Zouhair El Assal

SYNTHESIS AND CHARACTERIZATION OF CATALYSTS FOR THE TOTAL OXIDATION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS
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University of Oulu Graduate School; University of Oulu, Faculty of Technology; University of Chouaib Doukkali El Jadida, Morocco

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University of Oulu, P.O. Box 8000, FI-90014 University of Oulu, Finland

Abstract

The harmful emissions of chlorinated volatile organic compounds (CVOCs) originate only from man-made sources. CVOCs are used in a variety of applications from pharmaceuticals production to decaffeination of coffee. Currently, CVOC emissions are limited by strict legislation. For these reasons, efficient CVOC abatement technologies are required. Catalytic oxidation is very promising option for this purpose, since catalysts can be tailored to each case to maximize the efficiency and minimize the formation of unwanted products, such as dioxins or Cl2.

The goal of this thesis was to study the role of the physico-chemical properties of catalysts in dichloromethane (DCM) oxidation. To reach the aim, several catalytic materials were prepared and characterized, and their performance was tested in total oxidation of DCM. The catalytic materials used were powders of four single metal oxides (γ-Al2O3, TiO2, CeO2, MgO), three mixed oxides (Al2O3-xSiO2) washcoated on a cordierite monolith and four active phases (Pt, Cu, V, Mn).

At first, support properties were studied. It was found that the DCM conversion and HCl production are dependent on support acidity when the studied single oxides are considered. The best DCM conversions and HCl yields were observed with the support having the highest total acidity (γ-Al2O3). Further, the quality of the by-products formed was dependent on the type of the acid sites present on the support surface. Secondly, the impregnation of the active compound was observed to improve the selectivity of the material. From the tested active phases, Pt presented the best performance, but also V2O5 and CuO showed almost equal performances. Especially CuO supported on γ-Al2O3, that had less formation of by-products and is less toxic than V-containing oxides, seems to be a promising alternative to Pt. Concerning stability, no deactivation was observed after 55h of testing of Pt/Al2O3. Furthermore, in the used reaction conditions, the formation of CuCl2 is not thermodynamically favoured. Finally, the good characteristics of the powder form catalysts were successfully transferred to the monolith. The performance of the Pt/90Al2O3-10SiO2 catalyst in DCM oxidation was improved when the channel density was increased due to an increase in geometric surface area and mechanical integrity factor, and a decrease in open fraction area and thermal integrity factor.

Keywords: acidity, catalytic oxidation, CVOC, DCM, dichloromethane, monolith, noble metal catalyst, transition metal oxide catalyst
Tämän väitöskirjatyön tavoitteena oli selvittää katalyyttien fysikaalis-kemiallisten ominaisuuksien yhteyksiä dikloorimetaanin (DCM) hapetukseen. Tavoitteen saavuttamiseksi valmistettiin useita katalyyttejä, jotka karakterisoitiin ja testattiin DCM:n kokonaishapetuksessa. Työssä tutkittiin neljää jauhemaista metallioksidia (γ-Al_2O_3, TiO_2, CeO_2 ja MgO) kolmea metallioksidiseosta (Al_2O_3-xSiO_2), jotka pinnoitettiin kordieriittimonoliitille, sekä neljää aktiivista ainetta: Pt, Cu, V ja Mn.


