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# Molecular and Atomic Layer Deposition of Hybrid Inorganic-Organic Materials – Deposition on Porous Substrates

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#### ACADEMIC DISSERTATION

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"You may encounter many defeats, but you must not be defeated. In fact, it may be necessary to encounter the defeats, so you can know who you are, what you can rise from, how you can still come out of it."

Maya Angelou

### Abstract

This thesis focuses on increasing the general knowledge of molecular layer deposition (MLD) research, developing novel low-temperature MLD coatings and on the preparation of inorganic-organic hybrid materials by atomic layer deposition (ALD) and MLD on porous substrate materials. In addition, characterization of the chemical and physical properties of the produced materials is of interest, and thus further the development of novel applications for example in the field of clothes with added functionalities, construction and packaging materials and catalysts. For example, in the case of packaging materials ALD and MLD coatings can provide enhanced barrier properties against moisture and oxygen transmittance. Furthermore, ALD/MLD can be used for adding antimicrobial properties for example on technical masks and medical textile products. In the case of catalysts, ALD can be used for implementing active metal nanoparticles on the catalyst support or ALD/MLD can be used for depositing a protective overcoating on the catalyst surface to protect the active metal particles from fouling, sintering, or leaching.

Atomic and molecular layer deposition are thin film deposition techniques where sequential pulses of gaseous precursors react in a self-limiting way on the solid surface forming conformal coatings. The greatest advantage of ALD and MLD is the possibility to coat 3D surfaces with a wide range of materials, different shapes and high aspect ratios, with accurate layer thickness.

When studying the ALD growth on porous nonwoven fibrous substrates, electrospun polyethylene sulphone, poly-L-lactic acid and cellulose acetate and foam-formed cellulose, it was observed that only a few cycles of  $Al_2O_3$ , ZnO or  $TiO_2$  was often the best option for modifying the physical properties of the prepared materials to the wanted direction. In the case of electrospun polymeric fibres, protection against thermal degradation was achieved with ALD  $Al_2O_3$  and ZnO, whereas the hydrophobicity, moisture resistance and compression strength of foam-formed cellulose were improved with ALD  $TiO_2$ . Differences between the traditional ALD and vapor phase infiltration were clarified and new insights about ALD on porous substrate materials were obtained.

The study on ALD and MLD overcoatings on porous powdery Fischer-Tropsch catalysts revealed enhanced activity of the overcoated catalysts. Furthermore, protection against leaching in multiphase FT synthesis was provided by both ALD ( $Al_2O_3$ ) and MLD (alucone, TMA + ethylene glycol) coatings.

The study on the development of new MLD processes with aromatic precursors (phenol, 3-(trifluoromethyl)phenol (3F) and 2-fluoro-4-(trifluoromethyl)benzaldehyde (4F)) revealed that the aromatic ring structures can be opened by ozone in the case of all precursors tested. Furthermore, phenol, 3F and 4F can be used as organic precursors in continuous MLD processes, and fluorine can be incorporated into the film structures. Low deposition temperatures could be used, since the MLD growth was observed at the temperature range of 75-150 °C, with the exact temperature depending on the precursor.

### Preface

This research and experimental work were carried out in VTT Technical Research Centre of Finland. The main part of the research was done in the project "Understanding nanostructure growth in ALD/MLD", funded by Academy of Finland (ID 288212). Part of the work was carried out within the framework of the COST Action MP1402 - HERALD. In addition, catalytic performances were studied in the project "ICO2CHEM - From industrial CO2 streams to added value Fischer– Tropsch chemicals", funded by European Union's Horizon 2020 research and innovation programme under grant agreement No (ID 768543). The effect of TiO2 ALD on foam-formed fibres was studied in the project "Piloting alternatives for plastics", funded by EU Regional Development Fund (Grants A73089 and A73092). I could have not done this work alone. For that reason, I wish to thank:

First, my original supervisor in VTT and University of Helsinki, Professor Matti Putkonen. Your guidance and encouragement during this research have been everything. Also, my official supervisor, Professor Mikko Ritala, thank you for the opportunity to reach for the title of PhD and support during the journey. Furthermore, I wish to thank all my managers in VTT (Pekka, Janne and Alexander). Thank you for the opportunity for reaching out the title of PhD and all the support during the way. I would also like to thank my other colleagues at VTT. Thank you for all the practical help and guidance and all the mental support during these years! And my dear friends along the way who have been there for me this whole time, I owe you all so much!

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Espoo, November 2023 Laura Keskiväli

# List of abbreviations

ALD	Atomic Layer Deposition
ATR-FTIR	Attenuated Total Reflectance – Fourier Transformation Infrared Spectroscopy
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CA	Cellulose acetate
CAM	Contact Angle Measurement
СТМР	Chemi-Thermo Mechanical Pulp
CVD	Chemical Vapor Deposition
DEZ	Diethylzinc
DFT	Density Functional Theory
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive Spectroscopy
EG	Ethylene glycol
FT	Fischer-Tropsch synthesis
FTIR	Fourier-Transform Infrared Spectroscopy
GPC	Growth per cycle
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
MLD	Molecular Layer Deposition
MOF	Metal organic framework
NMR	Nuclear Magnetic Resonance Spectroscopy
PE	Plasma enhanced
PES	Polyethersulphone
PLLA	Poly-L-lactic acid
POCA	Powder coating cartridge
PVA	Polyvinyl alcohol
PVD	Physical Vapor Deposition
SEM	Scanning Electron Microscope

STEM	Scanning Transmission Electron Microscope
TGA	Thermogravimetric Analysis
TMA	Trimethylaluminum
TOF-ERDA	Time-of-Flight Elastic Recoil Detection Analysis
VPI	Vapor Phase Infiltration
XPS	X-ray Photoelectron Spectroscopy
XRR	X-Ray Reflectivity

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5	Conclu	isions and outlook	53
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## List of original publications

This thesis is based on the following publications:

I Low-Temperature Molecular Layer Deposition Using Monofunctional Aromatic Precursors and Ozone-Based Ring-Opening Reactions

Laura Svärd, Matti Putkonen, Eija Kenttä, Timo Sajavaara, Fabian Krahl, Maarit Karppinen, Kevin Van de Kerckhove, Christophe Detavernier, Pekka Simell

Langmuir 33 (2017) 9657–9665. The author prepared the MLD films and carried out the ellipsometry, CAM, FTIR, in-situ FTIR and XRR analysis. The author wrote the first draft and finalized the paper with co-authors.

#### II Molecular Layer Deposition Using Ring-Opening Reactions: Molecular Modeling of the Film Growth and the Effects of Hydrogen Peroxide

Laura Keskiväli, Matti Putkonen, Eini Puhakka, Eija Kenttä, Jeroen Kint, Ranjith K. Ramachandran, Christophe Detavernier, Pekka Simell

ACS Omega 3 (2018) 7141-7149

The author prepared the MLD films and carried out the in-situ FTIR analysis. The author wrote the first draft and finalize the paper with co-authors

III Comparison of the Growth and Thermal Properties of Nonwoven Polymers after Atomic Layer Deposition and Vapor Phase Infiltration

Laura Keskiväli, Pirjo Heikkilä, Eija Kenttä, Tommi Virtanen, Hille Rautkoski, Antti T. Pasanen, Mika Vähä-Nissi, Matti Putkonen *Coatings* 11 (2021) 1028

The author prepared the ALD coatings. The author wrote the first draft and finalized the paper with co-authors.

IV Atomic layer deposited TiO<sub>2</sub> on foam-formed fibres – Effect on hydrophobicity and physical properties

Laura Keskiväli, Tiinamari Seppänen, Paavo Porri, Elina Pääkkönen, Jukka Ketoja

*BioResources* 18 (2023) 7923-7942

The author planned the ALD coatings prepared by P. P.. The author wrote the first draft and finalized the paper with co-authors.

#### V The effect of Atomic Layer Deposited overcoat on Co-Pt-Si/γ-Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch catalyst

Niko Heikkinen, Laura Keskiväli, Patrik Eskelinen, Matti Reinikainen, Matti Putkonen

Catalysts 11 (2021) 672

The author planned the ALD and MLD coatings prepared by P. E.. The author contributed in her part in writing the paper (ALD and MLD sections) that was mostly written by N. H.

VI Effect of water on Co-Pt-Si/γ-Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch catalyst enhanced with Atomic Layer Deposited or Molecular Layer Deposition overcoating

Niko Heikkinen, Laura Keskiväli, Jasmiina Palo, Matti Reinikainen, Matti Putkonen

ACS Omega 7 (2022) 7725-7736

The author planned and prepared the ALD and MLD coatings. The author contributed in her part in writing the paper (ALD and MLD sections) that was mostly written by N. H.

Other related publications:

VII Modelling atomic layer deposition overcoating formation on a porous heterogeneous catalyst
 Niko Haikkingan, Juba Lahtangan, Laura Kaskiväli, Jihong Vim, Shuotha

Niko Heikkinen, Juha Lehtonen, Laura Keskiväli, Jihong Yim, Shwetha Shetty, Yanling Ge, Matti Reinikainen, Matti Putkonen *Physical Chemistry Chemical Physics* 24 (2022) 11

The publications are referred to in the text by their roman numerals.

### **1** Introduction

Porous materials are all around us and play important roles in our everyday lives. Porous materials are defined as materials containing voids or regions of empty space between solid or liquid materials, into which quest molecules can be selectively adsorbed. These characteristics have made porous materials useful in many applications, such as separation membranes, textiles with added functionalities, batteries, fuel cells, solar cells and other energy storages and power generation materials, and heterogeneous catalysts. Porous materials can be classified to inorganic, organic and inorganic-organic hybrid materials, and they can be for example crystalline solids (zeolites, catalyst powders, MOFs (metal organic frameworks)), synthetic polymeric fibres, and natural fibres or clays (Figure 1). From the beginning of research and development of porous materials, researchers have been interested in the modification of their structure and characteristics and adding additional functionalities to enable all the multiple applications.

Thin films are nanoscale materials formed of one or several ultrathin layers. They are essential part of the materials science research area. There are multiple methods for producing thin films. They can be produced with chemical methods from liquid phase such as sol-gel, spin coating, plating or from gas phase with chemical vapor deposition (CVD) or atomic layer deposition (ALD), or with physical vapor-based methods, such as physical vapor deposition (PVD), sputtering and evaporation. Thin films can be utilized for example as protective or functional coatings, antifouling materials, and tunable biomaterials. The list of potential applications for thin film materials is almost endless, varying from microelectronics, semiconductors and displays to catalysts, biocompatible implants, and medicine. Current developments in materials science and in thin films are focused for example on quantum technologies and different hybrid materials (inorganic-organic), aiming at modifying physical and chemical characteristics of components utilized in modern science and technology.



Figure 1 Classification of porous materials (inorganic, chemistry organic, inorganic-organic) and the evolution of atomic arrangement in porous materials science. COFs: covalent organic frameworks, POCs: particulate organic carbons, PCPs: coordination polymers, MOPs: metal-organic polyhedra. Copyright (2021), Springer Nature. Ltd https://doi.org/10.1038/s41563-021-00957-w.

One of the most accurate thin film deposition technique, ALD, is a surfacecontrolled layer-by-layer process based on sequential, saturative gas-solid surface reactions between volatile precursors and a surface of a solid substrate. As a result, pinhole-free uniform films are produced with self-limiting reactions. The greatest advantages in ALD are the purity and uniformity of the films, even when deposited on complex 3D structures and porous materials. As a subtype of CVD, ALD is a deposition method where the gaseous precursors react on the substrate surface to produce a solid film. However, in the case of ALD the precursors are introduced on the surface in turns with purge steps in between, inhibiting excess gaseous reactions between the precursors and ideally enabling the deposition of one atomic layer at the time, and finally a uniform and pinhole-free film. Furthermore, especially in the case of molecular layer deposition (MLD), significantly lower deposition temperatures compared to CVD technique enable the manufacturing of more complex and variable materials in both the coating and substrate wise.

Traditionally, ALD is about inorganic films deposited on inorganic substrates, such as silicon wafer or glass. In the most typical ALD process, Al<sub>2</sub>O<sub>3</sub> is produced

from sequential pulses of trimethylaluminum (TMA) and H<sub>2</sub>O. This is a well-known process, which can be performed even at room temperature allowing the use of temperature sensitive substrates. Alternatively, as a variation of ALD, in MLD, organic or hybrid inorganic-organic materials are produced by one molecular layer at a time. The first polymer films, polyimides, deposited by the MLD technique were presented in the beginning of the 1990s, and since then MLD processes for a vast number of different coating materials, including polymers such as polyimides, polyamides, and polyureas, as well as hybrid materials and structures such as metalcones, and barrier layers have been presented. A growing interest towards organic and hybrid inorganic–organic nanomaterials has accelerated the development of various thin film materials produced by MLD techniques.

The goal of this thesis was biseptate. Firstly, deposition of ALD and MLD materials on different porous substrates and further development of inorganicorganic hybrid materials was of interest. The porous substrates in these materials were nonwoven electrospun polymeric fabrics, cellulose-based foam-formed fibres and ceramic powder catalyst supports. Secondly, the focus was on fundamental research on the growth and structure of novel molecular layer deposited films. More specifically, the aim was to study the structure and reactions during the growth of MLD films deposited with monofunctional aromatic structures containing fluorine functionalities.

