittiin ALD-kasvumekanismia. Kasvumekanismi noudatti pääasiallisesti Vollmer-Weber -mallia, jossa metallit tarttuvat helpommin kantajan pinnalle, jos pinnalla on jo metallia valmiiksi muodostaen metallisaarekkeita. Katalyyttien stabiilisuutta alkoholien sähkökemiallisessa hapetuksessa pystyttiin muokkaamattaan ja deaktivoitumisnopeutta hidastamaan vaihtelemalla prekursorien syöttöjärjestystä katalyytin valmistuksessa.

Acknowledgements

Contents

List of Abbreviations and Symbols

AES   atomic emission spectroscopy

ALD   atomic layer deposition

CNF   carbon nanofiber

CNT   carbon nanotube

CVD   chemical vapour deposition

DMSO   dimethyl sulfoxide

EDS   energy-dispersive spectroscopy

GC   gas chromatograph

HMF   hydroxyl-methyl furfural

HR-TEM   high-resolution transmission electron microscopy

LC   liquid chromatograph

MIBK   methyl isobutyl ketone

MWCNT   multi-walled carbon nanotube

SWCNT   single-walled carbon nanotube

TEM   transmission electron microscopy

TPD   temperature programmed desorption

XPS   X-ray photon spectroscopy

XRD   X-ray diffraction

List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals

Emma Sairanen neé Rikkinen

I Sairanen, Emma; Karinen, Reetta; Borghei, Maryam; Kauppinen, Esko I.; Lehtonen, Juha. 2012. Preparation Methods for Multi-Walled Carbon Nanotube Supported Palladium Catalysts. Wiley-VCH Verlag GmbH & Co. ChemCatChem, volume 4, issue 12, pages 2055-2061. ISSN 1867-3899.DOI: 10.2002/cctc.201200344.

II Rikkinen, Emma; Santasalo-Aarnio, Annukka; Airaksinen, Sanna; Borghei, Maryam; Viitanen, Ville; Sainio, Jani; Kauppinen, Esko I.; Kallio, Tanja; Krause, A. Outi I. 2011. Atomic Layer Deposition Preparation of Pd Nanoparticles on a Porous Carbon Support for Alcohol Oxidation. ACS Publications. The Journal of Physical Chemistry C, volume 115, issue 46, pages 23067-23073. ISSN 1932-7447. DOI 10.1021/jp2083659.

III Sairanen, Emma; Figueiredo, Marta C.; Karinen, Reetta; Santasalo-Aarnio, Annukka; Jiang, Hua; Sainio, Jani; Kallio, Tanja; Lehtonen, Juha. 2014. Atomic Layer Deposition in the Preparation of Bi-metallic, Platinum-based Catalysts for Fuel Cell Applications. Elsevier B.V. Applied Catalysis B: Environmental, volume 148-149, pages 11-21. ISSN 0926-3373. DOI 10.1016/j.apcatb.2013.10.045.

IV Sairanen, Emma; Vilonen, Kati; Karinen, Reetta; Lehtonen, Juha. 2013. Functionalized Activated Carbon Catalysts in Xylose dehydration. Springer. Topics in Catalysis, volume 56, issue 9-10, pages 512-521. ISSN 1022-5528. DOI 10.1007/s11244-013-0013-6.

Other relevant publications

Santasalo-Aarnio, Annukka; Sairanen, Emma; Arán-Ais, Rosa M.; Figueiredo, Marta C.; Hua, Jiang; Feliu, Juan Miguel; Lehtonen, Juha; Karinen, Reetta; Kallio, Tanja. 2014. The Activity of ALD-prepared PtCo Catalyst for Ethanol Oxidation in Alkaline Media. Elsevier B.V. Journal of Catalysis, volume 309, pages 38-48. ISSN 0021-9517. DOI 0.1016/j.jcat.2013.08.027.

He, Maoshuai; Chernov, Alexander I.; Fedotov, Pavel V.; Obraztsova, Elena D.; Rikkinen, Emma; Zhu, Zhen; Sainio, Jani; Jiang, Hua; Nasibulin, Albert G.; Kauppinen, Esko I.; Niemelä, Marita; Krause, A Outi I. 2011. Selective Growth of SWNTs on Partially Reduced Monometallic Cobalt Catalyst, The Royal Society of Chemistry. Chemical Communications, volume 47, issue 4, pages 1219-1221. ISSN 0009-241X. DOI 10.1039/c0cc02751k.

Author's Contribution

Publication I: Preparation Methods for Multi-Walled Carbon Nanotube Supported Palladium Catalysts

Author planned the experiments together with the co-authors, prepared the catalysts, carried out part of the catalyst characterization, tested the catalysts in model reactions, and wrote the first version of the manuscript.

Publication II: Atomic Layer Deposition Preparation of Pd Nanoparticles on a Porous Carbon Support for Alcohol Oxidation

and

Publication III: Atomic Layer Deposition in the Preparation of Bi-metallic, Platinum-based Catalysts for Fuel Cell Applications

Author planned the experiments together with the co-authors, prepared the catalysts; carried out part of the physical characterization of the catalysts; and analysed the results and wrote the manuscript together with the co-authors. Author did not carry out electrochemical characterization or analysis of the electrochemical results.

Publication IV: Functionalized Activated Carbon Catalysts in Xylose dehydration

Author planned the experiments together with the co-authors and carried out part of the experiments. Author analysed the results together with the co-authors and wrote the first version of the manuscript.

1. Introduction

1.1 Carbon as a catalyst material

There is a growing demand to find sustainable ways to produce chemicals and energy. The role of catalysts in creating more efficient and sustainable solutions is remarkable. If the production of chemicals, fuels and energy from renewable sources could utilize heterogeneous catalysts, it would follow the principles of green chemistry and be more sustainable. Carbon materials have many suitable properties that could be advantageous in catalysis applications and can offer a solution to these challenges [1 ,2]. Different type of carbon materials, such as activated carbon and carbon black, are widely used as catalysts or catalysts supports. Other carbon materials, like carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphenes, have also been recently studied for catalyst applications. Typical reactions for carbon catalysts are hydroprocessing of petroleum feedstocks, hydrogenation reactions, ammonia synthesis, environmental catalysis, and electrocatalysis [1].

1.1.1 Preparation of carbon materials

Carbon materials are prepared from various carbon sources using various methods. The properties of prepared materials depend on the used carbon source and preparation method. Activated carbon, carbon black, and carbon nanotubes present different type of carbon materials which all have their own advantages in catalyst applications.

  Activated carbon is prepared from several carboneous materials like wood, coal, coconut shell, nutshell, synthetic polymers, or petroleum processing residues [3, 4]. Activated carbons are prepared by two preparation methods: chemical and physical activation. In the chemical activation method, the raw material is carbonized and activated during a single process step at temperatures between 600-800 °C. In the carbonization, carbon source material is heated to form solid carbon material. No oxygen is present during this step. Activation is achieved using an agent added to the process before heating. Typical activation agents are various acids; bases; or salts, such as phosphoric acid or zinc chloride

[3 , 4]. In physical activation activated carbon is prepared using a two-step process: carbonization is carried out at 600-800 °C without oxygen by thermal decomposition of the carbon source. The activation step is carried out with oxygen source like oxygen, steam, or carbon dioxide at 800-1100 °C after the carbonization step. Activated carbons typically have very large surface areas, around 800-1200 m²/g and the pore size distribution can be very wide. The surface area varies as a function of the degree of activation of the material. The pore structure can in some extent be varied with the raw material choice [3, 4]. Typically activated carbons have high micro- and mesoporosity but rather low macroporosity [5]. Activated carbon used in catalyst applications have typically mean particle sizes between 10 to 50 micrometers [6]. The surface structure of activated carbon has a similar surface as graphite but it also contains disorganized areas. In addition to hexagonal rings of carbon atoms, there are pentagons and other non-hexagonal rings on the surface [3, 4]. Activated carbon contains impurities. The type and amount of impurities vary depending on the carbon source and preparation method used [3].

Carbon black is prepared by pyrolysis or incomplete combustion. In the pyrolysis, the carbon source is heated without oxygen present in the system. In the incomplete combustion, there is a limited amount of oxygen present in the system. There are many carbon sources for carbon black preparation, for example methane, acetylene, naphthalene, oil, and tars [3, 7]. A common method for preparation of carbon black is to burn the carbon source with a limited amount of air at temperatures around 1400 °C [3]. Carbon black has a surface area of 10-1500 m²/g. Carbon black consists of separate non-porous particles with a diameter of 5-100 nm. The shape of these particles varies. The porosity of the material is attributable to the empty spaces between these particles. The structure of the outermost surface of these particles is quite close to graphene and the proportion of this ordered structure decreases towards the inner parts of the particles which are a more amorphous carbon material. Similarly to activated carbon, the surface area depends on the carbon source used and the preparation method [3, 7].

Carbon nanotubes can be single-walled, double-walled, or multi-walled tubes. The surface structure of carbon nanotubes is equivalent to graphene sheets rolled in a cylinder. In double- and multi-walled carbon nanotubes there are two or more sheets rolled around each another. Carbon nanotubes can be prepared using various methods the main ones being arc discharge, laser ablation, and chemical vapor deposition [8]. The most widely used method is chemical vapor deposition (CVD). In CNT preparation by CVD, metals, typically nickel, iron, or cobalt, are used as a catalyst [8]. The carbon source - typically methane, ethane, or carbon monoxide - is added in the gas phase. The nanotubes are grown at temperatures of 800-1500 °C on the metal particles [8].

The carbon nanotube properties depend on the size of the metal particle used for the growth of the tube, growth conditions, and carbon source. Especially the catalysts used for growing the carbon nanotubes have a remarkable impact on the structure and properties of the tubes. Multi-walled carbon nanotubes (MWCNTs) are more widely used in catalyst applications than single-walled

carbon nanotubes (SWCNTs). The main reason for this is the easier production of MWCNTs. CNT growth takes place in high temperatures which easily causes metal sintering on the catalyst. With larger metal particles, MWCNTs are formed, whereas SWNTS are grown on small metal particles. The preparation of SWCNTs with single chirality is a widely studied topic because the metal-lic/conductive properties of tubes depend on the chirality [9, 10]. When defining carbon nanotubes as tubes which are rolled from graphene sheet, sing chirality means that the all the tubes in the sample are rolled-up at same angle leading the nanotubes being uniformly either metallic or semiconductive in a similar way [11]. SWCNTs with single chirality would be desirable in catalytic applications because the controlling properties of the catalyst support material could be utilized in different catalyst applications. Catalysts with small metal particles with narrow metal particle size distribution are thus far the most promising alternative for preparation of this type of tubes [8, 12, 13].

1.1.2   Properties of carbon materials

When carbon materials are applied as catalysts or catalyst supports in the place of traditional catalyst materials, such as oxide materials, several benefits can be found: carbon materials are stable and inert in both acidic and basic conditions. Carbon surfaces are relatively easy to modify by creating different functionalities that modify the catalyst acidity, polarity, and hydrophobicity. Many carbon materials, for instance activated carbon, have large surface areas. Metal recovery from metal catalysts using a carbon support is efficient because the support can be burned off to recover the metals. Different type of carbon materials offer alternatives for many applications because carbons can be manufactured in various shapes, for example pellets, powders, monoliths, fibres, and mats with various size and dimensions [1].

   In aqueous conditions, i.e. when using water as a solvent in liquid phase reactions, carbon catalysts might offer a solution to challenges which are encountered with traditionally used solid acid catalysts, such as different oxides. These challenges include, for example, the possible dissolution of acid sites to the water [14] and changes in surface structures which might take place on the catalyst in water. For example, in the case of Al_2O_3 oxygen on the catalyst surface can be hydrated to surface hydroxyl groups changing the gamma-alumina to boehmite. These groups can act as Brönsted sites and the acid-base properties of the material are changed in water [15]. The good water tolerance of carbon materials might offer a solution to these difficulties relating to heterogeneous catalysis where water is the solvent or a reagent in the system [16].

   The amount of impurities is one of the main differences of CNTs compared to activated carbon and carbon black. The amount of impurities on carbon nanotubes is very low because the carbon raw material has lower amount of impurities. The main impurities in the tubes are metals which are residues originating from the catalysts used for the nanotube growth. If the application of the CNTs

requires it, the removal of most of these metals with different acid treatments is possible [17].