Asiassanat: CVOC, DCM, dikloorimetaani, happamuus, jalometallikatalyyttikin, katalyyttinen hapetus, monoliitit, siirtymämetallikoordinatiokatalyyttikin
To my family
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The characterization technicians at Poitiers University, at the Environmental and Chemical Engineering and at the Center of Microscopy and Nanotechnology are kindly acknowledged for the characterization of the materials and for their appreciated discussions’. GTK Espoo Finland and financial support from the Academy of Finland through the RAMI infrastructure project (293109) is acknowledged for the X-ray tomography results. PHC Volubilis (No. 24618ZJ), Thule, Oulu University Scholarship Foundation (Yliopiston apteekin rahasto) and
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Oulu, October 2018
Zouhair El Assal
List of symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Alumina, Al$_2$O$_3$</td>
</tr>
<tr>
<td>Ce</td>
<td>Ceria, CeO$_2$</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>D</td>
<td>Mean size of crystallites (XRD)</td>
</tr>
<tr>
<td>d$_{ch}$</td>
<td>Channel size</td>
</tr>
<tr>
<td>Dp</td>
<td>Average pore size (N$_2$-physisorption)</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Particle diameter (TEM)</td>
</tr>
<tr>
<td>e$_{ch}$</td>
<td>Wall thickness</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium, MgO</td>
</tr>
<tr>
<td>Mn</td>
<td>Manganese</td>
</tr>
<tr>
<td>mol-%</td>
<td>Mole percentage</td>
</tr>
<tr>
<td>n</td>
<td>Channel density</td>
</tr>
<tr>
<td>$S_{BET}$</td>
<td>Specific surface area [m$^2$ g$^{-1}$]</td>
</tr>
<tr>
<td>Si</td>
<td>Silica, SiO$_2$</td>
</tr>
<tr>
<td>T$_{50}$</td>
<td>Temperature of 50% conversion [$^\circ$C]</td>
</tr>
<tr>
<td>T$_{90}$</td>
<td>Temperature of 90% conversion [$^\circ$C]</td>
</tr>
<tr>
<td>Ti</td>
<td>Titania, TiO$_2$</td>
</tr>
<tr>
<td>V</td>
<td>Vanadium</td>
</tr>
<tr>
<td>vol-%</td>
<td>Volume percentage</td>
</tr>
<tr>
<td>wt-%</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>Sigma summation operator</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Alpha phase of alumina</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Full-width at half-maximum FWHM (XRD)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Gamma phase of alumina</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Delta phase of alumina</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Eta phase of alumina</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Bragg angle (XRD), theta phase of alumina</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Kappa phase of alumina</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength (XRD)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Vibration mode</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Chi phase of alumina</td>
</tr>
<tr>
<td>AlSix</td>
<td>($Al_2O_3$)$_{1-x}$(SiO$_2$)$_x$</td>
</tr>
<tr>
<td>BAS</td>
<td>Brønsted acid site</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller (model to calculate specific surface area)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>BJH</td>
<td>Barret-Joyner-Halenda (model to calculate pore size distribution)</td>
</tr>
<tr>
<td>CB</td>
<td>Chlorobenzene, C₆H₅Cl</td>
</tr>
<tr>
<td>CF</td>
<td>Chloroform, CHCl₃</td>
</tr>
<tr>
<td>COP</td>
<td>Conference of the Parties related to the pollutant emission</td>
</tr>
<tr>
<td>CVOC</td>
<td>Chlorinated volatile organic compounds</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2-Dichloroethane, C₂H₄Cl₂</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane, CH₂Cl₂</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas hourly space velocity</td>
</tr>
<tr>
<td>GSA</td>
<td>Geometric surface area</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma-optical emission spectroscopy</td>
</tr>
<tr>
<td>LAS</td>
<td>Lewis acid site</td>
</tr>
<tr>
<td>MC</td>
<td>Methyl chloride, CH₃Cl</td>
</tr>
<tr>
<td>MIF</td>
<td>Mechanical integrity factor</td>
</tr>
<tr>
<td>OFA</td>
<td>Open fraction area</td>
</tr>
<tr>
<td>PCE</td>
<td>Perchloroethylene, Tetrachloroethylene, C₂Cl₄</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>TCE</td>
<td>Trichloroethylene, C₂HCl₃</td>
</tr>
<tr>
<td>TCM</td>
<td>Tetrachloromethane, Carbon tetrachloride, CCl₄</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA-DTA</td>
<td>Thermogravimetric and differential thermal analysis</td>
</tr>
<tr>
<td>TIF</td>
<td>Thermal integrity factor</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature programmed reduction</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
</tbody>
</table>
Hazard identification phrases

H315  Causes skin irritation
H319  Causes serious eye irritation
H335  May cause respiratory irritation
H336  May cause drowsiness or dizziness
H351  Suspected of causing cancer
H373  May cause damage to organs (liver, blood, central nervous system) through prolonged or repeated exposure
Original publications

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


El Assal has been the main author of all Papers I–IV. In Paper I, El Assal planned and did the catalyst preparation, did some of the characterization and did the testing of the studied catalysts in DCM oxidation. In paper II, El Assal was responsible for the data analysis, testing of the catalysts, and writing the paper. In paper III, El Assal was responsible for results analyses, re-preparation of the catalysts and evaluation of the catalyst performance in DCM oxidation. In publication IV, El Assal prepared the monoliths, did characterizations and testing of the performance of the catalysts.
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1 Introduction

Globally, air pollution has been recognized as the major threat to the environment and human well-being. According to studies, household air pollutants (indoor) cause 4.3 million deaths annually and 3 million deaths are caused by ambient air pollution (outdoors from traffic, industrial sources, waste burning or residential fuel combustion), which corresponds to 23% of total deaths in the world (WHO, 2017). It was forecasted that the global temperature has raised by 0.99 °C by 2016, which was the warmest year since 1880 (NASA, 2017) causing ice melting, for example. The major air pollutants (indoor and outdoor) are nitrogen oxides (NO, NO₂), carbon monoxide, volatile organic compounds (VOC), sulphur oxides, particulate matter, and pesticides. (Ming-Ho, 2005)