Traditionally, fluorine doping in inorganic ceramic materials has been used for improvement of structural, optical and electronic properties.<sup>1–3</sup> For example in transparent conductive oxides (ZnO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, CdO, etc.), fluorine is used as a dopant for improving electronic properties by replacing O<sup>2-</sup> ions and supplying free electrons for the n-type conduction of metal oxide:F thin films.<sup>4</sup> In organic and hybrid materials, the usage of fluorine dopants is increasing for example in electronics as well, such as semi-conductors and transistors.<sup>5,6</sup> All in all, novel organic and hybrid materials are constantly needed for new types of solutions and breakthroughs.

Different kinds of hybrid materials, such as ALD coated electrospun polymeric fibres and foam-formed fibres, are of interest due to the modified properties of the fibres or so-called composites. Many of this kind of hybrid materials have been studied during the resent years.<sup>7–9</sup> However, since the synthesis route of the polymer and ALD deposited material is different in every combination, the outcome for resulting materials and properties is hard to predict. For this reason, the knowledge base remains limited and further effort to study these materials for novel applications is needed.

ALD has been exploited in catalyst production and research already since the late 80's, when Tuomo Suntola and Suvi Haukka started the development work on heterogeneous catalysts in Microchemistry Ltd.<sup>10</sup> Since that, ALD has been used for active metal deposition, catalyst support modification and for different kinds of

overcoatings, where the ALD/MLD coating serves as a protective coating against sintering, leaching and poisoning.<sup>11–16</sup> Normally, ALD catalysts are used merely in gas phase reactions, since the durability of the overcoating and active metal particles can be ensured better. However, in the Fischer-Tropsch synthesis reaction, synthesis gas (CO and H<sub>2</sub>) is converted to hydrocarbons (CnH<sub>2n+2</sub>), *i.e.* chemicals and fuels in a reaction where water is a side product. Being involved in the reaction, water adds its own challenges for the catalysts and overcoatings, bringing at the same time an apparent need for the modification of the catalyst surface to maintain its activity and selectivity against sintering, coking and leaching. By today, ALD and MLD has been exploited in FT synthesis fairly rarely, and mainly for depositing the active metal, cobalt, instead of the overcoating.<sup>17,18</sup> In this thesis, studies on ALD and MLD overcoated Co-Pt-Si/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts are described.

This thesis is constructed in the following manner. Chapter 2 elaborates the background of porous materials, theory of ALD and MLD in general and theory of ALD/MLD studied in this thesis. In Chapter 3, the practical experiments and techniques carried out and utilized in this thesis are described, and Chapter 4 summarizes the main results achieved in the three different "work packages" (ALD on porous nonwovens, ALD/MLD on porous FT catalysts, and novel MLD on silicon wafers) and contains the discussion. Finally, in Chapter 5, conclusions and outlook into the future are given. For clarification, the background and experimental part of this thesis are presented in a flow chart, Figure 2.



**Figure 2** Background and research of this thesis in a flow chart. Everything takes the positions under the porous materials. ALD and MLD are chosen as the methods for modification of surface properties and are exploited on electrospun and foam-formed non-woven fibres and Fischer-Tropsch catalysts. Furthermore, vapor phase infiltration was carried out with electrospun fibres. Finally, novel MLD processes were developed, and these could potentially be used for modifying surface properties as well, as pointed out finally in the outlook.

### 2 Background

#### 2.1 Porous materials

Synthetic porous materials have history from the early 1900s, when activated charcoal and aluminosilicates and other zeolites were developed. After that various hybrid materials, organometallic polymers and extended networks were invented in the 1950s, and gradually MOFs (metal-organic frameworks), PCPs (porous coordination polymers) in the 1990s and others followed. Porous materials can be also liquids and glasses. Porous liquids possess both porosity and fluidity. First porous liquids were developed in 2015.<sup>19</sup> Generally, the pores of porous materials are classified into three categories: micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm) (Figure 3). The most advantageous and obvious aspect of porous materials is the large surface area, which can be even over 7000 m2/g (MOFs).<sup>20</sup>



**Figure 3** A visual representation of different pore sizes defined by IUPAC. The pores are arranged within a particle and macropores formed between particles known as interparticle pores. Reprinted from https://wiki.anton-paar.com/my-en/pore-size-measurement/##data-imagegroup-39109-1 at 25.7.2023.

Since the early development phase of porous materials, the work has been concentrating on the rational design of the crystalline solid state, enabled largely by the X-ray diffraction analysis. Over time, it has become clear that the presence of defects could provide additional characteristics and functionalities to these porous structures.<sup>19</sup> Controlled introduction of elements and structures to crystalline materials is in a key role of controlling the properties of the materials, for example in catalytic applications, biomedicine, and in adsorption and separation techniques. Despite the long history of research on porous materials, these aspects continue to be an intense area of scientific research.

There are multiple different methods to modify porous materials and substrates. Impregnation, sol-gel-process (with aqueous or organic solvent media), spincoating and plating as wet chemical methods and chemical and physical vapor depositions (thermal and plasma CVD, PVD, sputtering, evaporation) as gas phase methods are well known techniques to add for example metal oxide nanoparticles and coatings on ceramic porous substrates, such as catalyst powders and other structures. Then again, acid oxidation, alkali treatment and esterification can be used for modifying the properties of fibrous porous materials. However, all these methods are lacking the precise controllability and conformality brought by atomic layer deposition. Furthermore, most of these frequently used techniques are wet chemistry modifications having drawbacks including solvent exchange processes and the need of complex disposal of large amounts of waste solvents. For these reasons, ALD is the weapon of choice when wanting to alter the properties of porous materials efficiently, precisely, and environmentally friendly way.

### 2.2 Atomic layer deposition (ALD)

ALD is a coating method where self-limiting film growth takes place via alternate saturative surface reactions of alternately supplied gaseous precursors. Ideally, ALD produces conformal and pinhole-free coating with a thickness that can be selected with the accuracy of one atomic or molecular layer. The process is typically carried out in a heated reactor and in low pressure.

ALD is a modification of the CVD technique. The difference between these two techniques is in the reaction site, since in traditional CVD, the precursors meet each other already in the vapor phase in the reaction chamber since they are led to the chamber at the same time. In contrast, in ALD, the precursors are pulsed sequentially to the chamber, reactions happen on the substrate surface only, after which the chamber is purged and only after then the next precursor is pulsed to the chamber. In this way, no gas phase reactions are taking place. Reactive chemicals, i.e., precursors can be in gaseous, liquid, or solid phase at room temperature. The vacuum system enables evaporation of solid and liquid precursors and transportation of the precursors to the reaction chamber via lines. Normally, heating and carrier gas (argon, nitrogen) is used for the transportation to enhance the process and to prevent the condensation of the precursors to the lines and valves. Schematic pictures of ALD tools for flat substrates are presented in Figure 4. ALD tools for porous substrates, such as ceramic powders, are presented in Figure 5. In the fixed-bed reactor the particles rest on a fixed bed, without any agitation (Figure 5, a). In the fluidized bed reactor, the porous particles are mechanically agitated, for example with gas feed, which is directed vertically from the bottom to the top (Figure 5, b), vibrating ultrasound or with a rotating mixer. In the fluidized bed reactor, the obvious advantages are particle separation, good mixing of the particles, and heat transfer resulting in conformal coating of high surface area particles.



Figure 4 Examples of ALD reactors for flat substrates. A: Crossflow reactor, B: Perpendicular-flow reactor, shower head, C: Roll-to-roll reactor



Figure 5 Examples of ALD reactors for porous powder substrates. A: Fixed-bed reactor. Reproduced from Topics in Catalysis, vol. 7-11, page 612, P. Voigt et al.<sup>21</sup> "Nickel Supported on Mesoporous Zirconium Oxide by Atomic Layer Deposition", Copyright (2019), Springer. https://doi.org/10.1007/s11244-019-01133-w. B: Fluidized bed reactor, preproduced from Inorganics, vol. 6, page 9, T. Onn et al.<sup>22</sup> "Atomic Layer Deposition on Porous Materials: Problems with Conventional Approaches to Catalyst and Fuel Cell Electrode Preparation", Copyright (2018), MDPI. https://doi.org/10.3390/inorganics6010034. Schematics of one ALD cycle of the most studied ALD process, trimethylaluminum (TMA) and water, is presented in Figure 6. The first step illustrates the TMA precursor dose and the ligand protonation reactions between -  $CH_3$  functionalities of TMA and surface OH groups. In the second step, the film growth is self-terminated and the excess reactants and formed byproduct,  $CH_4$ , are purged away. In the third step, oxygen precursor ( $H_2O$ ) is introduced and finally the excess water and  $CH_4$  are purged away in the step 4. Ideally, there should always be reactive sites on the substrate surface for the precursors to react with, but if this is not the case, the growth of the first ALD layers can happen via chemisorption reactions. Furthermore, two-dimensional layer-by-layer growth and formation of a complete monolayer and uniform atomic layers during the first reaction cycles is not always the typical type of the growth. More probably, there is first island growth, and the film becomes more regular and uniform after several reaction cycles.<sup>23,24</sup>



Figure 6 One ALD cycle of the TMA and H2O process. Copyright (2019), preproduced from Applied Physics Reviews, vol. 6, page 021302-2, V. Cremers et al.<sup>25</sup> "Conformality in atomic layer deposition: Current status overview of analysis and modelling", Copyright (2019), AIP Publishing. https://doi.org/10.1063/1.5060967.

The greatest advantages of ALD are excellent conformality, accurate film thickness and composition control, reproducibility, and large area uniformity. Coatings with accurate thickness are relatively easy to produce on uniform and smooth surfaces, but the greatness in ALD relies in its capability to produce coatings with accurate film thickness on nonplanar and patterned substrates as well. A good example about this was published by Ritala et al. (1999) (Figure 7).<sup>26</sup>



Figure 7 Cross-sectional SEM image of a 300 nm Al2O3 film deposited on patterned silicon substrate. Reprinted from Chemical Vapor Deposition, vol. 5, page 8, M. Ritala et al.<sup>26</sup>
 "Perfectly Conformal TiN and Al2O3 Films Deposited by Atomic Layer Deposition", Copyright (1999), WILEY-VCH Verlag GmbH, D-69469 Weinheim. https://doi.org/10.1002/(SICI)1521-3862(199901)5:1<7::AID-CVDE7>3.0.CO;2-J.

One of the most important factors on the ALD growth is the deposition temperature. The temperature range where the growth is ideal, self-limiting, and saturated surface reactions occur, is often called ALD window. If the deposition temperature is out of this window, the growth is often disordered and cannot be called ALD type of growth. Out of the window physical condensation or adsorption, precursor decomposition and desorption are taking place (Figure 8). The ALD window is specific for each individual process and is dependent on the precursors and reaction chemistry.



**Figure 8** The possible temperature dependency of an ALD growth process. a1) Physical condensation or adsorption, a2) Temperature limits reactions, b1) constant, temperature independent growth rate of the material as a function of temperature (ALD window), b2) self-limiting growth with temperature dependent rate, c1) Precursor decomposition, c2) Precursor desorption.

### 2.3 Molecular layer deposition (MLD)

As mentioned already in the Introduction, MLD is sort of an ALD method, where organic or hybrid-inorganic-organic materials are produced from organic and inorganic precursors. Typically, organometallic precursors (TMA, DEZ,  $TiCl_4$ ) are combined with organic precursors producing so called metalcones, such as, alucone (TMA+EG (ethylene glycol)). In the case of MLD, temperature plays even more critical role than with the purely inorganic ALD materials. MLD produces organic or hybrid inorganic-organic materials, and properties of thermally restricted organic precursors and substrates need to be taken into a consideration. Selection of organic precursors is not endless either since sufficient vapor pressure needs to be achieved without excessive heating and risk of thermal degradation. In addition, in MLD, precursor pulses are typically longer (precursors can be "stickier" than organometallics) for achieving the saturation of the reactions on the surface. Besides the deposition temperature and pulse lengths, other factors affecting the film growth are pressure in the reaction chamber (affects the reaction chemistry), purging times (enough time for the excess precursors to be purged out) and the number of cycles. If the growth is linear as a function of the number of cycles, it is more likely ALD type of growth, and no condensation or CVD growth is taking place.

#### 2.4 ALD and MLD on porous substrate materials

The concept of porous substrate materials in ALD and MLD research is wide. When discussing the ALD and MLD on porous substrate structures and materials, it brings clarity to define the type of the porosity. Porous substrates can be, for example, mesoporous ceramic thin films, opal structures, metal organic frameworks (MOFs), porous powders with multiple different sizes and structures of pores, or porous polymer films and fibres, natural and synthetic ones. For example, in the recent decades, different battery and power generation materials, such as Li-ion batteries and solid oxide fuel cells (SOFC), have been of high interest in the area of ALD research, as an illustration of porous substrate materials. In these applications ALD has been utilized for example for surface passivation, diffusion barriers and corrosion protection. In fuel cells ALD research has been proceeding in alcohol conversion and hydrogen production. Due to the wide concept of porous substrates, in this thesis the topic was narrowed down to the selected two porous materials: nonwoven polymeric fibres and ceramic catalyst powders. Section 2.4 is concentrated on these topics.