Carbon black is widely used in fuel cell applications. The main benefit of the carbon black is low price. Drawback is the high amount of impurities which might affect the catalyst properties. MWCNTs are suitable catalyst supports because of their well-oriented and homogeneous surface structure which makes it easy to see the effect of functionalization and active metals on catalyst activity. MWCNTs have very low amounts of impurities. Drawback of the MWCNTs in catalyst applications is the high price of the material. Activated carbon is widely available support, commercially used in many applications, and it has rather low price. Drawback in the use of activated carbon as catalyst material is the possible impurities which might effect to catalyst activity.

1.2   Carbon surface functionalities

Carbon materials as such are inert but certain functionality can exist or can be created on the surface. Active sites on the surface can be defects on the surface; surface groups containing heteroatoms (for example oxygen-, sulphur-, or nitrogen-containing surface sites); or metal particles added on the surface. Typical surface defects or active sites are disorientated areas of the surface structure; edges of the carbon structure; and in the case of carbon nanotubes and fibres, ends of the tubes. Surface sites can be acidic, neutral, or basic. Different types of groups are active in different applications. The surface defects and the surface sites created by functionalization can either act as active sites for the reaction or as anchoring sites for the metal atoms added on the support. The modified surface properties can be utilized in catalysis applications.

Common heteroatoms on carbon surface are oxygen, sulphur, hydrogen, and nitrogen [18]. These heteroatoms can either be located in the ring form of the carbon structure or in surface groups of the carbon surface (see Figure 1). Heteroatoms can be added on the surface by many methods, the most widely used methods are various gas and liquid phase oxidations. In liquid phase oxidations commonly used oxidation agents are nitric acid and sulphuric acid. In gaseous phase oxidation, typical agents are O_2, O_3, and CO_2. The choice of oxidation agent, oxidation treatment time, and oxidation temperature have an effect on the type and amount of the sites created on the surface [19, 20].

Oxygen-containing surface sites are the most typical heteroatom containing sites on the carbon surface [18]. Oxygen-containing surface sites contain carbon-oxygen bonds, carbon-oxygen double bonds, and/or OH-groups. Typical oxygen-containing surface sites are carboxyl groups, phenolic groups, and ketone groups. The most common types of oxygen-containing functionalized groups on carbon supports formed in the gas phase oxidation are hydroxyl and carbonyl surface groups and in the liquid phase oxidation carboxylic acid surface groups [21]. The acidic or basic nature of oxygen-containing surface groups

is widely discussed in the literature. Generally it is proposed that carboxylic, lactone, and anhydride groups are acidic while phenol, quinone, and carbonyl groups are basic [18, 22-24]. The surface hydrophilicity decreases and polarity increases as a function of increasing number of oxygen-containing surface groups [25].

Nitrogen-containing groups are either added to the surface by including it with the carbon precursor in the preparation phase or on the carbon surface using a variety of reagents, such as ammonia, urea, or melamine [18]. Nitrogen-containing sites are different amine, nitro, and pyridine groups. Hydrogen in the surface is present either as chemisorbed water; on numerous surface groups containing hydrogen like in carboxylic acid groups, phenolic groups and amines; or as part of the carbon structure, for instance in aromatic compounds. Sulphur-containing groups can be added to the surface with sulphur-containing gases; such as H_2S, CS_2, and SO_2; or with liquid sulphuric acid. Sulphur-containing groups are typically sulphide, thiophenol, sulfoxide, and quinone sites [18].
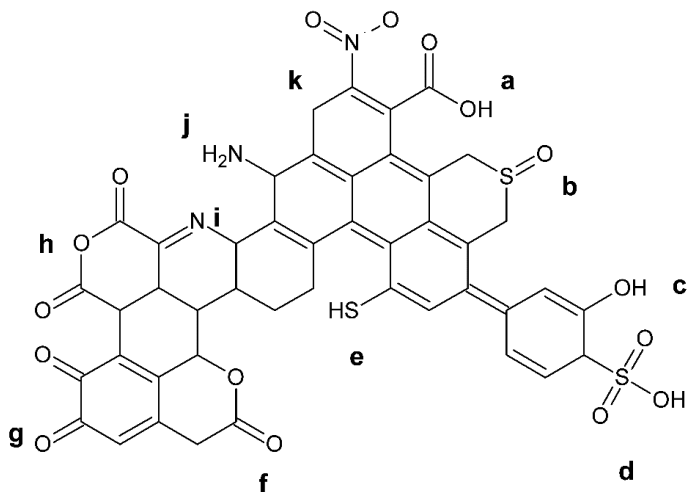
Figure 1. Carbon surface with different kinds of typical oxygen- and sulphur-containing surface groups: (a) carboxyl, (b) sulfoxide, (c) hydroxyl, (d) sulfonic acid, (e) thiophenol, (f) lactone, (g) quinone, (h) carboxylic anhydride, (i) pyridine, (j) amine, and (k) nitro.

1.3   Supported metal catalyst preparation

Carbon materials are widely used as catalyst supports. As supports, their large surface area, varying pore size distribution, and different surface functionalities can be utilized. Various parameters of heterogeneous metal catalysts effect catalytic activity. These parameters include metal, metal loading, metal dispersion,

and metal particle size. In the case of bi-metallic catalysts, the distance of different metals from one to another on the surface is also significant for the catalytic activity. In catalyst preparation, these properties can be altered with different catalyst preparation parameters.

Traditionally widely used and simple metal deposition methods for catalyst preparation are dry impregnation and wet impregnation. Gaseous phase catalyst preparation methods such as chemical vapour deposition (CVD) and atomic layer deposition (ALD) are more recently studied and applied to catalyst preparation. ALD was invented in Finland in the 1970s [26]. In Finland, ALD method has been studied in catalysts preparation since the 1980s [27-29].

In traditional impregnation methods metal precursor is either added on the surface as liquid metal precursor without additional solvent or solid precursor added to a small amount of solvent (dry impregnation), or precursor is dissolved in the solvent (wet impregnation). Liquid is later removed from the catalyst after metal deposition [30]. In gaseous catalyst preparation methods a metal containing precursor is evaporated and it reacts with the catalyst surface alone (CVD), with other gaseous precursor (CVD), or with another reacting compound, like other metal precursor or with gas like air or hydrogen (ALD). In the ALD, the surface is saturated with the absorbed reacting components in all the ALD cycles [31, 32].

Different catalyst preparation methods give different properties for the catalysts and have their own advantages and disadvantages. With dry impregnation good control of the metal loading on the catalyst is obtained and metal precursor is not lost. A disadvantage is that metal particles can easily cluster if the mixing is not efficient [30, 33]. In wet impregnation advantages are the mild preparation conditions and easy preparation methods. Disadvantages are the poorer control for metal loading and the possible loss of precious metal precursor during the preparation steps [1, 34]. With ALD, an advantage is the narrow particle size distribution obtained with small particles [35]. Because precursor is added in gas phase, it can also distribute more easily on the surface and lead to high metal dispersion on the surface. During one ALD cycle, the support surface, chosen precursor, and the deposition temperature affect the metal loading obtained [36]. A disadvantage is the cost and availability of suitable precursors needed for gas phase deposition. In addition, there are special equipment requirements for the ALD method when it takes place at a reduced pressure [35].

In preparation of carbon supported metal catalysts, some kind of anchoring sites for metal particles to attach on the carbon support are needed [16]. Without functionalization, the carbon catalyst surface is hydrophobic. Increasing the number of surface groups modifies the carbon towards higher hydrophilicity which increases the surface wettability. In catalyst preparation, when using liquid precursors containing water or other polar substances, increased surface wettability and polarity helps the metal precursors to attach more easily and more uniformly on the surface [30, 37]. In the controlling of metal loading and dispersion, the anchoring sites on the surface have significant role on carbon catalysts. With oxygen-containing functionalities, the metal loading and metal dispersion increases with increasing oxygen concentration on the surface [24].

If anchoring sites are evenly distributed on the surface, it also causes the metals to distribute more evenly on the surface leading to high metal dispersion. The anchoring site location on the surface depends on the carbon material and the used oxidation treatment and oxidation time. For example, in the case of carbon nanotubes, with shorter oxidation times, anchoring sites are more typically at the ends of the tubes than on the walls of the tubes [38, 39].

In preparation of bi-metallic catalyst, one of the main challenges is to get different metal particles near to each other or even to form bi-metallic particles on the catalyst support surface instead of forming separate mono-metallic clusters. The carbon surface is mainly inert towards metal precursors and that is why precursors are attached more easily to specific active sites on the surface. This can help also in bi-metallic catalyst preparation. In the literature it has been proposed that because there is only little or no interaction between the carbon surface and the precursor, it is easier for the metals added in preparation of bi-metallic catalysts to attach close to the metals already on the surface. This facilitates the creation of bi-metallic particles on the surface [1, 4].

1.4   Hemicellulosic sugar dehydration

New biorefinary concepts are studied to find alternative ways to produce chemicals and fuels from biobased materials. Hemicellulose and cellulose sugars, C5 monosaccharides, like xylose and C6 monosaccharides, like glucose, are one possible source which could be applied in chemical production [40, 41]. Dehydration of these sugars leads to production of furfural and hydroxylmethyl furfural (HMF). These products can be used as such or as intermediates in the production of bio-based transportation fuels and chemicals. For example, about 60% of commercially produced furfural, is used for furfuryl alcohol production. Tetrahydrofuran and tetrahydrofurfural are other main chemicals produced from furfural [42].

Dehydration reactions require acidic conditions for the reactions to proceed. In commercial production, liquid mineral acids such as sulfuric acid are used. Many different homogeneous acids are studied as catalysts in sugar dehydration [43]. From the green chemistry perspective it would be beneficial to use solid catalysts which would be easier to remove from the process. A wide variety of different solvents, for example methyl isobutyl ketone (MIBK), dimethyl sulfoxide (DMSO), acetone, and alcohols, are studied in dehydration reactions [43, 44]. Using water as a solvent instead of organic solvents in the process would follow the green chemistry principles as water is clean, safe, and non-toxic. The use of a solid catalyst with water as a solvent would modify the process to be more environmentally friendly. Carbon catalysts are one option to meet these requirements.

Sugar dehydration reactions form a complex reaction network which also includes other reactions than dehydration, as seen in Figure 2 where xylose dehydration is presented as an example. These reactions are sugar isomerization,

fragmentation, condensation, and resinification (Figure 2). In isomerization, a sugar isomerizes to other sugars which can further react in the same reactions as the sugar fed in to the system. In fragmentation reactions furfural decomposes to acids and in condensation and resinification reactions solid products, humins, are formed from furfurals and the intermediate products. In condensation reactions, humin formation takes place via the polymerization of furfurals and intermediate products. In resinification reaction humins are formed from furfurals which react with other furfural molecules [44]. Because the majority of these reactions are acid catalyzed modification of the system to achieve furfural production with high selectivity is challenging.
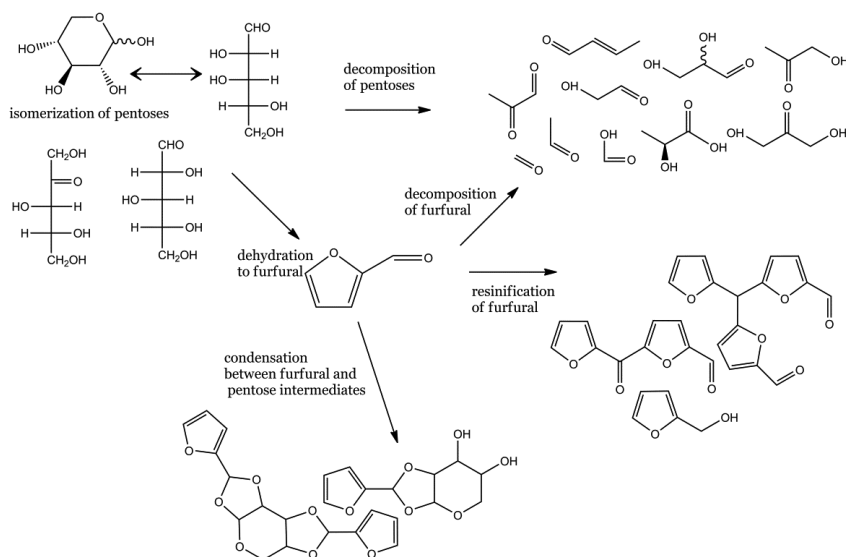
Figure 2. Xylose dehydration reaction scheme.