In ALD research, the conformality is often mentioned as in the central motivation of the study. In the introduction part of papers and presentations, conformality is almost always mentioned in the same package with pinhole-free structures, self-limitation, and possibility to prepare a coating with one atomic layer

at a time. However, especially with challenging porous substrate materials with varying pore types and sizes, the verification of the conformality is often highly demanding. To advance the conformality analysis, lateral high aspect ratio (LHAR) test structures have been developed.<sup>27</sup> They allow investigation of thin film thickness and properties in highly demanding aspect ratios (>10 000:1) and obtain accurate information of film thickness and properties.<sup>25,27–31</sup>

Similar to the conformality, also conformal and pinhole-free structures are extremely challenging to create with only a few ALD cycles on porous substrate materials. The most important factor in this is the amount of reactive surface functionalities on the substrate surface. For example, some polymer materials may have a low density of reactive surface sites resulting in an island-like growth instead of a conformal pinhole-free coating growing on a substrate with high density of reactive surface sites.<sup>32–34</sup>

In addition to the conformality aspects, different reaction chemistries and kinetics are important factors affecting the ALD growth and structure of the deposited materials. It has been studied, for example by Gregory et al., that the process kinetics in capillary structures with metal alkyl (TMA, DEZ) precursors is diffusion-limited and with metal halides (TiCl<sub>4</sub>) the kinetics is reaction-limited.<sup>35</sup> With the diffusion limited precursors the reactions are faster, and they react more easily on the pore walls. These reactions consume the precursors before they can diffuse further inside the pores. In contrast, reaction limited precursors have lower likelihood of reaction with the pore walls, leading to multiple adsorption and desorption events on the walls instead of reactions. This often leads to more conformal coatings in the capillary type of pores with reaction limited precursor since the coating grows deeper in the pore already during the first cycles (Figure 9). However, finally the diffusion limited process results in uniform coating as well.



Figure 9 Schematic illustration of the theory of diffusion-limited transport and reaction-limited transport of gaseous precursors in high-aspect-ratio capillaries. Reprinted from Langmuir, vol. 36, page 1638, S. Gregory et al. <sup>35</sup> "Single-Cycle Atomic Layer Deposition on Bulk Wood Lumber for Managing Moisture Content, Mold Growth, and Thermal Conductivity" Copyright (2020), American Chemical Society. https://dx.doi.org/10.1021/acs.langmuir.9b03273.

Due to the widely varying porous substrate surfaces and the challenges of getting conformal and pinhole-free ALD/MLD coatings produced, if desired, modeling is almost an inescapable part of modern ALD/MLD research. Various ALD processes on porous materials have been modeled extensively.<sup>36–40</sup> There are modeling studies about ALD on porous ceramic structures, such as those in microelectronics and batteries<sup>41</sup>, about ALD/MLD on porous natural polymers and fibres39, and furthermore, about ALD/MLD on porous powders, utilized for example in catalysts.<sup>42,43</sup> Important questions are what kind of a ALD/MLD process is used, what is the reaction chemistry between the precursors and reactive surface sites, and is the process diffusion-limited or reaction-limited. Cremers et al. have done extensive work studying and reviewing approaches to the modeling of ALD on porous nanostructures.<sup>25</sup> These include ballistic, Monte-Carlo, continuum, analytical and semi analytical models. The work is a continuation for the studies of Yanguas-Gil et al.<sup>36,37</sup> However, concentrating more on the aspects of modeling of ALD processes on porous substrates is out of the scope of this research, where we want to focus more on the process development, properties of the prepared inorganic-organic hybrid materials and utilization of these materials. In this research, Al<sub>2</sub>O<sub>3</sub> and ZnO ALD on porous electrospun fibres, TiO<sub>2</sub> ALD on porous foam-formed cellulose fibres, and Al<sub>2</sub>O<sub>3</sub> ALD and alucone (TMA+EG) MLD on porous supported catalysts are studied. Therefore, the theory of ALD on polymers and fibres and ALD/MLD on porous catalysts is discussed in the next sections.

#### 2.4.1 ALD on polymers and fibres

The high porosity of polymeric fibres and fibrous materials is a useful property for new applications in many areas, such as catalytic supports, pharmaceutical and chemical manufacturing, membranes, sensor techniques and materials, packaging materials, printed electronic textiles with added functionalities and others. When using these materials as substrates for ALD treatment, it is important to define the need for modification of the surface of the material. Is the aim to change the hydrophobicity or barrier properties, is there a need to bring protection against heat or UV-light? Maybe there is a need to change electrical properties, such as conductivity, or maybe the purpose is to bring catalytic properties or biocompatibility to the material. Whatever the need, these wanted properties and added functionalities determines the characteristics of the ALD coating and deposition conditions.

ALD coated electrospun nonwoven polymers as hybrid materials are of interest due to the novel properties of the coated composites. However, the fabrication of these materials differs greatly from the ALD on ceramic substrates. ALD on polymers is a thermally restricted process due to the low glass transition and melting temperatures of the organic polymeric materials. The growth is often non-linear, especially at the beginning of the deposition process, when the precursors of the first cycles adsorb on to the surface and between the polymer particles or fibres.<sup>44–46</sup> Wilson et al. present in their study how TMA and H<sub>2</sub>O precursors are first trapped in the near surface region, after which the coalescence of  $Al_2O_3$  clusters happen, closing the space between polymer chains. Finally, the formation of a dense  $Al_2O_3$  film on the polymer surface happens (Figure 10).<sup>44</sup> The cluster formation and the island type growth has been noted in other studies as well.<sup>47–52</sup> In addition, structures of the coatings depend strongly on the polymer composition.<sup>46,53–55</sup> Furthermore, surface roughness, nucleation effects and unreactive adsorption sites can cause abrupt changes in the surface energy of the base material during the first deposition cycles.<sup>56,57</sup> In addition, reaction temperature, extent of precursor exposure and specific chemical interactions between the precursors and surface functionalities affect the extent of subsurface diffusion and deposition on porous polymers and fibres.<sup>45,46,58</sup>



**Figure 10** a) Cross section of a polymer film represented by loosely packed circles, b) Al2O3 nucleation clusters forming from H2O reaction with TMA trapped in the near surface region, c) coalescence of Al2O3 clusters and closure of space between polymer chains, and d) formation of a dense Al2O3 film that grows on top of the polymer surface. Reprinted from Chemistry of Materials, vol. 17, page 5634, C.A. Wilson et al. <sup>44</sup> "Nucleation and Growth during Al2O3 Atomic Layer Deposition on Polymers" Copyright (2005), American Chemical Society. https://doi.org/10.1021/cm050704d.

The most studied ALD process (TMA+H<sub>2</sub>O) is also the best option for thermal ALD on polymeric materials. This Al<sub>2</sub>O<sub>3</sub> process can operate even at 33 °C, with certain limitations, such as long purging times. Both half reactions in the TMA+H<sub>2</sub>O process are exothermic enabling low-temperature processing conditions. Nucleation and growth of Al<sub>2</sub>O<sub>3</sub> on various polymers have been studied widely.<sup>45,46,57–61</sup> For example, the Al<sub>2</sub>O<sub>3</sub> process has been studied on polystyrene (PS), polypropylene (PP), poly(methyl methacrylate) (PMMA), polyethylene (PE), and poly(vinyl chloride) (PVC). <sup>44</sup> Similarly, the growth of ZnO ALD coating on PP, PMMA, PC, PET and P<sub>3</sub>HT have been studied by several groups.<sup>50,62–70</sup> However, the main focus in these previous studies was on polymeric film substrates instead of non-woven fibres.

As with other substrate materials, also with fibres the limiting factor for a functioning ALD process is the reactive surface groups on the fibre surfaces. Typically, in the case of fibres, such as cellulose and other natural fibres, there is an extensive density of reactive Lewis basic sites, hydroxyl groups, on the fibre surface. These sites allow ALD reactions to begin efficiently, especially if Lewis acidic reactants (TMA, TiCl<sub>4</sub>) are used.<sup>71</sup> In addition to the reactive surface sites, temperature often plays a crucial role when coating polymer fibres with ALD. Depending on the temperature and density of surface functionalities, diffusion of the ALD precursors can happen on the fibre surface or into the sub-surface or bulk of the polymer. High density of reactive surface sites normally leads to efficient nucleation and formation of a dense coating on the fibre surface, but with lower density of surface reactants and at higher temperature, diffusion into the bulk of the polymer can happen causing nucleation in the subsurface region and swelling and roughening of the fibre structure. Finally, conformal and uniform coating is formed if the ALD process is continued.44-46,71

The self-limiting nature of ALD surface reactions can enable conformal coatings of polymer fibres, despite of the porous and nonplanar structures. However, specific attention is needed for sufficient precursor dosages and purging times so that, firstly, the whole large porous surface area is saturated and, secondly, the excess precursor molecules are desorbed and diffused out from the pore structures avoiding nonuniform CVD type of grow. In many cases, for example with nonwovens, the mean free path of gaseous precursors within the fibres can be close to or smaller from the fibre-fibre distance, leading to the Knudsen flow conditions.<sup>71</sup> In the Knudsen flow, molecules and other precursors are instantaneously adsorbed on and re-emitted from the pore walls. Thus, the Knudsen flow becomes dominant in small pores at low pressures, while in larger pores and at higher pressures diffusion occurs mainly by the viscous flow mechanism.<sup>72</sup>

Several groups have studied ALD and MLD processes on electrospun fibres to learn about the conformality of the coatings regarding to porosity, effect of temperature and other process conditions and reactions between ALD precursors and polymeric fibre materials. Musschoot et al. studied the saturation and conformality of ALD coatings on nonwoven fibres with SEM and EDX. The coverage of the ALD film on the nonwoven fibres as a function of depth in the test structure was determined. They saw that a longer precursor exposure time results in deposition deeper inside the nonwovens.<sup>73</sup> Peng et al. studied the growth of ALD Al<sub>2</sub>O<sub>3</sub> on electrospun PVA (poly(vinyl)alcohol) and silicon wafers, and found out that with sufficient reactant supply and purging times the ALD process yields uniform coverage with adjustable thickness over a relatively large area of the PVA surface despite the apparent topological complexity.<sup>7</sup> Oldham et al. explored ALD and MLD on electrospun nylon nanofibres and discovered different reactions with the polymer surface depending on the coating material. They found out that the fibres can be protected with conformal inorganic or inorganic-organic hybrid ALD/MLD coatings with stable physical properties under various chemical exposures.  $^{74}$ 

#### 2.4.1.1 Vapor phase Infiltration

As described previously, depending on the reactive surface sites on the fibres, ALD precursors can adsorb and nucleate on the surface of the polymeric fibre structure (high density of reactive surface sites) or absorb into the subsurface of the structure. Precursor absorption, diffusion and nucleation into the fibre substrates can be forced up to the certain point when performing "vapor-phase infiltration" (VPI). Thus, VPI does not follow the same self-limiting surface reaction rules as in ALD, but rather rely on diffusion of the precursors into subsurface area.<sup>75</sup> VPI is often more beneficial compared to the conventional layer deposition ALD, for example if improvement of mechanical strength is desired.<sup>50,75,76</sup> Then again, if the aim is to improve barrier properties of fibrous materials, often layer deposition on and among the fibres is sufficient enough.

#### 2.4.1.2 ALD on cellulosic based fibres - barrier and wettability properties

ALD and MLD are excellent tools for modifying properties and adding functionalities to natural polymer fibres. For example, ALD has been studied widely for modifying wetting and barrier properties of cellulose fibres, which have very high density of reactive hydroxyl groups on the surface.<sup>35,57,75,77–81</sup>

ALD coatings have excellent barrier properties.<sup>82,83</sup> By far the most studied ALD coating for barrier layers is aluminum oxide. With 10-50 nm thick ALD-grown  $Al_2O_3$  coating the oxygen and water vapor barrier properties of biopolymeric materials could be significantly improved.<sup>52,83,84</sup> When doing this with ALD coating instead of a conventional aluminum film, the inorganic-organic hybrid material achieves barrier property and maintains total biodegradability, due to the thinness of the  $Al_2O_3$  layer.<sup>84</sup>

In addition to the barrier properties, it is noted in several publications that often just a few deposition cycles are enough to adjust the hydrophobic/hydrophilic nature of porous fibrous surfaces.<sup>35,57,58,78–81</sup> This result is explained by adventitious carbon adsorption. It is likely that with a few cycles of ALD material (for example  $Al_2O_3$ , ZnO, TiO<sub>2</sub>), the coating is not entirely continuous and there are more less polar Al-O-C bonds on the surface. This leads to adventitious carbon adsorption which makes the surface hydrophobic.<sup>46,58,78,80,85</sup> With thicker coatings, polar hydroxylated metal oxide structures become more dominant, and the surface returns hydrophilic again.