1.5   Carbon-supported fuel cell catalysts

Fuel cells are a promising alternative for the production of energy. In fuel cells, chemical energy of various chemicals, like hydrogen or alcohols, is converted to electricity and product molecules. Chemical reactions take place on the two electrodes. Two different reactions take place: oxidation reaction produces electrons which give the current from the system. Protons formed in the oxidation reaction diffuse through membrane electrolyte to counter-electrode where reduction reaction takes place. On the electrodes, different kind of catalysts are used to enhance the reactions [45].

Advantages of fuel cells are the mild operation conditions and cleaner output streams. To obtain high efficiency and profitable fuel cells, optimization of the

cell components, including catalyst, is extremely important. Hydrogen is used as a fuel in fuel cells but because of its reactivity, its storage and usage contains risks. A range of alcohols, for example methanol, ethanol, and propanol, are studied as alternative fuels because they are safer and easier to transport and use. Methanol is a widely used alcohol for fuel cell use but a significant disadvantage is its toxicity [II, 46]. Ethanol and propanol are good options as a fuel because they are less toxic, they have higher boiling points and high reactivity has been reported in fuel cell tests [47-49]. Ethanol can also be readily produced from biomass. A disadvantage in the use of ethanol and propanol as fuels is the need to break the carbon-carbon bond to achieve total oxidation and the catalyst used has to be able to break this bond in order to give better performances in fuel cells.

To enhance alcohol oxidation, various metals, like platinum and palladium, are used as catalysts [50, 51]. The key parameters of the catalyst affecting the fuel cell activity are the metal loading and metal distribution. The optimized use of metal on the catalyst helps to lower costs and increase the fuel cell activity. In particular, reducing the metal loading needed on the catalyst helps to lower the costs. One method to lower the metal loading and enhance the oxidation reaction is to have a catalyst with high metal dispersions [35]. Bi-metallic catalysts are another approach that can be used to lower the costs of the fuel cell and to obtain desired products from fuel cell reactions. The bi-metallic catalysts can enhance fuel cell operation and lower costs via two different mechanisms: firstly, with bi-metallic catalysts, part of the valuable noble metal can be replaced with the less expensive metal to lower the total cost. Secondly, the presence of the second metal on the catalyst can change the catalytic activity of the precursor metal. Both metals on bi-metallic fuel cell catalysts are active sites. For example, with a pure platinum catalyst, alcohol oxidation is reported to mainly follow a partial oxidation reaction mechanism at low temperatures whereas with bi-metallic catalysts, total oxidation can take place. For methanol oxidation ruthenium together with platinum [52] and for ethanol oxidation tin together with platinum [53] are reported to be the most active for total oxidation. For example, on bi-metallic platinum-cobalt catalysts, on platinum, partial oxidation reaction takes place whereas on cobalt these partial oxidation reaction products can further react to total oxidation reaction products [46]. In partial electrochemical oxidation of ethanol, acetic acid can be formed as a product which is harmful for the fuel cell operation as it changes the pH in the fuel cell. If the reaction proceeds via total oxidation, the main product is carbon dioxide [54-57].

1.6   Scope of the research

The aim of this work was to prepare various carbon catalysts and study the effect of preparation methods on catalytic properties of carbon catalysts and carbon supported metal catalysts [I-IV]. Three different type of carbon catalysts were prepared and studied: Firstly, carbon catalysts without any added metals with

different type of functionalized groups acting as active sites for the reaction were studied [I]. Secondly, carbon was studied as a catalyst support in the preparation of mono-metallic catalysts by three different catalyst preparation methods, wet impregnation, dry impregnation, and ALD [II]. Thirdly, gas-phase catalyst preparation methods were further studied. Mono- and bi-metallic carbon supported catalysts were prepared by ALD and the catalyst preparation parameters, the growth mechanism of metals on the surface, and the catalyst properties were studies [III]. For carbon functionalization, activated carbon [IV] and MWCNTs [I] were studied as carbon materials. Carbon supported metal catalysts were prepared using MWCNTs [I] and carbon black [II, III]. The prepared catalysts were tested in two different applications: in the production of chemicals from lignocellulosic biomass sources by dehydration reactions using carbon as a catalyst [IV] and in electrochemical oxidation of alcohols [II, III].

Carbon surface modification was studied by applying liquid phase oxidation treatment to add different types of oxygen-containing surface sites on the carbon surface. The catalysts were characterized and the activity of these solid acid catalysts was tested in sugar dehydration reactions in water. The suitability of carbon materials as catalyst materials in aqueous phase sugar dehydration reactions was tested [IV].

2. Materials and methods

2.1 Chemicals

The chemicals used in this thesis are reported in Table 1. The experimental methods are described in detail in papers I-IV and only a short summary is given here.

Table 1. The chemicals used in preparation, characterization, and testing the catalyst.

Gases and chemicals	Use	Supplier	Purity / %	Publication
activated carbon, ROX 0.8	catalyst	Norit		IV
argon, Ar	catalyst preparation	AGA	99.999	I
carbon black, Vulcan XC72R	catalyst support	Cabot		II
carbon monoxide, CO	characterization	AGA	99.999	II
cinnamaldehyde, C_9H_8O	reagent	Sigma-Aldrich	99	I
cobalt acetyl acetonate, $Co(acac)_3$	catalyst preparation	Merck	98	III
ethanol, C_2H_6O	electrochemical characterization	AGA		III
FAA-2 solution	electrochemical characterization	Fuma Tech		II
H-mordenite HSZ 660	catalyst	Tosoh Corpora-tion		IV
hydrochloric acid, HCl	catalyst characterization	Merck	32	IV
hydrogen, H_2	reagent, catalyst characteriza-tion, catalyst preparation	AGA	99.999	III
hydrogen peroxide, H_2O_2	cleaning	Sigma-Aldrich		II
ion-exchanged milli-Q water	solvent	Millipore		II
multi-walled carbon nanotubes, MWCNT	catalyst, catalyst support	Showa Denko		I
nitric acid, HNO_3	catalyst preparation	Sigma-Aldrich	98	I
nitrogen, N_2	catalyst preparation	AGA	99.999	II
palladium nitrate, $Pd(NO_3)_2$	catalyst preparation	Alfa Aesar	7.97 mass-%	I
perchloric acid, $HClO_4$	cleaning	Merck		II
phenolphthalein	catalyst characterization	Sigma-Aldrich		IV
platinum acetyl acetonate, $Pt(acac)_2$	catalyst preparation	Volatec Oy		III
potassium permanganate, $KMnO_4$	cleaning	Merck		II

2-propanol, C_3H_8O	solvent, standard, electrochemical characterization	Sigma-Aldrich, Merck	99.5	I, II
sodium hydroxide, NaOH	electrochemical characterization, catalyst characterization	Merck		II
sulfuric acid, H_2SO_4	electrochemical characterization, catalyst preparation	Merck		III
synthetic air	catalyst preparation	AGA	99.999	II
tetradecane, $C_{14}H_{30}$	catalyst testing	Sigma-Aldrich	99	I
2,2,6,6-tetramethyl-3,5-heptane dionate, $Pd(thd)_2$	catalyst preparation	Volatec Oy		II
titanium dioxide, TiO_2	catalyst	Alfa Aesar		IV
toluene, C_7H_8	catalyst preparation	Sigma-Aldrich	99.7	I
xylose, $C_5H_{10}O_5$	reagent	Sigma-Aldrich	99	IV

2.2 Catalyst preparation

2.2.1 Carbon materials

The studied carbon materials were activated carbon (Norit ROX 0.8), commercial multi-walled carbon nanotubes (Showa Denko VGCF-X), and carbon black (Cabot, Vulcan XC72R). Activated carbon was studied as carbon materials for carbon functionalization and as a catalyst in xylose dehydration [I]. Activated carbon was in the form of pellets with dimensions of 0.5 x 1.3 mm. MWCNTs were studied in carbon functionalization and as a support for Pd catalyst prepared with different methods [IV]. Carbon black was studied as catalyst support for ALD-prepared Pd, Pt, and Co fuel cell catalysts [II, III].

2.2.2 Functionalization

Oxygen-containing surface groups and sulphur-containing surface groups were created on the catalyst surface by liquid phase oxidation. Catalysts were refluxed in boiling nitric acid, sulphuric acid, or in the mixture of these acids from two to nine hours [I, IV]. After refluxing, the samples were washed with distilled water until the pH of the washing water was neutral. Finally, samples were dried at 80 °C overnight.

2.2.3 Dry impregnation

In dry impregnation the carbon support was first dried under reduced pressure at 70 °C for four hours. After drying palladium nitrate precursor was added to the support at atmospheric pressure and the sample was mixed overnight [I].

2.2.4 Wet impregnation

In wet impregnation $Pd(NO3)_2$ precursor was dissolved in toluene. The precursor solution was mixed with the carbon support overnight at room temperature

at atmospheric pressure. Then solvent was evaporated from the mixture at 40 °C under reduced pressure [I].

2.2.5 Atomic layer deposition

Atomic layer deposition was carried out in commercial F-120 reactor (ASM Microchemistry) at 180 °C. In the ALD-preparation method the support was first dried at 180 °C at a reduced pressure (0.5-1 kPa) with nitrogen. After drying, Pd(thd)$_2$ precursor was evaporated at 180 °C and fed through the catalyst support bed using nitrogen as a carried gas. Precursor feeding step was followed by flushing the ligands and non-reacted precursor from the surface by nitrogen [I-III] and oxidation or reduction treatment with air [II] or hydrogen [I].

2.3 Catalyst characterization

Various methods were applied for characterization of the catalysts prepared and commercial catalysts received. Catalyst metal loadings were characterized by atomic emission spectroscopy (AES) [I-III], energy-dispersive spectroscopy (EDS) [I- III], and X-ray photon spectroscopy (XPS) [II, III]. Microscopy images of samples were measured with transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM) [I-III], and scanning electron microscopy (SEM) [II, III] to analyze the metal particle size and distribution. Catalyst surface area, acidity, or type of surface sites was characterized with nitrogen physisorption [I, IV], CO chemisorption [III], XPS [II, III], temperature programmed desorption (TPD)[I, IV], X-ray diffraction (XRD)[II, III], and acid-base titration [IV].

2.4 Catalyst testing

The prepared catalysts were tested in cinnamaldehyde hydrogenation [I], hemicellulose sugar dehydration using xylose as a model compound [IV], and alcohol electrochemical reactions [II, III, 58].

2.4.1 Hemicellulose sugar dehydration

Xylose was used as a model compound for hemicellulose sugars. Xylose dehydration experiments were carried out in a 250 ml batch reactor with 0.1 g of solid catalyst. Stirring rates of 600, 1000, and 1400 rpm were tested and showed no significant effect on the reaction activity. 1000 rpm was chosen as stirring rate for the experiments. Xylose was diluted with ion-exchanged water used as a solvent to obtain sugar concentration from 2-5 mass-% for experiments. Reactions were carried out at temperatures between 160-220 °C with the reactor pressurised to 20 bar to keep the solvent in the liquid phase.

Before the reaction, 90 ml water was packed to the reactor. When the reactor achieved a temperature of 5 °C above the reaction temperature, xylose dissolved in 10 ml of water was added to the reactor and the experiment was started.

Conversion of the sugars was calculated from the sum of the all sugars measured in the reactor because sugar isomerization (see Figure 2) occurs simultaneously with the dehydration reaction and all the sugars formed can further react via dehydration.

2.4.2 Cinnamaldehyde hydrogenation

Cinnamaldehyde hydrogenation was carried out in 100 ml batch reactor with total liquid volume of 30 ml at 40 °C under 2 MPa hydrogen pressure. Cinnamaldehyde concentration in the reaction mixture was 0.1 mol/l and 2-propanol was used as a solvent with 0.030 g of catalyst. Catalyst was pretreated before the reaction by keeping it under nitrogen atmosphere for 0.5 hour and under hydrogen atmosphere for a further 0.5 hour. The reaction mixture was fed to the reactor after catalyst pretreatment.