#### 2.4.2 ALD and MLD on catalysts

Catalysts are used to accelerate the rate of chemical reactions, for example in various industrial processes, such as fuel and chemical production and pharmaceuticals. The global catalyst market was valued at USD 33.9 billion in 2019 and is expected to grow at a compound annual growth rate (CAGR) of 4.4% from 2020 to 2027. (Grand view research, GVR). Heterogeneous catalysts are in different phase than the reactive components in question. They are favored in industry, mostly because of being easy to separate from the reaction products. However, compared to homogeneous catalysts the selectivity of heterogeneous catalysts is often poorer.

As well as fibres and other polymeric materials, also ceramic catalyst supports are often and ideally highly porous materials and the aforementioned principles of sufficient precursor supply and purge times are still valid, and often even more so. Diffusion into the interior parts of the porous ceramic supports is considered to be highly challenging due to both high equivalent aspect ratio and very large surface areas (up to 2500 m<sup>2</sup>/g).<sup>25,86,87</sup>

As mentioned in the Introduction, ALD has been used in catalyst applications already from the late 80's. It can be exploited in different ways: for depositing the active metal, support modification and for depositing protective overcoating on top of the catalyst surface and active metal (Figure 11). The advantages of ALD in depositing the active metal are often better distribution of the metal particles and smaller active metal particle size with narrow size distribution.<sup>88–91</sup> MLD can be used for preparing catalysts as well. The biggest differences between ALD and MLD in catalyst preparation are probably the challenges of using organic precursors. In MLD sizes of the organic precursors are often larger, which might be an issue with small pores. Furthermore, vapor pressures of the organic compounds are often lower and the precursors can be "stickier", hampering the diffusion event in the pore structures especially at low temperatures.<sup>92</sup>

The advantages of ALD overcoatings are in inhibition of sintering and leaching, reduction of fouling and selectivity enhancement. Overcoatings can be considered as conformal coatings on supported catalysts (with thicker layer thickness) or thinner coatings with island-like growth and nucleation. Various ALD overcoatings have been studied widely for different catalytic applications.<sup>51,93–96</sup> For example Lu et al. studied alumina overcoating on supported Pd nanoparticles against sintering and deactivation by coking. They discovered remarkably reduced coke formation and no sintering at 675 °C for 28 hours. Furthermore, the yield of reaction product, ethylene, was improved on the Al<sub>2</sub>O<sub>3</sub> overcoated Pd catalysts.<sup>97</sup> Lee et al. studied TiO<sub>2</sub> overcoating on cobalt particles with TiO<sub>2</sub> support for aqueous-phase hydrogenation reactions. They managed to prevent leaching and sintering of cobalt, and with "decorative" non-continuous overcoating the catalyst preserved its activity.<sup>51</sup>



Figure 11 ALD in catalysis. a) nanobowl synthesis; b) metal nanoparticles isolated in nanobowls; c) Partial coating of nanoparticles, d) complete overcoating, followed by heating to induce nanoscale porosity. Gray: support material, Black: metal nanoparticle, Red: ALD overcoat, Green: removable grafting or template molecule. Reproduced from ACS Catalysis, vol. 5, page 1818, B. O'Neill et al.<sup>98</sup> " Catalyst Design with Atomic Layer Deposition" Copyright (2015), American Chemical Society. https://pubs.acs.org/doi/pdf/10.1021/cs501862h.

Unlike ALD overcoatings, there are less examples about MLD overcoatings for catalysts. The advantage of MLD overcoatings against ALD overcoatings is the coating structure with larger pores, i.e. looser structure. A dense and pinhole-free ALD coating can more easily decrease the catalyst activity. Previous examples of MLD overcoatings are about stabilizing Pt nanoparticles for oxidation reaction of CO, and Ni for dry reforming of methane (DRM). <sup>93,99,100</sup> The most extensively examined MLD overcoating is made with the two step AB process, where A stands for ethylene glycol (EG) and B for TMA. The film deposition with this combination of organic and aluminium precursor is often called "alucone" and was originally developed through a sol-gel technique.<sup>101</sup>

For Fischer-Tropsch synthesis catalysts ALD has been used mainly for depositing the active metal, cobalt.<sup>17,18</sup> The results reveal that small cubic  $Co_3O_4$  nanoparticles are formed by the ALD method, while larger spherical ones are made with the impregnation method. Furthermore, the catalyst made with a few ALD cycles showed 38% higher conversion, 30% higher  $C_{5+}$  selectivity and 28% less methane selectivity compared to the impregnated catalyst.<sup>18</sup>

# 2.5 Monofunctional MLD precursors and ring-opening reactions: Novel MLD materials

The biggest drawbacks in MLD are the limited availability of organic bifunctional monomers and the problem of restricted deposition temperatures and low vapor pressure of the precursors. These obstacles can be tackled with monofunctional aromatic compounds. Monofunctional aromatics, such as phenol, have often higher vapor pressures than heavily substituted precursors. Of course, when using monofunctional aromatics, the molecule is not active after it has adsorbed and reacted with the surface during the first half cycle using its only functional group. However, cyclic monofunctional aromatics can be opened and thus activated for the next precursor pulse. This allows a continuous MLD process with consecutive cycles. One possible reagent for the ring-opening is ozone (O<sub>3</sub>). In traditional organic chemistry, ozone has been utilized in oxidative cleavage of double bonds in aromatic ring structures, resulting in a formation of carboxylic acid groups (Figure 12).<sup>102–104</sup> Previously, ozone has been used for functionalizing structures in MLD processes, where alkene terminal groups were converted to carboxylic acids in the process with 7-octenytrichlorosilane, TMA and O<sub>3</sub> as precursors.<sup>105–107</sup>



**Figure 12** Opening of an aromatic ring structure with ozone and formation of carboxylic acid structures. Reconstructed from Journal of Hazardous Materials, vol. 150, page 719, Y. Shen et al.<sup>103</sup> "Effect of various gases and chemical catalysts on phenol degradation pathways by pulsed electrical discharges" Copyright (2008), Elsevier B.V.. https://doi.org/10.1016/j.jhazmat.2007.05.024

#### 2.5.1 Fluorinated MLD materials

As mentioned in the Introduction, fluorine doping has been used for improvement of structural, optical, and electronic properties of inorganic ceramics.<sup>1–3</sup> Fluorine dopants are used in organic and hybrid-based electronics as well, and the need for new types of solutions is constant. Thin film fluoropolymers are produced typically by CVD.<sup>108–110</sup> These materials are typically used for example for membranes,<sup>111</sup> and hydrophobic biomaterials.<sup>112</sup> The advantage of using MLD instead of CVD is obviously the conformality, uniformity and more controlled film thickness. In addition, the amount of fluorine can be adjusted more precisely, since in CVD the precursors decompose more easily during the deposition process and numerous fluorine groups can be flocked on the same spot in the film. In addition to this research, Closser et al. have published about MLD of fluorinated materials,<sup>113</sup> but otherwise there is no prior literature on MLD of fluorinated materials.

## 3 Experimental

In this section, summary of experimental procedures is given. More detailed descriptions can be found from the original research articles (appendixes I-VI). All the experiments were carried out during the years 2016-2023. All MLD and the majority of the ALD experiments were done with the Picosun SUNALE R-200 ALD-reactor (Figure 13). ALD infiltrations were done in CIC nanoGUNE research centre with the Savannah S100 ALD reactor.



Figure 13 Picosun SUNALE R-200 ALD-reactor in semi-clean room environment. This reactor was used in majority of the experiments during the thesis.

### 3.1 Processes

In this chapter all the fibre manufacturing processes, including electrospinning and foam forming, ALD processes and MLD processes, used in this research are described. Furthermore, incipient wetness impregnation method for Fischer-Tropsch catalyst preparation is described.

#### 3.1.1 Processes of electrospinning and ALD coatings on electrospun polymeric fibres

#### Electrospinning process for non-woven polymer fibres

Electrospinning is a method for producing nonwoven polymeric fibre materials with electrohydrodynamic phenomena and voltage-driven technique. In the most basic set up, a needle tipped syringe is filled up with polymer solution and pointed towards a collector. A potential difference between the needle and the collector is produced with a high voltage power source and alligator clips (Figure 14). In this thesis, the studied polymers were cellulose acetate (CA), polyethersulphone (PES) and poly-L-lactic acid (PLLA). CA and PES were dissolved within a magnetic stirrer directly into solvent mixture (Table 1). PLLA was dissolved first into CHCl<sub>3</sub>, and DMF was added to this solution. Technical details of the electrospinning processes are described in Table 1. SEM (scanning electron microscope) images of the electrospun materials are in Figure 15.

# Table 1 Electrospinning solutions and spinning parameters for cellulose acetate (CA), poly-L-lactic acid (PLLA) and polyethersulphone (PES).

Polymer	Concentration	Solvent system	Needle	Voltage	Distance	Fiber Ø
CA	16 wt%	Ac and DMAc 2.5:1	18 G	28 kV	14 cm	(430 ± 350) nm
PLLA	4.8 wt%	CHCl3 and DMF 9:1	19 G	15 kV	7.5 cm	(540 ± 270) nm
PES	30 wt%	DMF and NMP 1:1	19 G	17 kV	10 cm	(400 ± 270) nm



**Figure 14** Electrospinning set-up at VTT facilities and schematic illustration of the electrospinning process. Jetting occurs from the Taylor cone. After a short stable stage, instabilities start to bend the jet, which eventually leads to 3D looping within the envelope cone. Secondary and tertiary looping can also occur before the jet reaches the collector. Schematic illustration on the right reproduced from Thesis of P. Heikkilä "Nanostructured Fibre Composites, and Materials for Air Filtration",(2008), ISBN 978-952-15-2023-5.<sup>114</sup>



Figure 15 SEM images of electrospun CA, PLLA and PES fibres. Reprinted from Coatings, vol 11, page 3, L. Keskiväli et al.: "Comparison of the Growth and Thermal Properties of Nonwoven Polymers after Atomic Layer Deposition and Vapor Phase Infiltration", Copyright (2021), reproduced with permission from MDPI. https://doi.org/10.3390/coatings11091028.

#### ALD processes

ALD coatings were performed in the single wafer mode, in the Picosun R-200 ALD reactor. Nitrogen (> 99.999%) was used as a carrier gas.  $Al_2O_3$  was produced using trimethyl aluminum (TMA, Al(Me)<sub>3</sub>, Sigma Aldrich) with water or ozone. TMA was stored in a metallic container and evaporated at room temperature. The precursor dose/purge times (s) were  $0.2(TMA)/15/0.2(H_2O)/15$  for TMA+H<sub>2</sub>O and  $0.2(TMA)/15/2.5(O_3)/15$  for TMA+O<sub>3</sub>. For ZnO ALD using DEZ+H<sub>2</sub>O, (Diethylzinc Strem Chemicals) the dose/purge times (s)  $(Zn(Et)_2,$ were  $0.3(DEZ)/10s/0.2(H_2O)/10s$  (DEZ+H<sub>2</sub>O). The cycle numbers varied to achieve target thicknesses, approximately 2, 5 and 30 nm. The GPCs for these thermal ALD processes at 80 °C were approximately 0.9 Å (Al<sub>2</sub>O<sub>3</sub>) and 0.8 Å (ZnO).

The infiltration modification of the samples was performed in nanoGUNE, San Sebastian, in the commercial ALD reactor (Savannah S100, Cambridge NanoTech Inc). The infiltration was carried out at 100 °C under a constant nitrogen gas flow of 20 standard cubic centimeters per minute (sccm). DEZ (Strem Chemicals) and TMA (Strem Chemicals) were used as the metal source and demineralized water as the oxygen source. The substrates were exposed to the precursors for defined periods of time before purging, thereby allowing diffusion of the precursors into the polymer. An infiltration cycle consisted of Pulse (DEZ, 0.08 s)/ Exposure (30 s)/ Purge (N<sub>2</sub>, 30 s).

#### 3.1.2 Processes of foam-formed cellulose and TiO2 ALD films of foam-formed fibres

#### Foam forming process for non-woven cellulose fibres

The cellulose-based substrate materials were prepared by the foam forming technique115 (Figure 16 and Figure 17). The target density and the thickness of the samples were 60 kg/m<sup>3</sup> and 20 mm. The pulp and the surfactant, Simu sol SL10 with a dosage of 1.2 g/l, were placed in a vessel and foam was generated using a

laboratory mixer (Netzsch, Hedensted, Denmark). The target pulp content before the foam generation was 2.5%. The foam generation time was 5-10 minutes, with a rotational speed of 3800-5400 rpm, depending on the fibre mixture. The air contents of the wet foams varied between 54 - 65%. The fibre foam was poured into a hand sheet mold and was left to drain for 20 min in ambient conditions, and then dried in an oven at 70 °C. The dried sheets were rewetted to reach a dry matter content of 50% and compressed between metal plates with spacers to reach the target thickness. The samples were dried again at 70 °C in the oven.