2.4.3 Electrochemistry

For electrochemical oxidation catalyst inks were prepared from catalyst powders and used for preparation of electrodes. Electrodes were tested in a three-electrode electrochemical cell. Details of electrode preparation and experimental conditions are reported in publications II and III and in reference [58].

2.5 Analyses and calculations

Liquid samples from reactor experiments were analysed with gas chromatograph (GC) or liquid chromatograph (LC). In sugar dehydration experiments samples were analysed with LC (Agilent series 1100 HPLC, equipped with a refractive index detector and using an ion exchange column (Phenomenex Rezex Monosaccharide RHM H+) using 2-propanol as an external standard. The eluent used was 0.005 M sulphuric acid with 0.6 ml/min flow rate. In cinnamaldehyde hydrogenation liquid samples were analysed with GC (Agilent Technologies, 6890N equipped with HP-1 column) using tetradecane as an internal standard for the experiments.

In the calculation of analysis results, the following definitions were used for conversion, selectivity, yield, and product distribution. Conversion was defined as a ratio of the amount of consumed reactant to initial amount of reactant fed to the reactor (Equation 1).

$$X_A = \frac{n_{A0} - n_A}{n_{A0}} \tag{1}$$

where X_A is conversion of the component A, n_{A0} is the amount of the component A in the beginning of the reaction, and n_A is the amount of the component A at reaction time t.

Selectivity was defined as a ratio of an amount of product formed in the reaction to the amount of consumed reactant (Equation 2).

$$S_B = \frac{n_B}{n_{A0} - n_A} \tag{2}$$

where S_B is the selectivity of component B, and n_B is the amount of the component B at reaction time t.

Yield was defined as the product of conversion and selectivity (Equation 3).

$$Y_A = X_A \cdot S_A \tag{3}$$

where Y_A is the yield of component A.

Product distribution for a component was calculated by a ratio of component in product mixture and the sum of all the components in product mixture.

3. Functionalization of carbon surface

3.1   Carbon functionalization and characterization

Carbon catalysts were functionalized with oxidation treatment to increase the number of surface sites on the surface [I, IV]. Liquid acid oxidation is an effective way to create oxygen-containing surface sites. Depending on the oxidation agent, liquid acid oxidation can create both acidic and basic sites on the surface and the sites can contain different kind of heteroatoms. On carbon catalyst supports, carboxylic groups are preferred as anchoring sites for metals [59, 60]. In dehydration reactions, active groups for the reaction are reported to be carboxylic and sulfonic acid sites [61]. The purpose of the carbon functionalization was to increase the number of these sites. In this work, the widely used oxidation method with nitric acid was chosen as a functionalization method to create oxygen-containing surface sites [I, IV]. With nitric acid, especially carboxylic acid sites are obtained. To create sulphur-containing groups, sulphuric acid was used as an oxidation agent for carbon functionalization [IV].

TPD and XPS were used for characterization of the surface groups. To analyse the total amounts of surface groups on the carbon, MWCNT surface elemental oxygen concentration was determined by XPS and the total evolution of CO and CO_2 by TPD. In TPD, acidic oxygen-containing surface groups are presented to decompose from the surface as CO_2 and basic groups as CO [18].

The type of surface groups were analysed from the CO_2 or CO desorption temperatures (see Table 2 for temperature ranges for different groups). The amounts of different oxygen-containing surface groups were calculated by integrating the TPD profiles. Because there are several overlapping rate processes detected in TPD profiles and TPD peaks are not symmetric, the amount of different groups were simply integrated using the temperature ranges presented in Table 2. A typical TPD profile is shown in Figure 3.

Table 2. Surface groups desorbed in TPD and the temperature range integration limits.

Surface group	Desorbed in TPD as	T °C	Reference
strongly acidic carboxylic acids	CO_2	70-140, 140-200, 200-350	[62-64]
weakly acidic carboxylic acids	CO_2	350-550	[18, 59-61, 66]
lactone/anhydride	CO_2	550-680	[18, 60, 66]
anhydrides	CO	330-510	[18, 59, 60, 66]
phenolic/carbonyl/quinone	CO	510-780	[59, 60, 66]
thiophenol	SO	300-340	[65]
sulfonic acid, sulfoxide and/or sulfone	SO	360	[65]
sulphides	SO	500	[65]

The temperature ranges between detected peaks were also integrated to calculate how large a proportion of the detected surface groups were from the total amount of CO and/or CO_2 evolved. The amount of these proportions was typically 1-5 mol-% of the desorbed CO_2 or CO in $mmol_{gas}/g_{carbon}$; the maximum value was 10 mol-%. Because of the low proportions of unidentified groups during CO and CO_2 desorption, it was concluded that all the main surface groups created on the surface during functionalization were identified and quantified by TPD. Even though the same integration limits were used for all the samples, the method does not provide information about the actual amount of the different surface groups. Still, it enables the comparison of the surface group proportions between the samples.

3.2   Types of surface groups

Functionalization of MWCNTs was studied in publication I. For MWCNTs used as a catalyst support, the main oxygen-containing surface groups formed on the surface with nitric acid oxidation were carboxylic acid groups; anhydrides; and phenolic, carbonyl, or quinone groups (see Table 2) [I].

Functionalization of activated carbon was studied in publication IV. Functionalization of activated carbon was carried out with nitric acid, sulphuric acid, and with a mixture of these two acids. On the activated carbon, the groups formed by nitric acid treatment were mostly the same type as those formed on MWCNTs: nitric acid treatment created carboxylic acid groups; anhydrides; carbonyl, phenolic, or quinone groups; and lactone groups on activated carbon. With sulphuric acid different types of sulphur-containing groups were formed on the surface: thiophenol groups; sulfonic acid groups; and sulfoxide and/or sulfone groups. The sulphur-containing groups were different depending on whether only sulphuric acid was used as an oxidation agent or as a mixture with nitric acid. With a mixture of nitric acid and sulphuric acid, no thiophenol

groups were detected. All the other sulphur-containing groups which were obtained with pure sulphuric acid were obtained also with the H_2SO_4:HNO_3 mixture [IV]. TPD profiles of the activated carbon samples functionalized with nitric acid, sulphuric acid, and their mixture are presented in Figure 3 and a summary of the different groups on the catalysts is given in Table 3. The temperature ranges used for identification of different groups are presented in Table 2.
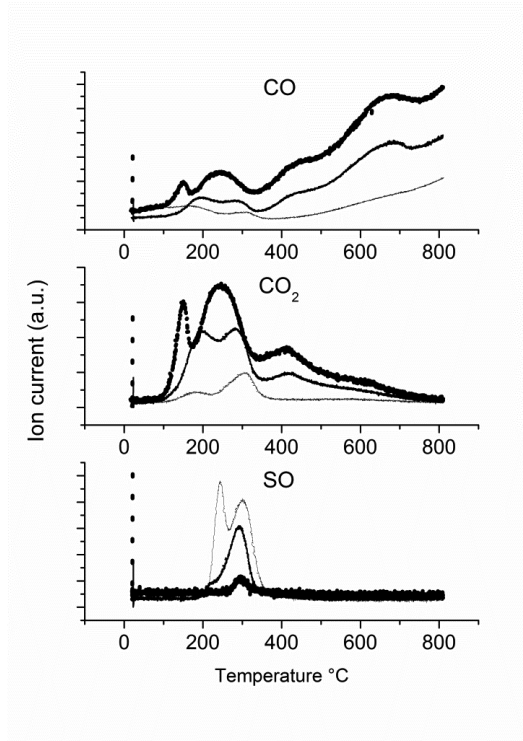
Figure 3. TPD profiles of functionalized activated carbon catalysts C(HNO₃) (bold black), C(H₂SO₄) (black), and C(H₂SO₄:HNO₃) (gray) [IV].

Table 3. Different surface groups on functionalized activated carbon.

Catalyst	C(HNO₃)	C(H₂SO₄)	C(H₂SO₄ : HNO₃)
Oxidation agent	HNO₃	H₂SO₄	3:1 mol ratio H₂SO₄:HNO₃
Detected oxygen-containing surface groups			
carboxylic acid groups	x	x	x
anhydrides	x	x	x
carbonyl, phenolic, or quinone groups	x	x	x
lactone groups	x	x	x
Detected sulphur-containing surface groups			
thiophenol groups		x	
sulfonic acid groups		x	x
sulfoxide and/or sulfone groups		x	x

3.3   Formation of groups as a function of time

In addition to oxidation agent, oxidation time and temperature are also reported to have an effect on the type and amount of surface sites. As a function of oxidation time, the number of sites increases rapidly at the beginning of the oxidation treatment and the formation rate stabilizes after that [20, 66]. To maximize the number of surface groups to which metal particles can attach for the catalysts prepared in publication I, functionalization was carried out with several oxidation times for MWCNTs [I].

The relation between the total amount of oxygen-containing surface groups and functionalization time was quantitatively analyzed by XPS and TPD (see Figure 4). The elemental surface concentration of oxygen and the amount of CO and CO_2 desorbed from the surface increased as a function of oxidation time with similar trends. Thus these two analytical methods supported one another. At the beginning of the oxidation, the oxygen content increased more rapidly and the rate decreased after 2-3 hours of oxidation. From this it was concluded that most of the groups were formed rather quickly at the beginning of the oxidation.
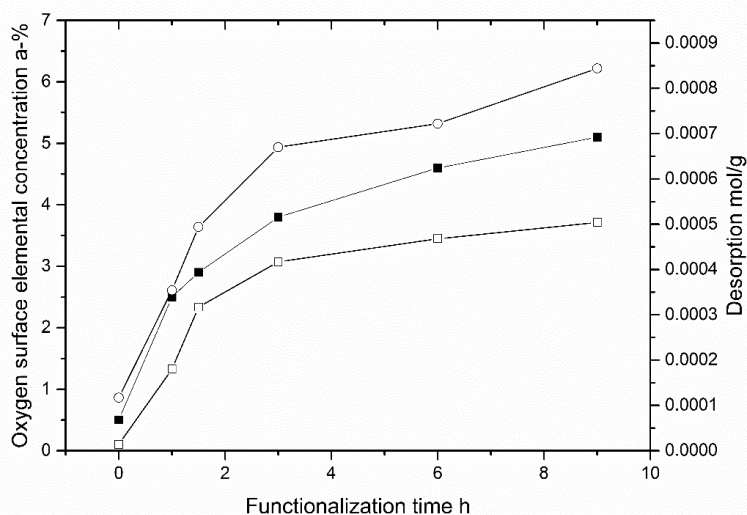
Figure 4. Elemental surface concentration of oxygen determined by XPS (■) and total desorption of CO_2 (○) and CO (□) in TPD as a function of functionalization time.

The amounts of different oxygen-containing groups are presented in Figure 5. The formation of each type of oxygen-containing groups started during the first hour of the oxidation. During the first hour of oxidation, the highest increase was observed in the amount of phenolic/carbonyl/quinone groups. The formation rate of carboxylic acids was second highest. In the literature, carboxylic acid sites are suggested to form via −OH groups [38]. This explains the detected formation rate order. On a non-functionalized MWCNTs (functionalization time

zero hours in Figure 5), small amounts of phenolic sites containing –OH groups were already detected. More -OH groups were also formed at the beginning of the oxidation and after that the formation rate of carboxylic sites increased. The distribution of the groups did not change after 1.5 hours oxidation time: after that the groups were formed in the same ratio and only the amount of groups increased.