**Figure 16** Foam generation at different scales. Left: A laboratory vessel with bubble size imaging, where one disk with two opposing bends is used as the blade in a mixer. Right: On a larger pilot scale, foam generation can be done in a pulper. Reprinted from Journal of Dispersion Science and Technology, vol. 43, page 1471, T. Hjelt et al. <sup>115</sup> "Foam forming of fibre products: a review" Copyright (2022), Taylor and Francis Group, LLC. https://doi.org/10.1080/01932691.2020.1869035



**Figure 17** The procedure of making lightweight structures. Left: After dewatering, the wet sample is removed from the mold with the forming fabric, and the rest of the water is evaporated in an oven. This results in highly porous fibrous structure with a thickness of 10-100 mm. Density depends mainly on consistency and air content. Right: Dried sample made from chemithermomechanical (CTMP) and softwood kraft pulps. Reprinted from Journal of Dispersion Science and Technology, vol. 43, page 1474, T. Hjelt et al. <sup>115</sup> "Foam forming of fibre products: a review" Copyright (2022), Taylor and Francis Group, LLC. https://doi.org/10.1080/01932691.2020.1869035

#### ALD

ALD coatings were performed in the single wafer mode, in the Picosun R-200 ALD reactor.  $TiO_2$  was produced using  $TiCl_4$  (titanium tetrachloride, Strem Chemicals) with water.  $TiCl_4$  was stored in a metallic container and evaporated at room temperature. The precursor dose/purge times (s) were  $1(TiCl_4)/60/1(H_2O)/60$ . The cycle numbers were 5, 15 and 50. The GPCs for these thermal ALD processes at 150 °C were approximately 0.6 Å/cycle, in agreement with the literature.<sup>116–118</sup>

# 3.1.3 Deposition Processes of ALD and MLD top-coatings on Fischer-Tropsch catalysts (IWI Co-Pt/ $\gamma$ -Al2O3)

#### Incipient wetness impregnation

Co-Pt-Si/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by incipient wetness co-impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (Puralox SCCa 5-150 Brunsbüttel, Germany) using cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and platinum nitrate (Pt(NO<sub>3</sub>)<sub>2</sub>) solutions. Tetraethoxysilane (C<sub>8</sub>H<sub>20</sub>SiO<sub>4</sub>) was impregnated in a following separate step on Al<sub>2</sub>O<sub>3</sub> support. In the preparation process the support was weighted and dried at 150 °C for two hours while generating below 15 mbar vacuum inside the flask. Cobalt nitrate and platinum nitrate solutions were poured onto the dried support material and left overnight. The catalyst was dried in a rotary evaporator (80 °C, 60 min) and calcinated in a quartz tube under continuous air flow (250 °C, ramp 2 °C/min, 4 h). After the calcination, the catalyst was sieved, and a 50–150 µm particle size fraction was collected. The resulting catalyst had 21.4 wt % cobalt, 0.2 wt % platinum, and 1.6 wt % silicon.

#### ALD

ALD and MLD coatings were deposited in single wafer mode, in Picosun R-200 reactor. A Picosun POCA powder coating system with quartz sinter was used (Figure 18). Al<sub>2</sub>O<sub>3</sub> overcoatings (15, 25, 35 and 40 cycles) were deposited with TMA and H<sub>2</sub>O and AB hybrid alucone MLD films with ethylene glycol (EG) and TMA (10, 15 and 20 cycles). Deposition temperatures were 150 °C (ALD) and 90 °C (MLD).


Figure 18 Picosun's powder coating POCA system. From the left: empty sinter, sinter with dark grey catalyst powder and sinter and POCA collet in the ALD reactor.

#### 3.1.4 Deposition Processes of MLD films on silicon wafers

MLD films were deposited in a single wafer mode. Si(100) wafers (Siltronic Corp.) were used as substrates throughout this study. Three and four-step (ABC, ABCD) processes were constructed from TMA (99.999% SAFC) as a metal precursor, ozone (generated by IN USA, Inc.,  $O_3$  generator from 99.99%  $O_2$ ), hydrogen peroxide (50 wt % in water, Sigma-Aldrich), and aromatic precursors including phenol (>96% Sigma-Aldrich), 3-(trifluoromethyl)phenol (99% Sigma-Aldrich) (3F), and 2-fluoro-4-(trifluoromethyl)benzaldehyde (98% Sigma-Aldrich) (4F) (Figure 19). TMA was stored in a metallic container and evaporated at room temperature. Phenol and 3-(trifluoromethyl)phenol were evaporated at 80 °C and 2-fluoro-4-(trifluoromethyl)-benzaldehyde was evaporated at 60 °C. Deposition temperatures varied between 75 and 200 °C. The recipes of the three MLD processes are described in Table 2.



Figure 19 Aromatic MLD precursors used in this research. From left: phenol, 3-(trifluoromethyl)phenol and 2-fluoro-4-(trifluoromethyl)benzaldehyde.

Process	Pulse / Purge (s)
TMA + phenol + O <sub>3</sub>	0.2/10 + 0.2/10 + 2/10
TMA + phenol + $O_3$ + $H_2O_2$	0.2/10 + 0.2/10 + 2/10 + 0.2/10
TMA + 3F + O <sub>3</sub>	0.2/10 + 0.2/10 + 2/10
$TMA + 3F + O_3 + H_2O_2$	0.2/10 + 0.2/10 + 2/10 + 0.2/10
$TMA + 4F + O_3$	0.2/10 + 0.2/10 + 2/10
$TMA + 4F + O_3 + H_2O_2$	0.2/10 + 0.2/10 + 2/10 + 0.2/10

 Table 2 Novel MLD processes (length of the precursor pulses and purges) developed in this research.

### 3.2 Characterization methods

Characterization methods and the objectives for using each characterization or analysis method in this research are listed in Table 3.

Table 3 Characterization methods used for the prepared ALD/MLD inorganic-organic hybridmaterials. Methods are categorized in three different categories: 1) MLD films on Si wafers,2) ALD coatings on electrospun fibres and 3) ALD/MLD coatings on catalyst.

ALD/MLD Coating on Substrate material	Objective	Method
1) MLD on Si wafers		
	Film thickness	Ellipsometry
		Sentech SE400adv
	Hydrophobicity/wetting properties	Contact angle measurement
		KSV CAM200
	Thickness and density	XRR
		X'Pert PRO PANalytical
	Chemical structure, functionalities	ATR-FTIR
		Nicolet iS50 FTIR
	Elemental compositions	TOF-ERDA
		University of Jyväskylä
	Chemical reactions during MLD	in-situ FTIR
	deposition	Bruker Tensor 27, Ghent University
2) ALD on electrospun fibres		
	Chemical structure, functionalities	ATR-FTIR
		Nicolet iS50 FTIR

	Morphologies and microstructures	SEM
		ZEISS Merlin FE-SEM
	Morphologies and microstructures	STEM
		FEI Titan G2 60-300, CIC nanoGUNE
	Film composition, coordination of Al	Solid state <sup>27</sup> AI NMR
		Agilent DD2 600 NMR
	Tensile strength of the ALD treated	Tensile strength
	fibres	Bruker Universal Mechanical Tester, CIC nanoGUne
	Thermal degradation properties	TGA/DSC
		Netzsch STA 440 F1 thermal analyzer
	Moisture content of the ALD treated fibres	Water vapor analysis, scale
	Compression strength of the ALD	Compression strength
	treated fibres	Lloyd LR10K Universal tester
3) ALD/MLD on catalysts		
	Surface area, pore size, pore volume	N2 adsorption and desorption
	of the ALD/MLD treated catalysts	BET
		BJH
		Micrometrics 3Flex 3500

Several characterization methods were used for analyzing the growth and structure of the deposited materials. Thicknesses of all the deposited MLD films and reference ALD films in the case of porous fibrous and powder materials on Si wafers were measured by ex situ ellipsometry (Sentech SE400adv).

There were different challenges in the characterization, depending on the materials. The novel MLD materials deposited on Si wafers were the most straightforward to characterize, especially in the case of physical properties and the basic characteristics (thickness, density, elemental composition) of the films. However, reactions during the deposition process and the actual precise structures of the prepared film were more challenging to determine. In this regard, molecular modeling methods based on density functional theory (DFT) were used to investigate the formation of MLD layers. The calculations were performed with the CAmbridge Serial Total Energy Package (CASTEP)22 code implemented into Materials Studio version 8.0 (Dassault Systèmes).

In the case of different porous substrate materials, the challenges were obviously the ones mentioned in the section 2.4. With polymeric fibre materials restrictions with temperature and common fragility of the fibre substrates caused challenges for the selection of characterization methods as well. Visual appearance and morphology, chemical structure, and functionalities as well as physical properties were quite straightforward to measure comparing to the growth of the film into the pore structures and subsurface of the fibre substrates. This same challenge applied with the porous catalyst powder substrates as well. In addition, in the case of the catalyst materials, the most challenging aspect was the combination of alumina overcoating on alumina support. However, in addition to the characterization of the growth and structure, especially in the case of porous materials, fibres and FTcatalysts, the main emphasis was in the modified physical properties and the applications, and not so much in the fundamental research of ALD and MLD film growth processes.

# 3.3 Catalytic activity tests with ALD and MLD top-coated FT catalysts

Fischer-Tropsch synthesis experiments were performed in a tubular fixed-bed reactor system (Figure 20) at a temperature of 200 °C, pressure of 20 bar and  $H_2/CO$  ratio of 2.0. Detailed description can be found elsewhere.<sup>119</sup>

The ALD or MLD overcoated Co-Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (3 g) was loaded in the reactor (Hastelloy C, 9.1 mm i.d.). During the FT synthesis reaction, CO and H<sub>2</sub> were reacted to methane, other hydrocarbons, and water. The heavy hydrocarbon products were separated in a hot trap (100 °C, at reaction pressure), while water and light hydrocarbons were collected in a liquid-liquid gas separator at 10 °C, and gaseous compounds were analyzed with an on-line gas chromatograph. During the experiments, the enhancement of the activity and selectivity of the ALD/MLD-overcoated catalysts was studied. Furthermore, the protection against leaching was estimated.



**Figure 20** On the left: Tubular fixed-bed reactor system for Fischer-Tropsch synthesis reaction testing. On the right: Two reaction furnaces containing reaction tubes.

## **4** Results and Discussion

This chapter is based on the original publications, presented as references I-VI at the end of this thesis. Subchapters 4.1 - 4.2 summarize the results of the studied subject areas (4.1 ALD and MLD on porous materials, 4.1.1 ALD on electrospun fibres, 4.1.2 ALD on foam-formed fibres, 4.1.3 ALD and MLD overcoatings on Fischer-Tropsch synthesis, 4.2 Novel MLD materials from monofunctional aromatic precursors).

### 4.1 ALD and MLD on porous materials

In this section and in references III-VI, ALD and/or MLD is done on three different porous substrate materials: electrospun fibres (III), foam-formed fibres (IV) and ceramic powder catalysts (V-VI). In this research the aim was to study the deposition processes and film growth on porous nonwovens and powders, but even more the focus was on the changed physical properties of the produced inorganicorganic hybrid materials and their possible utilization in different applications.

#### 4.1.1 ALD and VPI on electrospun fibres

Aluminum oxide and zinc oxide were deposited on three different electrospun fibre sheets: polyethersulphone (PES), poly-L-lactic acid (PLLA) and cellulose acetate (CA). Material growth in both layer deposition ALD and VPI was studied and compared. Morphology of the prepared materials was analyzed by SEM and STEM, and a novel way to study the reactions and structure of the Al<sub>2</sub>O<sub>3</sub> on polymeric fibre by solid state NMR was developed. Finally, the thermal properties were studied by TGA/DSC.

#### Reactions and structure of the ALD coated electrospun fibres

Fibre surfaces after the  $Al_2O_3$  and ZnO depositions on the three different electrospun nonwovens were studied by the SEM and STEM techniques. Two processes for aluminum oxide were tested, TMA+H<sub>2</sub>O and TMA+O<sub>3</sub>. The difference between the growth of  $Al_2O_3$  and ZnO ALD coatings was clearly observed with all the polymer materials (PES, PLLA, CA). The growth of  $Al_2O_3$  was uniform and visually detectable on all polymer fibres, whereas the growth of ZnO was relatively poor on all types of fibres. ZnO coating was not visible in SEM images (Figure 21), and STEM imaging showed non-homogeneous and granular deposition instead of smooth coating (Figure 22). However, pulsing of couple of cycles of TMA+H<sub>2</sub>O on the fibres before the DEZ+H<sub>2</sub>O enhanced the growth of ZnO significantly on all types of fibres.