Figure 5. The amount of the oxygen-containing surface groups on MWCNTs as a function of functionalization time in nitric acid. Strongly acidic carboxylic acid group (○), weakly acidic carboxylic acid group (●), lactone/anhydride (CO_2 evolution (□), anhydride (CO evolution), (■), and phenolic/carbonyl/quinone (▲)

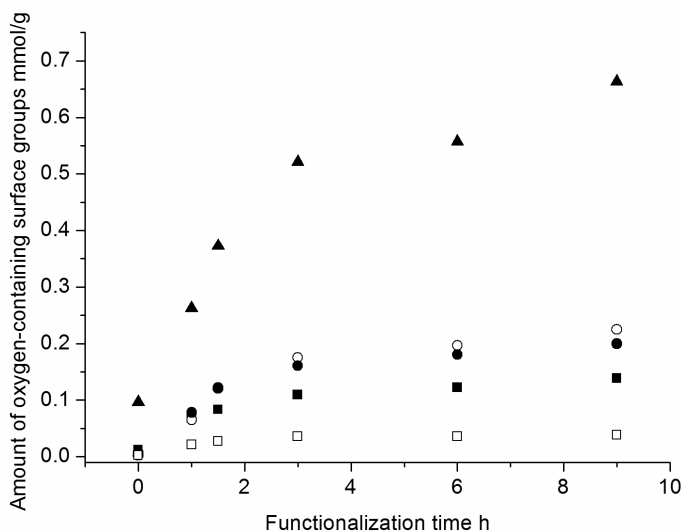It was observed, that there is a remarkable change in the amount of sites between non-treated and samples oxidized for three hours but further continuation of oxidation up to nine hours did not significantly increase the amount further (see Figure 5) [I]. These results are supported by reports in the literature that the majority of sites are created on the surface during the first hours of the oxidation after which the formation rate of oxygen-containing groups on the surface decreased. In particular, higher formation rates for carboxylic acid groups and phenol/carbonyl/quinone groups at the beginning of the functionalization are reported [19, 66-68]. In the case of carbon nanotubes, the formation of surface groups on the MWCNTs is proposed [38, 39] to start from the surface defects of the MWCNTs, followed by the formation of surface groups at the ends of nanotubes. During this step, the ends of nanotubes are opened by the acid treatment but the other parts of nanotube structure remain the same. Finally surface groups are formed at the walls of the MWCNTs. Because site formation is easiest at the defects and tube ends, the formation rate at the beginning of oxidation was faster.

For the MWCNTs used as a catalyst supports [I], a three hour functionalization time was chosen because during that treatment time the major amount of

oxygen-containing surface groups was formed. Especially carboxylic acid site groups, which are supposed to be the most active site for metals to attach, were mainly formed during the first three hours and after that the amount of those remained nearly constant.

4. Carbon supported metal catalyst preparation

4.1 Liquid and gas phase deposition methods for metals

Carbon supported metal catalysts were prepared with various catalyst preparation methods: the widely used impregnation methods based on liquid precursors and the less commonly used gas phase deposition method, ALD. Gas phase deposition of metal particles by ALD was further studied in more detail during preparation of mono- and bi-metallic catalyst.

In publication I, dry impregnation, wet impregnation, and ALD were studied in preparation of MWCNT supported palladium catalysts. The functionalization and characterization of MWCNTS used as a support for these catalysts is discussed in Chapter 3. With liquid $Pd(NO_3)_2$ precursor, i.e. in dry impregnation and wet impregnation, metal particle diameters were larger and therefore metal dispersions were lower than with ALD using gaseous $Pd(thd)_2$ precursor at 180 °C. Metal particle size was highest with wet impregnation. In wet impregnation, it is reported that the solvent used with the precursor tends to move the precursor to the outermost surface [30]. Because of this, there is more metal containing precursor on the outermost surface of the support, and this leads to larger metal particles. On the basis of detected particle sizes, this phenomenon took place on the catalysts reported in publication I. Of these three methods, ALD led to the smallest particle size with a narrow particle size distribution and high metal dispersion.

4.2 ALD-prepared mono-metallic Pd catalysts

High metal dispersions lead to efficient use of the valuable metals because of the high metal surface areas obtained. As ALD was found to be a good preparation method for preparing highly dispersed MWCNT supported Pd catalysts in publication I, it was chosen as a preparation method for carbon black supported Pd

catalysts for alcohol electrochemical oxidation [II]. Palladium was chosen as the active metal instead of the more widely used platinum because of the lower price of palladium. The characteristics of the prepared ALD-catalyst were compared to similar commercial Pd catalyst [II]. In Figure 6 the TEM-images of ALD-prepared and commercial catalyst with particle size histograms are presented. The average metal particle size of the ALD catalyst was 2.6 nm with a standard deviation of 1.3 nm and for commercial catalyst 3.4 nm and 1.3 nm, respectively. Palladium on the both ALD-prepared and commercial catalyst was mainly in the metallic state [II].
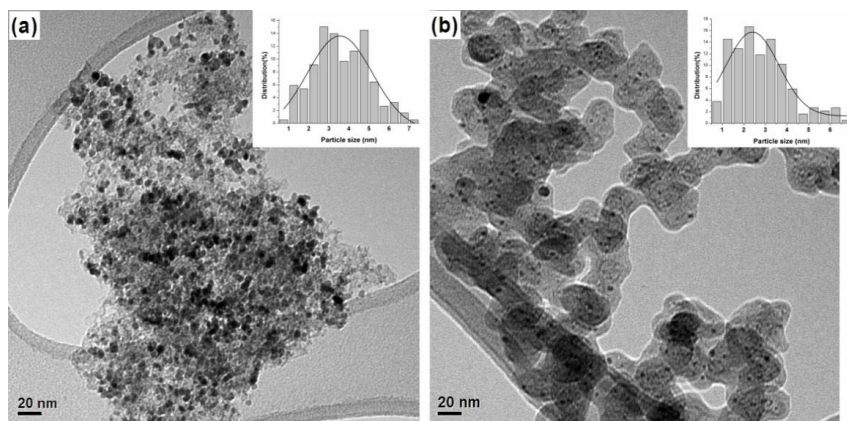
Figure 6. TEM images of (a) commercial Pd/C catalyst and (b) ALD-prepared Pd/C catalyst [II].

4.3   ALD-prepared bi-metallic PtCo catalysts

Bi-metallic PtCo catalysts were prepared by ALD on carbon black support and compared to a mono-metallic Pt catalyst in paper III (see catalyst preparation details in publications II, III, and reference [58]). In preparation of bi-metallic catalysts, the control of metal location on the surface is important, especially if the aim is to prepare catalysts with bi-metallic particles. The first phenomenon to study was to find out whether bi-metallic particles are formed in the preparation of bi-metallic catalysts or are the different metals located as mono-metallic areas on catalysts prepared by ALD. Secondly, the growth mode taking place during the particle growth was studied.

The number and order of the precursor cycles in ALD is reported to affect the metal particle size and the metal availability on the surface [69]. Three primary growth modes exist during thin film growth: a layer-by-layer mode (Frank-van der Merve mode), an island mode (Vollmer-Weber mode), and a random growth mode. Also combination of these different modes can exist, for example, a layer-plus island mode. The main difference between the different growth modes is whether the metal is more strongly attached on the catalyst support (layer-by-

layer mode) or on the metals which already are on the surface (island mode). On random growth mode metals attach as strongly on both surface sites and metals on the surface. On the layer–plus-island mode first a complete metal layer is formed on the support and after that, metal islands are formed on top of the metal monolayer [70-72]. The growth mode can be identified by characterization of the prepared materials between the ALD cycles and analyzing the changes in metal particle locations and metal loadings.

4.3.1 Metal location on the surface

The metal distribution on the surface of bi-metallic PtCo catalysts was mainly studied by EDS and XRD [III]. XPS analysis was carried out to support these results. In EDS, the metal loadings were measured over several areas of the catalyst surface. Pt and Co metal loading ratios on these small areas were found to be similar in all the measurement points and from these results it was concluded that both of the metals were distributed evenly over the surface. In XPS, both Pt and Co were detected. With XPS, metals are detected only on the outermost 10 nm of surface of the sample [73] and thus the results supported the EDS results that both metals are located on the carbon surface.

With XRD, it is possible to detect whether bi-metallic samples have metals as metal alloys or bi-metallic particles. With PtCo catalysts, it has been reported in the literature that formation of metal alloys shifts the XRD reflections to higher detection angles when comparing mono-metallic Pt and bi-metallic PtCo samples [70]. With ALD-prepared Pt and PtCo catalysts, this shift was not detected which indicated metals deposited as bi-metallic particles on the surface and not as metal alloys.

4.3.2 Growth mechanism

The metal particle growth mode in preparation of bi-metallic PtCo catalysts was studied by following the metal loading difference; the metal particle sizes; and the metal distribution on the surface. The increase in the metal loading during one ALD cycle was linear as a function of metal loading on the catalyst used as a support for ALD (Figure 7). The more metal present on the surface before the ALD cycle, the more metal was attached on the surface during the following ALD cycle. This result fits best to the island growth mode where metals deposited during ALD cycles are more strongly attached on other metals than on the support material.
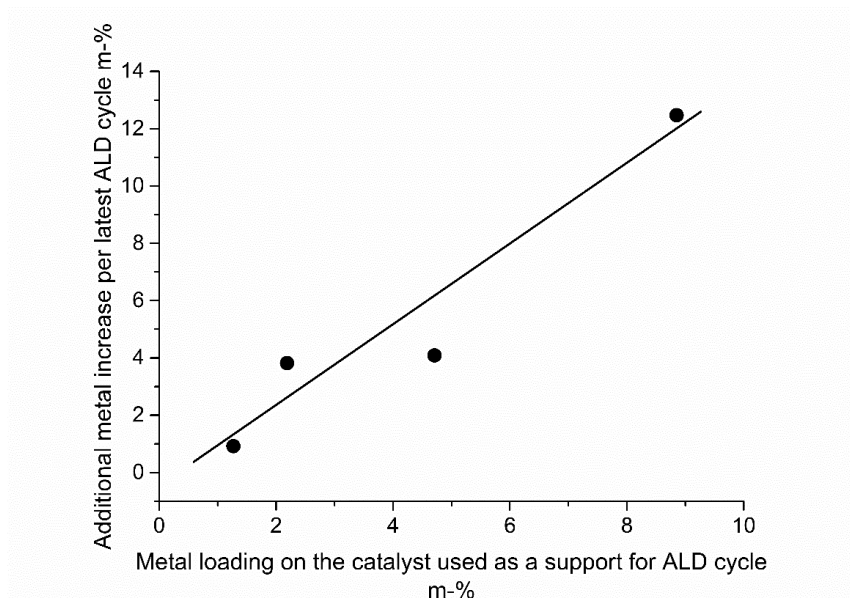
Figure 7. Metal loading added to one ALD cycle as a function of metal loading on the support before the cycle [III].

4.3.3   Metal particle size

Analysis of particle size change as a function of ALD cycles was carried out to further analyse the metal location on the surface and the particle growth mode taking place. Metal particle size was determined by TEM. Two different cases were studied: difference between mono- and bi-metallic catalysts and the effect of the number of ALD cycles when performing additional Pt cycles on a bi-metallic PtCo sample.

When comparing Pt catalyst with one ALD cycle and PtCo catalyst with two ALD cycles, the average metal particle size increased and the metal particle size distribution shifted to larger particles on PtCo catalyst (Figure 8). This indicated that metal was attached on the metals already present on the surface from the first ALD cycle on the sample. Because the metal loading difference between these samples was quite low (total metal loading on Pt catalyst 13.97 mass-% and on PtCo 15.16 mass-%), part of the larger particles were perhaps attributable to sintering of smaller Pt particles formed during the first ALD cycle. In TEM images, also some new cobalt particles were detected to be formed during the second cycle. Nevertheless, these changes cannot explain all the differences detected in the particle size histograms (Figure 8), so the formation of bi-metallic PtCo particles was taking place.

To further study how the metal particles attached on the surface when more ALD cycles were added on the catalyst preparation, catalysts with three and four ALD cycles were prepared (for details, see publication III). On these catalysts, firstly bi-metallic PtCo sample was prepared and on that sample one or two additional Pt deposition cycles were performed to obtain catalysts PtCoPt and PtCoPtPt. On these catalysts, part of the Pt added on the PtCoPt catalysts to obtain PtCoPtPt was still attached to the bi-metallic PtCo particles. This was detected as the weakened Co signal in the XPS measurements because in XPS, only the metals on the outermost surface are detected.