Figure 21 SEM micrographs of CA fibres (a) before ALD and, (b) with 2 nm Al2O3, (c) 30 nm Al2O3, (d) 2 nm ZnO, (e) 30 nm ZnO, and (f) 1 nm Al2O3 + 30 nm ZnO. Reprinted from Coatings, vol 11, page 5, L. Keskiväli et al.: "Comparison of the Growth and Thermal Properties of Nonwoven Polymers after Atomic Layer Deposition and Vapor Phase Infiltration", Copyright (2021), reproduced with permission from MDPI. https://doi.org/10.3390/coatings11091028



**Figure 22** STEM images of: CA fibres coated with (a)  $Al_2O_3$  and (b) ZnO, PES fibres coated with (c)  $Al_2O_3$  and (d) ZnO, and PLLA fibres coated with (e)  $Al_2O_3$  and (f) ZnO. The target thickness in all cases was 30 nm. Reprinted from Coatings, vol 11, page 7, L. Keskiväli et al.: "Comparison of the Growth and Thermal Properties of Nonwoven Polymers after Atomic Layer Deposition and Vapor Phase Infiltration", Copyright (2021), reproduced with permission from MDPI. https://doi.org/10.3390/coatings11091028

Samples were analyzed by ATR-FTIR to verify the presence of the coating material and discover the functionalities on the nonwoven fibre sheets as well as to reveal possible infiltration carried out by VPI. The results were quite parallel with all the polymer types and support the observations made with SEM and STEM. The Al<sub>2</sub>O<sub>3</sub> coating was detectable already with the smallest thickness (2 nm) on all CA, PLLA and PES. When ozone was used as the oxygen precursor, Al-formate and other carbon containing species (methoxy, carbonate) were detected. This is a common temperature dependent phenomenon when O<sub>3</sub> is used and can be prevented with processing temperatures of 380 °C or more.<sup>65,120</sup> In the case of ZnO, as mentioned with morphology studies, the detection was more challenging. ZnO depositions were detectable only with thicker 30 nm coatings on all three polymers. With that thickness the characteristic stretches and vibrations were detected with all three polymeric fibres.

In addition, according to ATR-FTIR spectroscopy of the infiltrated samples, the infiltration resulted in detectable interactions between some of the polymers and one of the ALD precursors or the complete processes. The ATR-FTIR results from vapor phase infiltration were similar to layer deposited samples. Infiltration was detectable with TMA precursor solely (when fibres were exposured only to TMA precursors) and also with  $Al_2O_3$  coating on CA fibres. With PLLA partial degradation occurred during the infiltration procedure, but infiltration during the TMA+H<sub>2</sub>O deposition was detectable. In the case of DEZ and ZnO on PLLA, clear infiltration was observed. In the case of PES, no clear evidence of infiltration of TMA,  $Al_2O_3$ , DEZ or ZnO could be detected. Based on these SEM/STEM and ATR-FTIR characterization results, the best combination for ALD treated electrospun hybrid material was  $Al_2O_3$  on CA, and it was selected for further studies with <sup>27</sup>Al Solid state NMR to clarify more thoroughly the structure of the material and coordination of Al, and with TGA/DSC for revealing the modified thermal properties.

The solid state  ${}^{27}$ Al NMR spectra revealed a difference in the growth mechanism of the Al<sub>2</sub>O<sub>3</sub>. In the analysis 4-, 5- and 6-coordinated aluminum structures were compared between the ALD and VPI prepared samples. In the infiltrated samples the concentration of five-coordinated aluminum was higher than in the corresponding conventional ALD samples (Figure 23). Based on the differences between layer deposition and vapor phase infiltration processes (longer pulsing times leading to larger dosages), it can be speculated that the higher amount of 5-coordinate aluminum can be attributed to the interactions between the deposited layers and the first infiltrated Al<sub>2</sub>O<sub>3</sub>.



**Figure 23** <sup>27</sup>Al NMR spectra of (a) Al<sub>2</sub>O<sub>3</sub>, deposited on CA and (b) Al<sub>2</sub>O<sub>3</sub> infiltrated into CA. Reprinted from Coatings, vol 11, page 13, L. Keskiväli et al.: "Comparison of the Growth and Thermal Properties of Nonwoven Polymers after Atomic Layer Deposition and Vapor Phase Infiltration", Copyright (2021), reproduced with permission from MDPI. https://doi.org/10.3390/coatings11091028

#### Thermal behavior

Thermal behavior was studied with TG and DSC analysis. Thermal degradation of  $Al_2O_3$  treated CA fibres occurred in the temperature range of 30-400 °C. The analysis showed the effect of both ALD and VPI on the polymeric fibres, since the curves differed from the TG curve of the untreated CA fibre. It seems that the layer deposited aluminum oxide protects the fibres better from the thermal degradation than the infiltrated  $Al_2O_3$ , since the degradation starts earlier with the infiltrated fibre. In addition, an extended exposure times to ALD precursors appear to degrade the CA fibres, as discussed already earlier. This phenomenon was observed in DSC curves as well, since the greater the amount of aluminum oxide, the lower the temperature of the endothermal peak (Figure 24). With this in mind, it appears that a small amount of ALD material protects the fibres, but a thicker coating has already an opposite effect.



Figure 24 TGA and DSC curves of CA fibres with  $Al_2O_3$  of variable amounts infiltrated into them. Reprinted from Coatings, vol 11, page 16, L. Keskiväli et al.: "Comparison of the Growth and Thermal Properties of Nonwoven Polymers after Atomic Layer Deposition and Vapor Phase Infiltration", Copyright (2021), reproduced with permission from MDPI. https://doi.org/10.3390/coatings11091028

Novel insights of traditional layer deposition by ALD and vapor phase infiltration on electrospun polymeric fibres were developed during this research. Differences in growth mechanisms were enlightened by SEM, STEM and ATR-FTIR techniques and solid-state NMR technique was developed for further understanding the reactions during the film growth and structures in the prepared materials. However, procedures to interpret all the steps even further from nanostructure formation, film growth and materials performance are still needed, and characterization techniques should be developed, especially *in situ* -techniques to study the reactions during the film growth. After all, this research brings new knowledge to the research and development work of inorganic-organic hybrid nonwoven materials and their utilization in various applications mentioned earlier in the chapter 4.1.

#### 4.1.2 ALD on foam-formed fibres

To the knowledge of the authors of the reference IV (submitted), ALD coatings were deposited on the foam-formed cellulose for the first time in this research. We wanted to study the growth and reactions of ALD on this type of nonwoven fibre material and most importantly, see the effect on physical properties important in the typical areas of usage of this material. Foam-formed cellulose can be used for example as an insulating material for replacing plastic foam, and in this applicational scope low water vapor absorption and high compression strength are assets. These properties, hydrophobicity, low water vapor absorption and enhanced compression strength were pursued with  $TiO_2$  ALD coating using the  $TiCl_4 + H_2O$  process. Coatings deposited with number of cycles between 5-50 were studied.

#### Growth and structure

Validation of the growth of  $TiO_2$  coating on foam-formed cellulose was carried out by SEM and TEM. With both methods, the  $TiO_2$  coating was observed on the surface of the fibre structure (Figure 25 a). Furthermore, the growth of the  $TiO_2$  coating inside the foam-formed fibre block (20 mm thickness) was verified nicely by TEM (Figure 25 b).



Figure 25 a) TEM images of the sample with 100 cycles of  $\text{TiO}_2$ . The sample was taken from the surface of the foam formed block. b) TEM image of the sample with 100 ALD cycles. The sample was taken from inside the foam-formed fibre block with a thickness of 2 cm. Copyright (2023) BioResources, https://doi.org/10.15376/biores.18.4.7923-7942

As recently discovered in the literature in the case of cellulose-based fibres, also in this research the desired hydrophobicity was reached with only a five cycles of ALD  $TiO_2$  on the foam-formed cellulose. When increasing the number of deposited cycles to 15, material turned back to hydrophilic (Figure 26). On the uncoated reference samples the contact angles could not be measured due to the rapid disappearance of the ionized water droplet inside the fibre surface.



Figure 26 Comparison of the water contact angles of 5 and 15 cycles of ALD  $TiO_2$  on 50% BSKP + 50% BSKP SR90, sample set 3. Copyright (2023) BioResources, https://doi.org/10.15376/biores.18.4.7923-7942

Water vapor absorption and compression strength were both measured in the relative humidity (RH) of 50% and 90%. The titanium oxide ALD coatings had effects on both properties, and the effects were more clearly seen in the 50% RH. Differences between different cycle numbers were small, but altogether, the moisture content of the ALD-treated samples decreased in the case of all sample sets (1-4) in the 50% RH. When compression strength was measured, ALD coating seemed to influence the compression strength through the moisture content at 50% RH. When combining these two, a clear trend between the moisture content and mechanical strength was detected since the compression strength increased with decreasing moisture content (Figure 27).



Figure 27 Combined data of compression strength (kPa) and Moisture content (%) in both 50%<br/>and 90% RH. Copyright (2023) BioResources,<br/>https://doi.org/10.15376/biores.18.4.7923-7942

It has been discussed previously in the literature that the stage of refinement that affects fibre size, fibre surface area and bonding between fibres also affects the permeability and absorption of gases. When the fibre size is decreased due to the refining, the surface area is increased, which enhances bonding between the fibres and therefore results in denser fibre network with smaller pores and uniform dimensions. This increases the tortuosity in the substrate and thus lowers the permeability. In our study, the foam-formed cellulose material had loose fibre network causing high porosity and relatively high permeability for water vapor. This was observed in the water vapor measurements since our ALD treatment had only mild effect on the moisture content and further on compression strength. However, differences between sample sets with different levels of refinement were observed, these were in line with the literature, since also in this research the moisture resistance was the highest in the case of the fibre sample with the highest level of refinement (CTMP). On the other hand, ALD treatment had larger effect on wettability, *i.e.*, hydrophobicity, regardless of the refinement level and sample set, since already a small number of TiO<sub>2</sub> ALD cycles was enough to turn all the fibre blocks (sample sets 1-4) hydrophobic.

When comparing the results in references III and IV, on changing the physical properties of electrospun polymeric fibres and foam-formed cellulose-based natural fibres, in both cases exceedingly small amounts of the ALD coating, or even a few cycles of coating material, were enough to achieve the desired properties. Furthermore, in some cases (protection against thermal degradation and hydrophobicity) small amount of coating or cycles was not just enough, but better option, since with higher amount of deposited material the properties were either reversed or otherwise worsened. This phenomenon, "the thinner the coating the better the effect", applies in all the ALD processes in this research, differing from each other by reaction chemistry. As discussed in the Background section 2.4, TiO<sub>2</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub> differ from reaction kinetics in capillary structures. With metal alkyl precursors (TMA, DEZ), the coating is diffusion-limited and with metal halides (TiCl<sub>4</sub>) it is reaction-limited.

#### 4.1.3 ALD and MLD overcoatings on Fischer-Tropsch synthesis

In addition to the nonwoven fibres, ALD and MLD growth was studied on porous powder catalysts. As compared to fibre matrixes, where the challenges are in the reactions of the ALD precursors with the fibre surface functionalities, ALD growth inside the fibre network and possible infiltration to the fibre subsurface, with porous powders the challenges are in the widely varied pore structures and shapes, high aspect ratios with deep pores and long diffusion times of the ALD precursors. With this research we wanted to increase the knowledge in the field of catalysis by using ALD and MLD materials as protective overcoatings on porous catalysts, especially for the Fischer-Tropsch (FT) synthesis reaction. Catalyst overcoatings are expected to inhibit catalyst metal particles sintering, leaching, and poisoning, and by that way enhance the activity, lifetime and possibly selectivity of the catalysts. To the knowledge of the authors of the references V and VI, this was the first time ALD/MLD overcoatings were deposited on FT-catalysts.

In the references V and VI, ALD  $Al_2O_3$  (15-40 cycles) and MLD alucone coating prepared with TMA + ethylene glycol (10-20 cycles), were deposited on Co-Pt-Si/-Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch catalysts prepared by incipient wetness coimpregnation. After the deposition, the catalysts were annealed at 420 °C to modify the ALD and MLD coatings. The ALD coated catalysts were annealed in inert atmosphere, while the MLD coated catalysts were annealed in oxygen containing atmosphere to combust the carbon structures for achieving porous overcoating structures. Catalyst activity was studied in the FT synthesis in a tubular reactor. The effect of co-fed water was also studied, since in the FT processes remarkable amount of water can be present, coming from the feed as well as forming during the FT reactions.

According to the nitrogen adsorption/desorption analysis and calculated BET surface area (m<sup>2</sup>/gcat), pore volume (ml/gcat) and pore size (nm), ALD coating grew on the powder support, since the measured values decreased, and further, by annealing the values recovered. This can be seen in the case of 35 cycles of  $Al_2O_3$ , (Table 4). With 40 cycles, the surface area and pore volume were clearly lower

compared to the other catalyst indicating too thick coating and clogging of the pores. The differences between the catalyst support and catalyst (two first rows in the (Table 4) are due to the impregnation of the cobalt particles.

Catalyst	BET Surface Area (m <sup>2</sup> gcat <sup>-1</sup> )	Pore Volume (ml gcat <sup>-1</sup> )	Pore Size (nm)
Support (Puralox SCCa 5-150)	140	0.46	13.2
Catalyst	87	0.24	10.9
Catalyst + 15c + TA	88	0.23	10.5
Catalyst + 25c + TA	84	0.23	10.8
Catalyst + 35c + TA	89	0.24	10.7
Catalyst + 35c	13	0.03	8.0
Catalyst + 40c + TA	61	0.15	10.0

**Table 4** BET Surface area, pore volume and pore diameter analysis of catalyst powder support and different catalyst types.

Experimental error  $(\pm 2\sigma)$  for surface area was  $\pm 1.2 \text{ m}^2/\text{g}$ , pore volume  $\pm 0.01 \text{ ml/g}$  and pore size  $\pm 0.1 \text{ nm}$ . Uncertainty was determined from three independent runs for catalyst without overcoat.