Still, the average particle size decreased and particle size distribution shifted to smaller particles between PtCoPt and PtCoPtPt samples, indicating also the formation of new mono-metallic Pt particles (for histograms, see Figure 8, lower row). There was only a minor formation of new larger particles between these two samples. This indicated two phenomena: Firstly, the clustering of Pt to larger particles detected in preparation of Pt and PtCo catalysts was not taking place when there were more Pt cycles added after Co cycle. This was proposed to be due to the stabilizing effect of cobalt preventing the Pt particles from clustering on the surface. Secondly, not all the metal added to the catalyst attached to the metal particles. Instead, part of it attached to the carbon support. Due to the limited batch size during catalyst preparation, Pt and PtCo samples were from the one batch and PtCoPt and PtCoPtPt from another which explains the differences in histograms and total metal loadings.
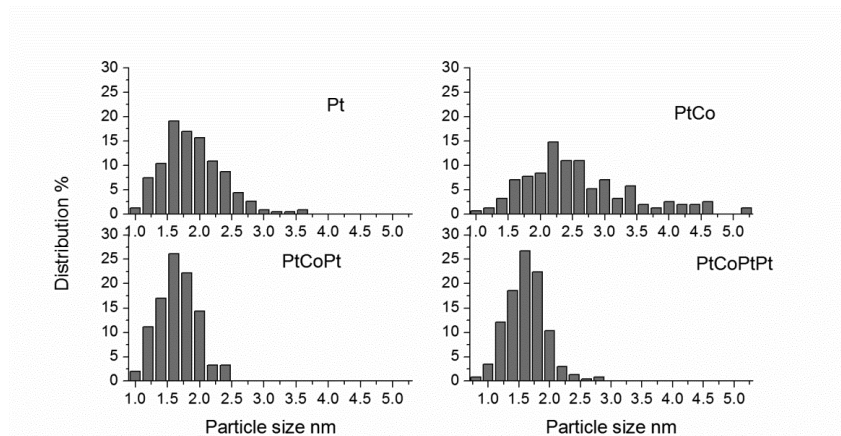
Figure 8. Particle size histograms of ALD-prepared catalysts [III].

Based on these results it was concluded, that with ALD, catalysts with small and well-dispersed bi-metallic Pt and Co particles were prepared. Both metals were distributed evenly over the catalyst support in close proximity to each other and there was a formation of bi-metallic particles on the support. The results indicated that island growth was the primary growth mode taking place,

but a part of the particles were attached on the surface randomly. These results are in agreement with the literature: in the literature, during preparation of catalysts on powder supports using gas phase deposition methods, island growth mode is mainly reported [71, 74].

5. Carbon and other solid acid catalysts in sugar dehydration

5.1 Sugar dehydration catalysts

Solid acid catalysts in an aqueous solvent are an environmentally friendly option for dehydration reactions. The dehydration reaction activity and selectivity depends on numerous different properties of heterogeneous catalysts; catalyst acidity, pore size, and water tolerance being the most important ones [75]. In the dehydration process, many reactions take place simultaneously (see Chapter 1.4 and Figure 2). The nature of the active sites on the heterogeneous catalyst affects the reactions occurring. For example, dehydration reactions take place on the acidic surface sites and sugar isomerization reactions on basic sites [76]. Homogeneous catalysts have shown to be very active in dehydration reactions [43]. However, tailoring the active sites on homogeneous mineral acids is more complicated than on heterogeneous catalysts. This makes solid acid catalysts an interesting option for dehydration reactions, in addition to any environmental aspects. As an example, reaction routes where sugars are firstly isomerized on basic sites to more reactive sugar isomers which are further dehydrated on acidic sites to furfurals, utilize the different type of surface sites on the catalyst.

A disadvantage in the use of solid acid catalysts is the ease of solid catalyst deactivation in water by the dissolution of acid sites [14]. In publication IV different solid acid catalysts – activated carbon, TiO_2, and H-mordenite type zeolite – were studied in xylose dehydration using water as a solvent. The effect of different carbon catalyst surface sites on the dehydration reaction was studied by testing carbon catalysts functionalized with different oxidation treatments in xylose dehydration. The functionalization and characterization of these carbon catalysts used in the dehydration reaction is discussed in Chapter 3.

Activated carbon was chosen for dehydration because of its good water tolerance and the modifiable surface which provides the possibility to create different type of active sites on the surface. H-mordenite and TiO_2 were studied because they both have high acidity. The acid site density measured by acid-base titration was highest on H-mordenite (41.98 mmol/cm²) and lowest on TiO_2 (6.06 mmol/cm²). For carbon catalysts the measured acid site density was 7.80 mmol/cm² [IV]. Zeolites and especially H-mordenites are also reported to be

active and selective and xylose dehydration [77]. TiO_2 is reported to be a water-tolerant catalyst support. In the literature it has been tested for example in cellulose sugars hydrogenation reactions in an aqueous solvent [78].

5.2   Dehydration activity of different solid acid catalysts

The activity of different solid acid catalysts; activated carbon, TiO_2, and H-mordenite; in xylose dehydration and isomerization were studied at the reaction temperature 200 °C and pressure 5 MPa (Figure 9) [IV]. High furfural selectivities in xylose dehydration were obtained with all the catalysts. Selectivity to furfural changed as a function of conversion. At the higher sugar conversions, furfural selectivity decreased. The detected decrease in selectivity was lowest with carbon catalysts. Notable differences discovered between the catalysts were in the isomerization activity (Figure 9) and catalyst deactivation (Figure 10). Isomerization was analysed by calculating the xylose/all sugars ratio: when the ratio was high, the formation of sugar isomers from xylose was low. Of the studied catalysts, the highest xylose/all sugars ratio was detected with carbon catalyst which indicated the lowest isomerization activity of the compared catalysts. Depending on the formed sugar isomers, isomerization can either enhance the furfural formation rate or slow it down. Ketosugars react more easily in dehydration reactions than aldose sugars [79, 80] and thus isomerization reactions enhance furfural formation if ketosugars are formed through isomerization. Ketosugar xylulose was not detected in the reaction mixture but aldose sugar lyxose was detected as a product (Figure 9). Because the detected sugar isomers for all the tested catalysts were aldose type sugars, this reaction route could not be utilized in the system. However, all the studied sugar isomers are reactive in dehydration.
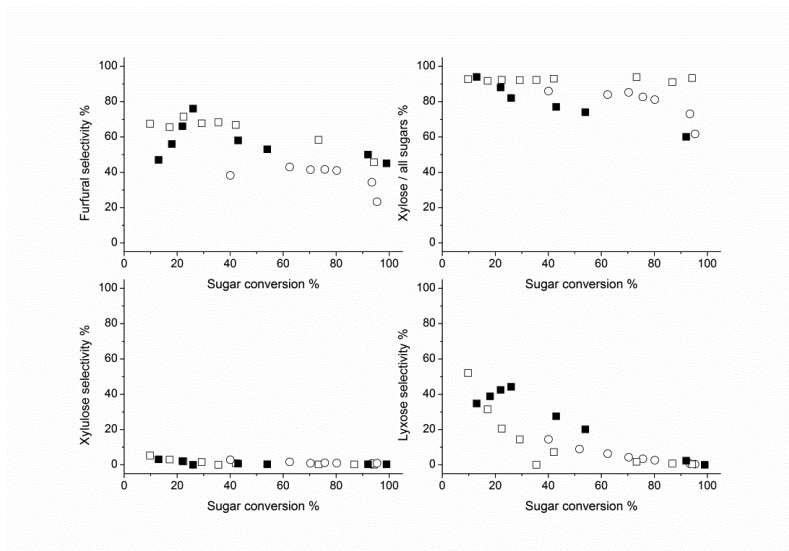
Figure 9. Furfural selectivity, xylose/sugars ratios, xylulose selectivity, and lyxose selectivity as a function of xylose conversion on C(HNO$_3$+H$_2$SO$_4$) catalyst (□), H-mordenite (■), and TiO$_2$ (○) on xylose dehydration experiment at reaction temperature 200 °C and pressure 5 MPa [IV].

The observed differences for the dehydration activity can be due to the total acidity of the catalyst, acid site density, distribution of acid sites type between Brönsted and Lewis acidity, or pore sizes [IV]. Acid site density has to be high enough for catalysts to have enough active sites for reactions to proceed efficiently. On the other hand, too high acid site density can enhance the side reactions consuming furfural. In condensation and resinification reactions furfural that is formed adsorbs back on the active sites and reacts further. These reactions can take place either on the same site as dehydration or on another active site on the surface. On the catalysts with high acid site density, furfural formed on the surface can react further more easily because after desorption there are surface sites available close to the original one making it easier to adsorb back on the active site. An indication of the acid site density affecting furfural selectivity was detected on H-mordenite in Figure 9: at the beginning of the reaction, the selectivity increase on the H-mordenite was the most significant compared to the other catalysts studied. On the other hand, the selectivity decrease on H-mordenite was the most rapid as a function of conversion. The acid site density on H-mordenite was the highest of the compared catalysts which is proposed to be the factor leading to high furfural selectivity at lower conversion levels as there was a high amount of active sites available for sugar molecules. Still, high active site density also caused the furfural formed to react further.

In addition to the total acidity of the catalyst, the type of acid sites affects the performance of the catalyst: Brönsted acid sites are reported to lead to high selectivity towards furfural, whereas Lewis acid sites lead to high sugar conversions but enhance the isomerization reactions. In water, Lewis acid sites can change to Brönsted sites [44]. Between H-mordenite and TiO$_2$ this difference

was seen in the dehydration results: on H-mordenite the selectivities were higher with the catalyst acidity being mainly Brönsted acidity, whereas with TiO_2 with mainly Lewis acidity, the selectivity was lower [81, 82]. On the other hand, because of the possible change of Lewis sites to Brönsted sites in water, the reason for differences in activity depends also on other catalyst properties than the surface site Brönsted/Lewis type acidity.

The catalyst pore size distribution can also change the product distribution. Optimal activity for dehydration reaction is achieved with catalysts pores that are large enough to enable the sugars and furfural to diffuse in and out to the pores and active sites. At the same time, pores have to be small enough so that sugar condensation products, humins, cannot be formed in the pores [76]. A catalyst pore size close to 0.8 nm is consider to be optimal in xylose dehydration [83]: the diffusion of xylose and furfural is possible but they are too small form humins. In the comparison of pore sizes of activated carbon, H-mordenite, and TiO_2, the smallest pore sizes were found with carbon catalysts, almost 46% of the pore volume is contained in pores with a radius of 1-2 nm. On H-mordenite the catalyst pores determined by BET-analysis were largest with 61% of pore volume being in the 5-10 nm range and 29% of pore volume in the 10-20 nm range. On TiO_2 the pore size distribution was widest with all kind of pores ranging from 2 to 30 nm [IV]. The high proportion of smaller pores on carbon catalyst is one reason for the highest furfural selectivity obtained over the entire conversion range when compared to other catalysts studied.

Catalyst stability and deactivation were studied by carrying out experiments twice with the same catalyst and observing the changes in conversions and selectivity (Figure 10). Based on these results, for carbon catalysts the lowest amount of deactivation among the studied catalysts was observed: both sugar conversion and furfural selectivity remained at the same level compared with the previously tested catalyst. With TiO_2 sugar conversion decreased when using the spent catalyst. With H-mordenite, the sugar conversion remained on the same level but the furfural selectivity decreased with the spent catalyst. These results indicate that in water, carbon catalyst retains its activity in xylose dehydration. Thus carbon catalysts were the most suitable for use in an aqueous environment.
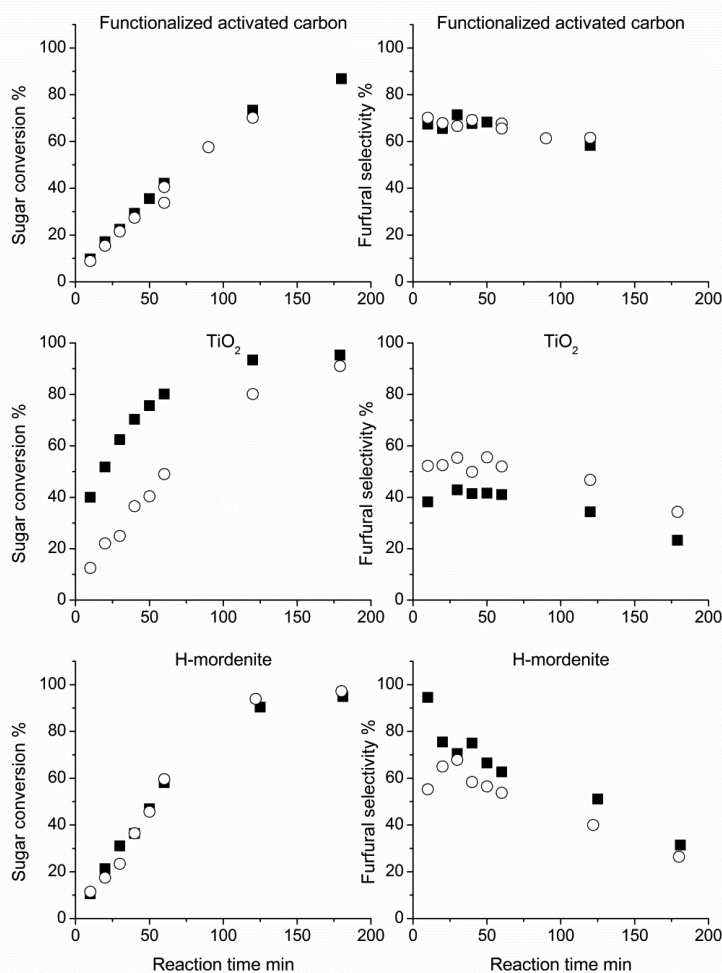
Figure 10. Sugar conversion and furfural selectivity on fresh (■) and used (○) catalysts for C(HNO₃+H₂SO₄) catalyst, H-mordenite, and TiO₂ on xylose dehydration experiment at reaction a temperature of 200 ° C and a pressure of 5 MPa [IV].

5.3 Active sites on carbon surface

Different types of oxygen-containing acidic groups and sulphur-containing groups are reported to be active in xylose dehydration [84]. Three different acid combinations in functionalization treatments were tested with activated carbon catalyst (see Chapter 3). The aim was to create oxygen-containing surface groups, sulphur-containing surface groups, and their combination to compare

their activity in dehydration. The types of the surface groups on the functionalized catalysts with the tested acid combinations are presented in Table 3.

The surface sites on carbon catalyst were shown to affect the performance of the catalyst in dehydration (Figure 11). The highest furfural selectivity was obtained on the catalyst which was functionalized with both nitric acid and sulphuric acid, $C(H_2SO_4:HNO_3)$. The total acidity of this catalyst was 15.77 mmol/cm^2. The more specific role of different type of groups was studied by comparing catalysts functionalized separately with HNO_3 and with H_2SO_4. The acidity of the $C(HNO_3)$ sample was 20.43 mmol/cm^2 and $C(H_2SO_4)$ 14.83 mmol/cm^2 [IV]. Oxygen-containing surface groups in both catalysts were of a similar type (Table 3) and the main difference was that with $C(H_2SO_4)$, there were also sulphur-containing surface sites which did not exist on the C(HNO3) catalyst. On the catalyst with sulphur-containing groups, furfural selectivity was higher than on the catalyst without them even though the total acidity of $C(HNO_3)$ catalyst was higher than $C(H_2SO_4)$. Based on these results it was concluded that for xylose dehydration on carbon catalysts, the type of surface groups and the catalyst acidity affected the furfural selectivity. The sulphur-containing groups were more selective towards furfural than oxygen-containing groups. When the catalyst contained both oxygen- and sulphur-containing groups, higher furfural selectivity was obtained with the more acidic catalyst (Figure 11).

The total amount of sugar isomerization was similar for all carbon catalysts. This is detected from the ratio of xylose to the total amount of sugars in the reactions system (Figure 11). In general, the isomerization activity of carbon catalysts was rather low and most of the sugars in the reaction mixture, approximately 90 mol-% of all sugars, were xylose. The sugar isomers formed varied with different type of sulphur-containing groups on the catalyst: the ketosugar xylulose was detected only on the catalyst which had thiophenol groups ($C(H_2SO_4)$ catalyst) (see Figure 1 for a picture of the groups). On the other catalysts, $C(HNO_3)$ and $C(H_2SO_4:HNO_3)$, the aldose sugar lyxose was the only detected sugar isomer. The difference between these three catalysts was the thiophenol groups on the $C(H_2SO_4)$ catalyst. The difference in isomerization activity of surface groups towards aldose/keto sugars could be used in two step dehydration mechanisms where xylose is first isomerized to more reactive ketosugars and dehydration takes place after that [76].
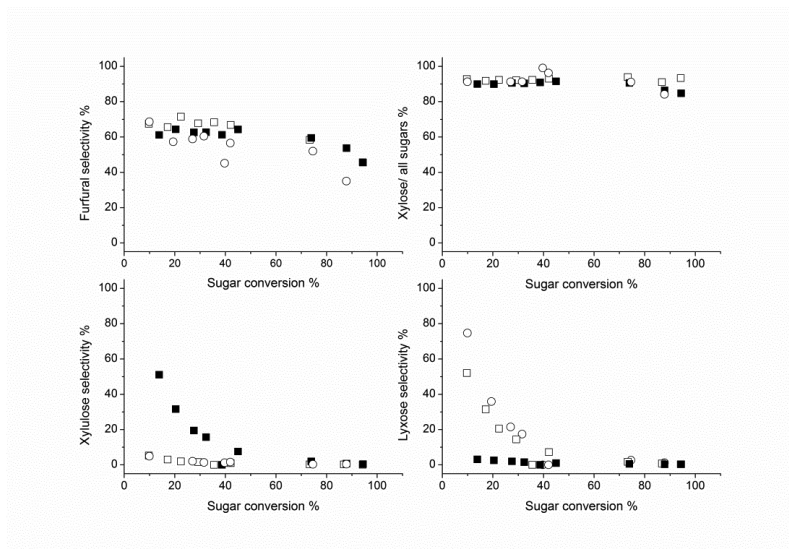
Figure 11. Furfural selectivity, xylose/sugars ratios, xylulose selectivity, and lyxose selectivity as a function of xylose conversion on activated carbon catalyst functionalized with 3 M H₂SO₄:HNO₃ 3:1 (□), 3 M H₂SO₄ (■), and 3 M HNO₃ (○) on xylose dehydration experiment at reaction temperature 200 ° C and pressure 5 MPa [IV].

The water-tolerance of carbon catalyst in this reaction was shown to be better compared to the other catalyst studied. With a suitable solid acid catalyst, it is possible to modify the dehydration reaction mechanism to obtain higher selectivity towards the desired products.

6. Carbon catalysts in hydrogenation

Hydrogenation of α, β-unsaturated aldehydes is a widely used reaction in many applications because unsaturated alcohols are intermediates in the production of fine chemicals and pharmaceuticals. Hydrogenation of the C=C bond is easier than the C=O bond because of the lower activation energy but often unsaturated alcohols obtained by hydrogenation of the C=O bond are the desired products [85, 86]. Examples of these reactions are cinnamaldehyde hydrogenation [85] and prenal hydrogenation [86]. Cinnamyl alcohol from cinnamaldehyde hydrogenations (Figure 12) is used in the production of fragrances, pharmaceuticals and fine chemicals [86, 87]. Prenol from prenal hydrogenation is used in fragrances, in flavouring, and in pharmaceuticals like in vitamin A production [86]. Because the reaction products formed in these reactions depend strongly on the reaction mechanism and the mechanism is affected by the catalyst properties, hydrogenation reactions of α, β-unsaturated aldehydes are suitable model reactions for catalyst screening. To support the physical characterization results of the catalysts prepared with different techniques in publication I, catalysts were tested using cinnamaldehyde hydrogenation as a model reaction.

Hydrogenation reactions commonly require metallic catalysts for reactions to take place efficiently. These catalysts are either mono- or bi-metallic. Platinum [86] and other platinum group metals such as ruthenium and palladium are commonly used in hydrogenation [II, 59, 86]. Palladium is reported to be an active metal in cinnamaldehyde hydrogenation making this a suitable model reaction to test the prepared catalysts, as reported in publication I (see Figure 12 for reaction scheme). The preparation and physical characterization of these catalysts is presented in Chapter 4.

Different kinds of carbon materials, for example activated carbon and carbon nanotubes, are widely used and studied as supports for hydrogenation catalysts. The chemical nature of the support material surface is shown to affect the activity in the reaction. In the case of cinnamaldehyde hydrogenation, the polarity of the support caused by oxygen-containing surface groups leads the cinnamaldehyde phenyl ring being rejected from the surface. With this type of support, the C=O bond is more easily hydrogenated than C=C bond [88].
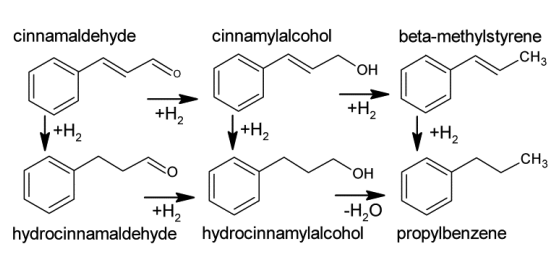
Figure 12. The reaction scheme for cinnamaldehyde hydrogenation [IV].

Cinnamaldehyde hydrogenation is widely used as a model reaction to study the properties of supported metal catalysts because the product selectivity changes clearly as a function of metal particle size [59, 85, 88]. With smaller metal particles, both the C=C and C=O bond are hydrogenated leading to hydrocinnamyl alcohol as a product. With larger metal particles, only the C=O or C=C bond is hydrogenated leading to hydrocinnamylaldehyde and cinnamyl alcohol products [89, 90]. These products can still be further hydrogenated to beta-methylstyrene or dehydrated to propylbenzene (Figure 12).

Catalysts in this study were prepared either by dry impregnation, wet impregnation, or ALD [I]. With dry impregnated and ALD-prepared catalysts, significantly higher proportions of hydrocinnamyl alcohol were detected in the product distribution than with wet-impregnated catalyst [I]. With wet-impregnated catalyst, the proportion of hydrocinnamaldehyde in the product distribution was high whereas with other catalysts it was not detected. The obtained product distribution results supported the characterization results of particle sizes: with smaller metal particles, both double bonds in the molecule were hydrogenated.

The consumption rates of cinnamaldehyde were 1.25, 0.53, and 2.45 mmol/(g$_{Pd}$min) for the wet-impregnated, dry-impregnated, and ALD-prepared catalysts, respectively [I]. The high surface area of the active components increases the reaction rate. The smaller metal particles sizes and higher surface area of metal found for ALD-prepared catalysts was noticeable in these results, as the cinnamaldehyde consumption was highest on ALD-prepared catalyst. This supports the conclusion drawn from the characterization results that with similar metal loadings, smaller metal particles enhance the higher catalyst activity [I].

7. ALD-prepared catalysts in alcohol electrochemical oxidation

7.1 Carbon supported catalysts for fuel cell applications

Carbon black supported ALD-prepared catalysts were tested for electrochemical oxidation of different alcohols to determine if the advanced properties of these catalysts, small metal particles and high metal dispersion, could be utilized for fuel cell applications. Catalyst preparation and physical characterization details are discussed in Chapters 4.2 and 4.3. With a mono-metallic Pt ALD-catalyst the effect of higher metal dispersion on catalyst activity in alcohol oxidation was studied. For bi-metallic PtCo catalysts, the activities of mono- and bi-metallic particles and the differences in reaction mechanisms with various metal ratios and structures on the bi-metallic particles were compared.

7.2 Mono-metallic ALD-prepared catalysts

ALD-prepared Pd/C catalyst with a metal loading of 3.5 mass-% (details described in publication II) was tested in ethanol and isopropanol electrochemical oxidation in alkaline media and its electrochemical activity was compared to a commercial Pd catalyst with a metal loading of 20 mass-% [II].

The reaction rate on the catalyst directly affects the onset potential. If the activation energies for the oxidation and reduction reactions are high, the potential to obtain a given current from the anode is higher. This lowers the overall fuel cell potential and the total efficiency of the fuel cell. With the ALD-prepared catalyst the onset potential was 50 mV lower than with commercial catalyst indicating that the smaller metal particles on ALD-prepared catalyst were more active in oxidation reactions than the larger particles on the commercial catalyst.

With an ALD-prepared catalyst, 2.5 times higher oxidation currents were obtained than with commercial catalyst when currents were scaled by the metal loading on the catalyst (see Figure 13). This result suggests the catalyst with higher dispersion and thus with higher electrochemically active surface area is more active for the oxidation reaction. Because of the higher currents obtained with ALD-prepared catalyst, it can be concluded that with the ALD method it could be possible to decrease the metal loading and still achieve high currents.

This would make it possible to reduce the fuel cell catalyst costs by using catalysts with a lower metal loading.