Typically, thermal treatment is carried out at higher temperatures, at 700 °C or above to crystallize amorphous ALD Al<sub>2</sub>O<sub>3</sub>, but we wanted to test the effect of milder annealing, partly to avoid possible sintering of the cobalt particles. Previous studies have shown that already upon annealing at lower temperatures ALD coatings densify, resulting in a mass loss and change of chemical composition,<sup>121,122</sup> meaning evaporation of excess oxygen, hydrogen and carbon residues. This causes coating densification and thinning. All this changes the chemical reaction environment on the catalyst surface affecting the activity and selectivity of the catalyst. In Figure 28 the effect of annealing (at 420 °C) on the catalyst activity can be seen clearly in the case of catalyst with 35 cycles of Al<sub>2</sub>O<sub>3</sub> ALD. In Figure 28 the conversion of carbon monoxide (CO, %) is presented as a function of space-time (the time required to process one reactor volume of feed into a reactor at the inlet conditions).



Figure 28 Effect of thermal annealing on catalyst activity. Activity presented as carbon monoxide conversion (%) as a function of space-time (h). Reprinted from Catalysts, vol 11, page 9, N. Heikkinen et al.: "The Effect of Atomic Layer Deposited Overcoat on Co-Pt-Si/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch Catalyst", Copyright (2021), reproduced with permission from MDPI. https://doi.org/10.3390/catal11060672

In the case of ALD overcoatings without co-fed water, the most positive effect on the catalyst activity was observed with 35 cycle ALD catalyst without compromising selectivity towards heavy hydrocarbons. In Figure 29, it is illustrated how catalysts with 15 and 25 cycles of ALD overcoating already have a positive effect on the catalyst activity, and with 35 cycles the activity still increases, but then with 40 cycles of overcoating the effect is changed to lowering the activity. The same result is repeated when testing catalysts overall reactivity during the reaction start-up phase and stabilization during 40 hours time-on-stream with fixed reaction conditions (Figure 30). In this test the catalyst with 35 cycles of ALD overcoating had the best activity as well.



**Figure 29** Effect of the ALD overcoating thickness on the catalyst activity. The activity is presented as carbon monoxide conversion (%) as a function of space-time (h). Reprinted from Catalysts, vol 11, page 7, N. Heikkinen et al.: "The Effect of Atomic Layer Deposited Overcoat on Co-Pt-Si/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch Catalyst", Copyright (2021), reproduced with permission from MDPI. https://doi.org/10.3390/catal11060672.



**Figure 30** Catalyst overall reactivity during the reaction start-up phase and stabilization during 40h time-on-stream with fixed reaction conditions (200 °C, 20 bar, and total flow 6.6 nl/h). Catalyst bed contained 603, 603, 613, 609 and 601 mg of catalyst respectively to nonovercoated catalysts, 15c, 25c, 35c and 40c catalysts. Reprinted from Catalysts, vol 11, page 7, N. Heikkinen et al.: "The Effect of Atomic Layer Deposited Overcoat on Co-Pt-Si/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch Catalyst", Copyright (2021), reproduced with permission from MDPI. https://doi.org/10.3390/catal1060672.

When the effect of co-fed water was studied, the ALD catalyst with 40 cycles of aluminum oxide and the MLD catalyst with 10 cycles of alucone increased the activity the most during 144 hours time-on-stream with fixed reaction conditions (Figure 31). Previously, it has been studied that in the case of FT synthesis the moderate added water partial pressure increases  $C_{5+}$  selectivity and lowers  $CH_4$ selectivity.<sup>123,124</sup> Furthermore, the added water lowers the CO activation energy barrier and increases the carbon species  $(CH_x)$  surface coverage by enhancing the CO dissociation on the surface. By adding the 40 cycles of ALD or 10 cycles of MLD overcoating to the catalyst surface, the activity increased notably. According to the TPD (temperature programmed desorption) analysis, this was probably due to the enhanced CO-metal bond strength and adsorption of CO onto the active CO hydrogenation sites, followed by increased CO dissociation. Furthermore, in this research the effect of the ALD and MLD overcoatings on cobalt particle leaching was studied, and the results show inevitably vast effects of both coatings, since the concentration of cobalt in product water collapses even to a tenth with the 40 cycles of Al<sub>2</sub>O<sub>3</sub> (Figure 32).





**Figure 32** ICP–MS analysis results from water samples collected after 72 hours of process, before co-fed water addition. Reprinted from ACS Omega, vol 7, page 7727, N. Heikkinen et al.: "Effect of Co-fed Water on a Co–Pt–Si/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch Catalyst Modified with an Atomic Layer Deposited or Molecular Layer Deposition Overcoating", Copyright (2022), reproduced with permission from American Chemical Society. https://doi.org/10.1021/acsomega.1c06512.

In this research we observed the increased activity of the overcoated catalysts. Detailed reasons behind this increase were difficult to discover, since there were difficulties in characterization of the materials due to the porous powder structure and similarity of the substrate and coating materials, which both were aluminum oxide. However, it is likely that the overcoating was grown mainly onto the surface of the catalyst particles, and not so much into the pores of the particles resulting in an "eggshell" catalyst with different kind of gas diffusion properties during the catalytic reactions.<sup>125</sup> In the case of the slow Fischer-Tropsch reactions this is a positive change, as observed during the experiments. On the other hand, as a parallel theory, the deposited coating is probably structured like a decorative overcoating already before the annealing due to the catalyst particle structure and a quite few numbers of cycles.

With both polymeric fibres and ceramic powder particles, the growth during the first tens of cycles is probably island growth. In the case of polymeric materials, the ALD growth during the first cycles depends on the surface site functionalities on the fibre surface. In the case of ceramic particles, the early growth prefers to happen on low-coordination sites, such as steps and edges. What this means in terms of the FT reactions was difficult to discover due to the aforementioned challenges in characterization. However, with the ALD/MLD coating and pore formation and densification of the coating, the lower activity sites might have been modified towards increased activity for example by formation of defects acting as higher activity sites.

Finally, the ALD reactor set up plays a tremendous role in the growth of the ALD coating on porous powders. In our research, a relatively new and experimental Picosun's POCA powder coating set up was used. In POCA, the catalyst powder is placed in a quartz sinter vibrated by ultrasound to move the powder particles in the sinter during the coating process. Possible discontinuity in the ultrasound causing the decrease of movement of the particles can lead nonuniform ALD growth in and between the particles.

All in all, positive effects of the ALD and MLD overcoatings on catalyst activity and selectivity and against leaching were demonstrated. This research advances the ALD/MLD catalyst research in the field of Fischer-Tropsch synthesis. It also increases the understanding of the effect of co-fed water and brings an alternative for enhancing the catalyst activity and stability in the FT synthesis with multiphase conditions. When comparing to polymeric fibrous materials in references III and IV, slightly larger number of cycles of ALD/MLD material was needed for modifying the physical properties to the wanted direction. However, the better understanding of the film growth in the pores of the powder particles is desired and the research has been later continued and expanded for example to modeling studies (Modelling atomic layer deposition overcoating formation on a porous heterogeneous catalyst, Heikkinen et al. 2022, listed in the other related publications).

# 4.2 MLD materials from monofunctional aromatic precursors

In references I and II, novel MLD materials were developed using organic precursors which had not been utilized in MLD processes before. The aim was to test the ring-opening hypothesis, that is, opening of an aromatic ring structure with ozone, incorporation of fluorine into the film structures, and the effect of hydrogen peroxide as an additional precursor. With these approaches, we wanted to advance the vast area of MLD research, joint knowledge of aspects affecting MLD film growth and to bring novel alternatives to the MLD precursor selection. Furthermore, there is a constant need for novel MLD, and inorganic-organic hybrid materials utilized in various applications, for example in biocompatible coatings in medical applications, biosensors, textiles with added functionalities and many more. Hopefully this research is making its own contribution also to the field of tailored porous materials in the future.

#### 4.2.1 Film growth

Three and four-step (ABC, ABCD) processes were constructed from TMA as a metal precursor, ozone, hydrogen peroxide and aromatic precursors including 3-(trifluoromethyl)phenol phenol. (3F), and 2-fluoro-4-(trifluoromethyl) benzaldehyde (4F). In the three different MLD processes the aromatic compounds were used with TMA and ozone. The first half cycle reaction of TMA with phenol or 3F is straightforward and can be compared to the reaction between TMA and water, where TMA reacts through ligand exchange with the hydrogen atoms in surface OH groups, producing O–Al bonds and releasing methane (Figure 33). The reaction of TMA and 4F is described in Figure 34. In this reaction step TMA acts as a strong Lewis acid and attacks the nucleophilic carbonyl group in the 4F molecule, to break the ester bond and form aluminum alkyl oxide unit. After these steps (TMA with phenol, 3F or 4F), the ring-opening reaction with O3 takes place and activates the surface with carboxylic acid structures. This reaction step is discussed more thoroughly in the section 4 (results and discussion) with experimental and modeling results.



Figure 33 Ligand exchange reaction of the TMA reactant with surface OH groups. In the reaction gaseous CH<sub>4</sub> is released.



Figure 34 Reaction between TMA and 2-fluoro-4-(trifluoromethyl)benzaldehyde. Reprinted from Langmuir, vol 33, page 9658, L. Svärd et al.: "Low-Temperature Molecular Layer Deposition Using Monofunctional Aromatic Precursors and Ozone-Based Ring-Opening Reactions", Copyright (2017), reproduced with permission from American Chemical Society. https://doi.org/10.1021/acs.langmuir.7b02456.

Based on the ellipsometry results, GPC decreased with increasing temperature from 80 to 200 °C in all three processes (Figure 35). Phenol and 2-fluoro-4-(trifluoromethyl)benzaldehyde (4F) processes had similar trends, but the process with the 3-(trifluoromethyl)phenol (3F) precursor acted slightly divergently, although having the same decreasing trend with the temperature. The highest GPC (5.4 Å/cycle) was achieved with the TMA+phenol+O<sub>3</sub> process at 80 °C. The decrease of the GPC with increasing temperature is typical for MLD processes and is often explained by the decrease of reactive sites and temperature sensitive precursors. Furthermore, it is likely that the usage of ozone in these particular processes accelerates the decomposition of the precursors even more, as will be discussed more thoroughly later in this section.

When hydrogen peroxide was added as the fourth precursor, similar trends as without  $H_2O_2$  were observed (Figure 35). However, it seems that  $H_2O_2$  decreases the GPC, except for the phenol process at higher temperatures (100 – 200 °C). When  $H_2O_2$  was used as the fourth precursor, the highest GPC was approximately 80% of the value measured for the three precursor processes. In addition, there was a lot of variation in the results, which can be explained by increased decomposition of the precursors and as a consequence result increased randomness in the reactions as compared to the ABC processes.



Figure 35 a) GPC of ABC processes as a function of deposition temperature. b) GPC of ABCD processes. GPCs were calculated from thicknesses measured after 200 cycles. Reprinted from Langmuir, vol 33, page 9658, L. Svärd et al.: "Low-Temperature Molecular Layer Deposition Using Monofunctional Aromatic Precursors and Ozone-Based Ring-Opening Reactions", Copyright (2017), reproduced with permission from American Chemical Society. https://doi.org/10.1021/acs.langmuir.7b02456.

Saturation was tested as a function of the pulse length of the aromatic precursor. Relatively long pulse times were needed for the fluorinated organic precursors, but eventually the processes started to saturate. The process with the phenol precursor was saturated already with a pulse length of 0.2 s (Figure 36) and all three processes were concluded to be self-limiting. Furthermore, all three MLD process were found to be linear as a function of the number of deposited cycles.



Figure 36 GPC as a function of the phenol pulse length at 100 °C. Reprinted from Langmuir, vol 33, page 9658, L. Svärd et al.: "Low-Temperature Molecular Layer Deposition Using Monofunctional Aromatic Precursors and Ozone-Based Ring-Opening Reactions", Copyright (2017), reproduced with permission from American Chemical Society. https://doi.org/10.1021/acs.langmuir.7b02456.

#### 4.2.2 Film composition and reactions during the film growth

Structures of the deposited MLD coatings were investigated by ex-situ ATR-FTIR, in-situ FTIR and TOF-ERDA. By ATR-FTIR we found out that the coating contained hydroxyl groups,  $CO_2$ - and  $CO_2$ -Al groups, Al-O bonds and  $CO_3$  carbonyl and carboxylic acid groups, regardless of the process (phenol, 3F, 4F). Furthermore, with the 3F and 4F processes the presence of fluorine (C-F and CF<sub>3</sub> attached to benzene ring) was discovered (Figure 37).

The same structures were present when the processes were studied with the in situ FTIR method. Averaged-out difference spectra showed detailed reactions upon every precursor pulse and verified the ring-opening of the aromatic structures after the  $O_3$  pulse, since after the ozone pulse aromatic structures were replaced with carboxylic acid groups and carboxylate ions, shown in Figure 38, the blue spectrum. The incorporation of the fluorine containing species with 3F and 4F precursors was also detected.



Figure 37 ATR-FTIR spectra of the films deposited by the TMA + 3-(trifluoromethyl)phenol +  $O_3$ (blue) and TMA + 3-(trifluoromethyl) phenol +  $O_3$  +  $H_2O_2$  (red) processes.. Filmsdeposited at 100 °C. Reprinted from Langmuir, vol 33, page 9660, L. Svärd et al.: "Low-Temperature Molecular Layer Deposition Using Monofunctional Aromatic Precursorsand Ozone-Based Ring-Opening Reactions", Copyright (2017), reproduced withpermissionfromAmericanChemicalSociety.https://doi.org/10.1021/acs.langmuir.7b02456.



When the effect of hydrogen peroxide was studied with the in situ FTIR, a new peroxyacid structure (C(O)-O-OH) was discovered as a reaction product of surface carboxylic acid and  $H_2O_2$  in all three processes. The film growth was continuous with the fourth hydrogen peroxide precursor as well, but as mentioned earlier, the GPC was approximately 80% of the corresponding ABC processes. This lower GPC with  $H_2O_2$  can be explained with the changed surface species and reactions between TMA and OH groups in peroxyacid compared to the rection between TMA and OH group in carboxylic acid, with the latter being more favorable. Furthermore, based on the modeling results, discussed later in this section, there is some backbonding of the carboxylic acid structures to the surface. It is probable that this backbonding occurs with peroxyacid structures as well and even more abundantly causing the lower GPC. Furthermore, it has been studied previously, that  $Al_2O_3$  deposited by the TMA+ $H_2O_2$  ALD process is denser compared to that deposited by the TMA+ $H_2O_1^{126,127}$  In this research we added  $H_2O_2$  after  $O_3$ , and according to the XRR results, the films got denser when  $H_2O_2$  was used as the fourth precursor.

As was observed already with the ATR-FTIR and in situ FTIR measurements, fluorine was incorporated to the films with the 3F and 4F processes. This was confirmed with the TOF-ERDA measurements. Despite the amounts of fluorine in the precursors, the process with 3F incorporated more fluorine into the film compared to the 4F process (Table 5). When looking at the contents of Al, O, H and C and their ratios, one can see that the Al:O ratio in the films is lower (0.4) than the Al:O ratio in the bare aluminum oxide (0.7) (Table 6). In addition to the obvious

difference between MLD and Al<sub>2</sub>O<sub>3</sub> ALD films, this is probably due to the carboxylic acid formation during the ozone pulse and the ring-opening reaction. Furthermore, it is probable that a subsequent TMA pulse reacts with carboxyl groups forming bidentate and bridging complexes, resulting in an excess of oxygen in every cycle.

As discussed in the reference I, it is probable that the ozone pulse also affects the double bonds remaining deeper in the film structure in addition to the aromatic rings on the very surface. The subsequent ozone pulse breaks a second double bond in the carbon chain, thus forming a new carboxylic acid structure and decreasing the amount of carbon and fluorine in the film. Differences between the processes can be explained with the cleavages of double bonds in aromatic structures. The structural differences, the amount and position of fluorine atoms, between the 3F and 4F precursors produce varying steric hindrances between the molecules in the growing film resulting into different positions and angles of the precursors in the film. Furthermore, the steric hindrances and the energetically favorable reactions cause probably the difference in the cleavage reactions between the 3F or 4F precursor and subsequent ozone pulse.

The hypothesis was that the majority of the cleavages focus on the C3-C4 double bond in the case of 3F precursor, and on the C1-C2 double bond in the case of the 4F precursor (Figure 39). This explains the differences between the processes in the Al, O, H, C and F contents analyzed in the film with TOF-ERDA (Table 5 Table 6). Furthermore, this can be connected to the XRR density results as well, where 4F was concluded to result in films with the highest density. This can be due to the different reactions between TMA and 4F precursors during deposition, but also due to the secondary double bond cleavage caused by ozone leading to the lower content of organic moieties in the case of 4F. Secondary cleavages were studied by molecular modeling as well, and the results support the cleavage hypothesis, since the secondary cleavage was discovered to be energetically very favorable reaction. Modeling results are summarized in the next paragraph.

sample	Al	0	Н	С	Ν	F
TMA+phenol+O <sub>3</sub>	13±2	41±3	30±3	15±2	0.3±0.1	0
TMA+phenol+O <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	15±1	38±2	31±3	15±1	0.2±0.1	0
TMA+3F+O <sub>3</sub>	13±2	37±3	27±3	16±2	0.3±0.1	8±1
TMA+3F+O <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	13±2	36±3	25±3	18±2	0.6±0.2	7.4±1.0
TMA+4F+O <sub>3</sub>	16±2	45±4	26±3	10±1	0.7±0.2	1.9±0.5
TMA+4F+O <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	17±3	42±4	26±3	11±3	0.8±0.3	2.9±0.6

Table 5 TOF-ERDA measurements of the elemental compositions (atom %) of all processes.

Sample	Al/O	Al/C	C/H	F/C
TMA+phenol+O <sub>3</sub>	0.3	0.9	0.5	0
TMA+phenol+O <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	0.4	1.0	0.5	0
TMA+3F+O <sub>3</sub>	0.4	0.8	0.6	0.5
TMA+3F+O <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	0.4	0.7	0.7	0.4
TMA+4F+O <sub>3</sub>	0.4	1.6	0.4	0.2
TMA+4F+O <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	0.4	1.6	0.4	0.3

Table 6 Ratios between elements according to the TOF-ERDA measurements.



**Figure 39** Possible bond cleavages during the second ozone pulse. In the case of 3F, the majority of the cleavages focus on the C3–C4 double bond, whereas in the case of 4F the majority focus on the C1–C2 double bond. Reprinted from Langmuir, vol 33, page 9659, L. Svärd et al.: "Low-Temperature Molecular Layer Deposition Using Monofunctional Aromatic Precursors and Ozone-Based Ring-Opening Reactions", Copyright (2017), reproduced with permission from American Chemical Society. https://doi.org/10.1021/acs.langmuir.7b02456.

#### 4.2.3 Modeling

Molecular modeling results presented in the reference II support well the presented TOF-ERDA results and the hypothesis of the second double bond cleavage by ozone. Different variations of aromatic ring-opening and cleavages of the structures were presented, as well as theory of backbonding of the carboxylic acids. In backbonding reaction, carboxylic groups of the ring-opened phenols react with the surface Al atoms (Figure 40). Furthermore, chemical compositions and atomic ratios of different MLD films were obtained.

In addition to the discussion about atomic ratios and backbonding, the theory of backbonding brings insight to the measured contact angles and hydrophilicity as well. The 4F coatings had the largest contact angles, i.e. they were the most hydrophobic. In this regard, molecular modeling revealed the backbonding reactions, where fluorine functionalities form on the surface in the way leading to more hydrophobic surface compared to the 3F and phenol processes (Figure 40). In the case of 3F the additional fluorine atom is missing and with phenol the longer carbon chain balances the situation with the 3F process. Finally, backbonding affects also to the film densities, supporting the density results obtained by XRR. Based on the presented results, reactions during one cycle in the TMA + phenol +  $O_3$  process can be suggested as shown in Figure 41.



**Figure 40** MLD layers formed with the C5–C6 (above) and C2–C3 (below) openings of 4F. Pink: aluminum, red: oxygen, gray: carbon, white: hydrogen, and light blue: fluorine. Backbonding of the carboxyl group onto the surface Al atoms can be seen in the upper scheme. Reprinted from ACS Omega, vol 3, page 7146, L. Keskiväli et al.: "Molecular Layer Deposition Using Ring-Opening Reactions: Molecular Modeling of the Film Growth and the Effects of Hydrogen Peroxide", Copyright (2018), reproduced with permission from American Chemical Society. https://doi.org/10.1021/acsomega.8b01301.



**Figure 41** Suggested reactions during one cycle in the TMA+phenol+O<sub>3</sub>(+H<sub>2</sub>O<sub>2</sub>) process. Reprinted from Langmuir, vol 33, page 9663, L. Svärd et al.: "Low-Temperature Molecular Layer Deposition Using Monofunctional Aromatic Precursors and Ozone-Based Ring-Opening Reactions", Copyright (2017), reproduced with permission from American Chemical Society. https://doi.org/10.1021/acs.langmuir.7b02456.

The three monofunctional aromatic precursors studied in this research can be used for the MLD processes. Self-limiting growth was obtained. Depending on the aromatic precursors, depositions can be performed at temperatures as low as 75 - 100 °C, thus opening up new possibilities for coating temperature-sensitive substrates by MLD materials. According to the ATR-FTIR, in situ FTIR and TOF-ERDA measurements and molecular modeling results, fluorine was incorporated into the deposited films and ring-opening reaction occurred between the aromatic compounds and O<sub>3</sub>. When hydrogen peroxide was added as the fourth precursor after ozone, peroxyacid structure (C(O)-O-OH) was formed, and GPC decreased approximately 20%.

## **5** Conclusions and outlook

Porous materials with different variations of pore sizes and structures are everywhere. They are utilized in multiple applications, such as textiles with added functionalities, separation membranes and heterogeneous catalysts. ALD and MLD are especially suitable techniques for modification of structures and functionalities of porous materials due to the self-limiting surface reactions inducing conformality and accuracy in film thickness and composition.

The history of ALD catalyst research starts from the late 1980's when ALD was first implemented to heterogeneous catalyst preparation. Since that several different porous materials have been tailored by ALD. The history of MLD starts from the beginning of 1990's with the polyimide process and soon after the first hybrid inorganic-organic materials were developed. Thus, it can be said that the ALD/MLD research on inorganic-organic hybrid materials and deposition on porous substrates have been of interest for more than three decades today, and especially in the case of hybrid materials the growth has been exponential.

Despite the fast growth in the field, the nature of the ALD research demands thorough and often fundamental studies every time when new materials are developed, whether it is about new ALD/MLD processes and precursors, new substrate materials or their combination. The chemistry of these processes depends on vast number of different aspects, for which reason the adoption of previous results with different materials is often unfeasible. In addition, when an ALD/MLD process has been developed, the growth is taking place and the coating is conformal, the examination of properties starts. After this, possible new applications can be considered.

In this thesis, ALD and MLD on porous nonwoven fibres and porous ceramic catalyst powders were studied. In the case of electrospun fibres, the growth, structure and modified thermal properties of ALD  $Al_2O_3$  and ZnO were studied. The effects of traditional ALD and vapor phase infiltration on protection against thermal conditions were revealed, since slower depolymerization process and better thermal resistance were detected with both techniques, being slightly more pronounced with the vapor phase infiltration. For the foam-formed cellulose fibres, the growth and effects of ALD TiO<sub>2</sub> on wettability, moisture resistance and compression strength were studied. A clear trend between the ALD coatings and these physical properties was detected since the compression strength increased with decreasing moisture content caused by the ALD  $TiO_2$  modification. Furthermore, complete hydrophobicity was achieved with a few cycles of ALD  $TiO_2$ . And finally, in the case of porous powder catalysts the ALD  $Al_2O_3$  and MLD alucone (TMA+ethylene glycol) overcoatings and their effects on Fischer-Tropsch synthesis were evaluated. The overcoatings enhanced the activity and selectivity of the cobalt FT-catalysts and prevented the leaching of the catalyst metal particles in multiphase conditions.

MLD hybrid processes with organic molecules and organometallic precursors, such as TMA and DEZ, has been of great interest in materials research. Due to the limitations of MLD precursors and, at the same time, due to the urge of novel applications, there is still a constant need for new MLD processes. With this in mind, three new low-temperature MLD alucone processes were developed using phenol, 3-(trifluoromethyl)phenol, and 2-fluoro-4-(trifluoromethyl)benzaldehyde as organic precursors and the hypothesis of aromatic ring-opening with ozone was tested. And finally, the incorporation of fluorine atoms into the films was studied. Deposition temperature range varied between 75-150 °C depending on the process, and the growth per cycles decreased with increasing temperature. Furthermore, molecular modeling was carried out for deepening the knowledge of MLD film growth. The correspondence of the modeling results with the experimental data was excellent.

All in all, the purpose of this thesis was to increase the general knowledge of MLD research, obtain deeper understanding about fundamental interactions occurring during novel MLD processes and underlaying nanostructured materials. Furthermore, the purpose was to deepen the knowledge of ALD and MLD growth on different porous substrate materials and the modified physical properties. This work concentrated on the fundamentals of materials science, developing novel hybrid MLD/ALD materials, and finding suitable processes for nonwoven fibrous materials and for catalytic applications. Some breakthroughs were obtained, for example in understanding hybrid material formation during the processes, understanding the differences in growth mechanisms between traditional ALD and vapor phase infiltration (VPI), and comparison of atomic-scale modeling of the MLD growth and experimental data. Yet, detailed research for deeper understanding of the surface properties, growth and tuning of the surface chemistry and physics of nanostructures proved to be demanding tasks. Therefore, there are still open scientific questions left and need for interpreting all the steps from nanostructure formation, film growth and materials performance by developing new characterization methods and techniques. Furthermore, the possibility of modifying surface properties, such as hydrophobicity, with the MLD materials developed in this thesis should be recognized and tested.

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