Figure 13 presents the current obtained with different catalysts for ethanol and propanol oxidation at 0.7 V potential as a function of time. Even though higher initial currents were obtained with ALD-prepared catalysts, the catalyst activity on the ALD-prepared catalysts decreased faster than on the commercial catalyst. This could be due to surface poisoning by the intermediate products. Intermediate products reported in the literature are acetate and acetaldehyde for ethanol oxidation and acetone for isopropanol [50]. One alternative to reduce poisoning is the use of bi-metallic catalyst.

Bi-metallic catalysts can either reduce the adsorption of the intermediate products or can even oxidize them further thereby avoiding surface poisoning. To conclude, mono-metallic ALD-prepared catalysts led to promising results in alcohol oxidation but the stability of the catalysts against poisoning requires further improvements.
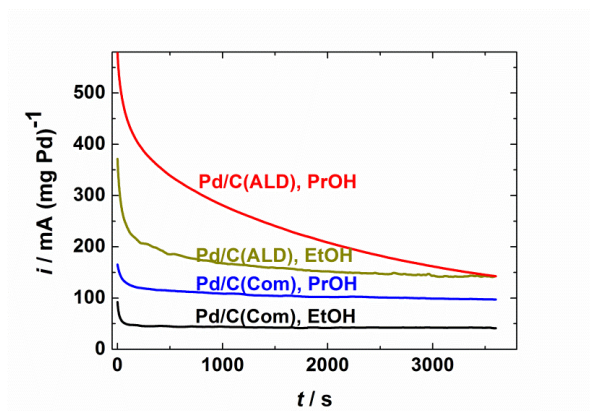

Figure 13. The currents obtained for ethanol and propanol oxidation at 0.7 V potential as a function of time in 0.1 M NaOH electrolyte [II].

7.3 Bi-metallic ALD-prepared catalysts

In fuel cells, in addition to decreasing the amount of precious metals, another important way to reduce the catalyst costs is to replace part of the noble metals with less noble metals [III]. It is reported in the literature, that bi-metallic particles can be more active for oxidation of alcohols than mono-metallic particles [91-93]. On bi-metallic catalysts, variation in the metals used alters the oxidation mechanism [58] which can make the catalysts less susceptible to poisoning by decreasing the amount of partial oxidation products which can poison the catalyst. Because the catalyst stability against poisoning was found to require further improvements for mono-metallic ALD catalysts [II], bi-metallic cata-

lysts were prepared by ALD to study the effect of adding Co on Pt catalysts. Preparation and physical characterization of these catalysts is discussed in Chapter 4.3.

7.3.1 Catalyst activity

Bi-metallic ALD-prepared catalysts were tested during methanol oxidation in acidic media [III] and ethanol oxidation in alkaline media [58]. Mono-metallic and bi-metallic catalysts were compared and the effect of partly layering the metals on each other by ALD cycles on catalyst activity and durability was studied.

There was a clear difference in activity detected between of mono-metallic Pt and bi-metallic PtCo particles in alcohol oxidation. With bi-metallic particles, the onset potential in methanol oxidation in acidic media was decreased by 50 mV and 1.5 times higher currents where obtained than with mono-metallic catalyst [III]. In ethanol oxidation in alkaline media, a similar decrease of the onset potential and increase in the activity between mono- and bi-metallic catalysts was also detected [58].

The number of ALD cycles changed the catalyst activity because the availability of the metals on the surface varied as a function of ALD cycles. When an additional platinum cycle was added on PtCo catalyst to obtain PtCoPt catalyst (see Chapter 4.3), part of the Co was covered with platinum and at the same time some new Pt particles were formed. Thus part of the cobalt was not directly available for reagents because it has been covered by Pt. Nonetheless, the cobalt below the platinum can change the catalytic properties of Pt. In the literature this phenomenon is known for example for the core-shell catalyst structures of Co and Pt [94]. In addition to changed availability of cobalt, the increasing number of mono-metallic Pt particles decreased the proportion of more active bi-metallic particles. In methanol oxidation this was detected as decreased activity by increased onset potential. The second Pt ALD cycle on the PtCoPtPt catalyst did not increase stability further as the catalyst was closer to mono-metallic Pt catalyst than to bi-metallic catalyst [III]. In ethanol oxidation, PtCoPt catalyst showed higher currents than Pt and PtCo catalyst. This was proposed to be because Pt atoms on the top of PtCo particles prevent cobalt dissolution from the surface and yet bi-metallic properties are still obtained [58].

In ethanol oxidation, the product distribution was analysed to further study the reaction mechanisms. The main products detected were carbon dioxide, acetaldehyde, and acetate. Carbon dioxide was detected as a product mainly for bi-metallic catalysts based on both platinum and cobalt and not with mono-metallic platinum catalysts. In addition, it was determined that the amount of CO_2 formed was lower on PtCoPt catalyst where an additional cycle of Pt was added on the bi-metallic PtCo catalyst. These results support the hypothesis of bi-metallic catalysts leading to total oxidation of the alcohol when compared to mono-metallic catalysts. Furthermore, the product distribution with multiple Pt cycles on Co was closer to the distribution obtained with mono-metallic catalysts than with bi-metallic catalysts. This result also supports the characterization results

of the ALD-prepared catalysts that indicated platinum partly covering the bi-metallic PtCo particles and bi-metallic PtCoPtPt catalysts being more similar to mono-metallic Pt catalysts than to bi-metallic PtCo catalysts [58].

7.3.2 Catalyst stability

One fuel cell deactivation mechanism is the dissolution of metals from the elec-trocatalyst due to oxidation of the less noble metal. It has been shown in the literature that alloying noble metals with a less noble metal, for example Pt with Co, can be used to decrease the amount of metal dissolution [95, 96]. However, it has also been reported that bi-metallic catalysts can experience severe leach-ing of the second metal from the particle [94]. With PtCo catalysts, the possible dissolution of the less noble metal can be decreased by adding noble metal on top of it. In the literature it has been reported, that core structure catalyst with cobalt core and platinum shell prevented cobalt dissolution [94]. With ALD-prepared catalysts, in this study, cycling the metals during the catalyst prepara-tion process was tested as a solution for the stability problem. As was shown in the physical characterization results (see Chapter 4.3), with ALD metals added on the catalyst surface were partially covering the metals from the previous ALD cycles leading to similar type of structures as in core-shell catalysts.

The activity and stability of mono- and bi-metallic catalysts was first com-pared, as the stability of mono-metallic ALD-prepared catalysts was shown to be less than commercial mono-metallic catalysts (see Chapter 7.2). The activity of mono-metallic catalyst decreased fastest at the beginning of the oxidation re-action which is in line with the stability results reported in the literature for mono- and bi-metallic catalysts during alcohol oxidation [94-96].

When studying the stability of bi-metallic catalysts prepared using different numbers of ALD cycles, differences between PtCo catalysts and PtCoPt and PtCoPtPt catalysts were detected. Even though the Pt on top of Co on PtCoPt catalysts decreased the catalyst activity compared to PtCo catalysts, it was found, that the stability of PtCoPt catalysts was higher than PtCo. This was sug-gested to be because Pt on the top stabilized Co on the particle decreasing the deactivation rate. This is one solution to lower the high deactivation rate de-tected with mono-metallic ALD-catalysts [III, 58].

On the PtCoPtPt catalyst, which was prepared by adding one more cycle of Pt on PtCoPt, the catalyst stability was not enhanced anymore and the catalyst was more similar to mono-metallic Pt catalysts than bi-metallic catalysts [III].

Based on the stability results it can be concluded that the layering of the metals by ALD helped increase the catalyst stability but the amount of platinum depos-ited on cobalt has to be optimized to ensure that the advantages of the bi-metal-lic properties of the catalyst are still obtained.

8. Summary

Various types of carbon materials can be utilized in catalyst applications because of their modifiable properties. Carbon materials studied as catalysts or catalyst support in this work were the widely used bulk carbon materials activated carbon and carbon black and the less widely used, newer material, multiwalled carbon nanotubes.

Three different types of carbon catalysts were prepared and studied: functionalized carbons with groups containing heteroatoms (oxygen and sulphur) as active sites on the catalyst; carbon supported mono-metallic Pt and Pd catalysts; and carbon supported bi-metallic PtCo catalysts. For the preparation of catalysts with heteroatoms as active sites, the effect of functionalization treatment parameters was studied. In metal-catalyst preparation, three catalyst preparation methods - dry impregnation, wet impregnation, and ALD - were studied in preparation of mono-metallic Pd catalysts. ALD was further studied for the preparation of bi-metallic PtCo carbon supported catalysts.

In carbon functionalization, the widely used technique of liquid acid oxidation with nitric acid and sulphuric acid was used in the creation of different types of oxygen- and sulphur-containing sites on the surface. A difference in the surface groups formed when using nitric acid and sulphuric acid alone and as a mixture in the oxidation agent was observed. In addition, the formation mechanism of different type of oxygen-containing surface groups was studied with nitric acid oxidation. The formation mechanism was shown to follow the principles presented in the literature with phenolic/carbonyl/quinone groups formed at the beginning of the functionalization followed the formation of carboxylic acid groups was proceeded from these. The amount and type of surface group changed as a function of time making it possible to optimize the catalyst surface sites. As the carboxylic acids were the desired groups, the functionalization time was optimized so that the amount of carboxylic acid sites was maximized.

Solid acid catalysts are environmentally friendly alternatives to homogenous acid catalysts in xylose dehydration. Carbon catalysts were tested in the xylose dehydration reaction together with two other solid acid catalysts, namely TiO_2 and H-mordenite type zeolite. Carbon catalysts were found to be more water tolerant than the other catalysts tested at the reaction conditions studied, making carbon materials a suitable alternative as dehydration catalysts.

The furfural selectivity was shown to vary with different surface groups on the catalyst. In addition, a clear indication of differences in the sugar isomerization

activity with different type of surface groups was found. When sulphur-containing groups were present on the surface, the more reactive keto-type sugars were formed. This functionality could be further utilized when aiming for a two-step dehydration route, where xylose is firstly isomerized to the more reactive keto-sugar and the ketosugar is then dehydrated to furfural.

In metal catalyst preparation, the gas-phase deposition method ALD was found to give excellent catalyst properties when compared to the catalysts prepared with liquid phase precursors in dry and wet impregnation. The physical characterization results of the catalysts prepared with these three methods were supported by using the cinnamaldehyde hydrogenation reaction as a model reaction to characterize catalyst properties further. ALD-prepared catalysts had higher metal dispersions and smaller catalyst metal particle sizes than catalysts prepared with liquid precursor.

In preparation of bi-metallic particles by ALD, metals were shown to be deposited over the whole support surface area and part of the added metals formed bi-metallic particles. Formation of bi-metallic particles instead of separate clusters of different metals is advantageous when the reaction catalysed takes place via multiply reaction steps on active sites consisting of different metals. In addition to bi-metallic particle formation, the growth mode of ALD-prepared catalysts was studied. For powder catalyst supports, and especially for bi-metallic samples, analysis of the growth modes is not as widely reported in the literature as for thin films. In this study, the growth was shown to mainly follow island growth mode.

The ALD-prepared mono- and bi-metallic catalysts were tested in alcohol electrochemical oxidation. Mono-metallic ALD-prepared catalysts were compared to commercial catalysts. The activity and stability of ALD-prepared bi-metallic catalyst was tested and compared to mono-metallic ALD-prepared catalysts.

The ALD-prepared mono-metallic catalyst with higher metal dispersion and small particle sizes with narrow particle size distributions led to higher catalyst activity in alcohol electrochemical oxidation when compared to commercial catalysts with lower dispersion. This is beneficial when aiming to lower the fuel cell catalyst costs because with an ALD-prepared catalyst, the same activity could be obtained with a lower metal loading when compared to commercial fuel cell catalysts.

In electrochemical oxidation on bi-metallic catalysts, metals can dissolve from the catalyst to electrolyte. With ALD-prepared bi-metallic catalysts, it was possible to modify the catalyst stability by the catalyst preparation parameters. This was done by cycling the metals on top of one another. Because of this, better stability and a lower catalyst deactivation rate were obtained.

In this study several type of carbons were shown to be suitable materials as catalysts and catalyst supports. Various catalyst preparation methods were tested and carbon catalysts and carbon supported catalysts showed advanced properties when compared to traditionally more widely used catalysts and catalyst preparation methods.

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