Considering Finnish and Moroccan actions towards a cleaner environment and diminishing the effects of climate change, the steps taken can be described as follows. Finland, as a European country, has adopted the European Union-wide directives and legislation related to environmental protection since Finland joined the European Union in 1995. Before that, Finland had its own environmental legislation. The Finnish Ministry of Environment was founded in 1983, and environmental issues were taken into account already in 1960’s legislation (Lindholm, 2002). Morocco began to take into account pollution prevention and protection of the environment in 1992, when Morocco participated in the United Nation’s Conference on Environment and Development (UNCED) in Rio de Janeiro on June 3–14, 1992. In 2001, Morocco organized the 7th session of COP (Conference of the Parties) and the conference participants implemented the Kyoto Protocol (2005). In 2015, a new law was created by the Moroccan State for the restriction of the use of plastic bag starting from July 1, 2016 (Royaume du Maroc, 2015). Prohibition of manufacturing, importation, exportation, sale and/or free distribution of plastic bags provided for individual use, such as use during shopping, is the main statement of this law. Use of other plastic bags, such as insulated (isothermal), freezing and garbage bags is restricted. The 22nd session of COP was organized in Morocco on November 7–18, 2016. In 2013, Morocco decided to start producing electricity by renewable resources, such as by creation of Solar Power Stations (SPS) with a total electricity production of 2000 MW by 2020. This is forecasted to reduce carbon dioxide emissions by 3.7 million tonnes per year (invest in Morocco, 2016; Ministry of Energy Mines Water and Environment, 2016a; NOOR, 2016). In addition, wind energy will be used in order to produce 2000 MW by 2020, which will reduce carbon dioxide emissions by 5.6 million tonnes per year.
The NOOR project was awarded during the 52nd meeting of the African Development Bank in Ahmedabad (India), the prize is one of the Africa Development Impact awards in the category “Light up and power Africa” (AfDB, 2017). All these actions aim to reduce the harmful effects of air pollutants and several countries outside Europe are taking steps towards a cleaner environment. The most recent agreement related to climate change was signed by Morocco and Finland. This agreement was adopted during the 21st session of the Conference of the Parties (COP 21) in Paris (Paris Agreement, 2016).

This thesis concentrates on one group of the major air pollutants, namely volatile organic compounds (VOCs), and within this group to one of the most harmful type of compounds, *i.e.* chlorinated volatile organic compounds (CVOCs).

### 1.1 Volatile organic compounds and chlorinated volatile organic compounds

VOCs have different definitions depending on the country. Even within the European Union, different definitions can be found from one directive to another. The Solvent Emission Directive (Directive 1999/42/EC) states that VOCs are compounds containing, in addition to carbon and/or hydrogen, oxygen, sulphur, phosphorous, silicon and nitrogen, which have a vapour pressure of 0.01 kPa or higher at 293.13 K or corresponding volatility under the conditions of use. Carbon oxides, inorganic carbonates and bicarbonates are excluded from this group (Directive 1999/13/EC, 1999; Directive 2010/75/EU, 2010). In Directive 2004/42/CE, the VOCs are defined as organic compounds with the initial boiling point less than or equal to 250 °C at 101.3 kPa as standard pressure. The definition, described in Directive 2001/81/EC, states that “the VOCs are all compounds arising from human activities, other than methane, which are capable of producing photochemical oxidant by reactions with nitrogen oxides in the presence of sunlight” (Directive 2001/81/EC, 2001).

CVOCs are VOCs, where one or several hydrogen atoms are substituted by chlorine (Directive 1999/13/EC, 1999). Chlorinated organic compounds are widely used in pharmaceuticals and electronics manufacturing as cleaning and degreasing agents, film coatings, aerosol and automotive products, decaffeination of coffee and also in insect sprays (Wexler *et al.*, 2005; EPA, 2011; CEPA, 1993; ATSDR, 2000; WHO, 2000; Krausova *et al.*, 2006; Manahan, 1991; Aranzabal *et al.*, 2014; WHO & IARC, 1999; NTP, 2016).
VOCs are emitted to the atmosphere in two ways: from natural and anthropogenic sources. The natural sources are related to emissions from plants at atmospheric temperature due to sun irradiation, forest fires, etc. The anthropogenic sources are related to human activities: industry, transportation, power generation, etc. (car, ships, aircraft, etc.) (Azalim, 2011; Maupin, 2011; Ojala et al., 2011). The anthropogenic emissions are higher than natural emissions in industrial areas and vice-versa for rural areas. When considering the emissions of CVOCs in particular, they are basically emitted only from man-made sources (Manahan, 2000). In European countries, the main CVOCs used are dichloromethane, tetrachloroethylene and trichloroethylene (ECSA, 2017).

1.2 Abatement of volatile organic compounds

As long as the air pollutant gases are emitted, they remain a problem for human wellbeing and the environment. Researchers, policymakers and industry are engaged in decreasing the amount of hazardous materials in the atmosphere. Currently, several techniques, both primary and secondary in their nature, are used. The primary approach is related to the avoidance of the formation of emissions. However, this is not always possible. In this case, secondary methods, also called end-of-pipe techniques, need to be employed. The most commonly used secondary techniques in VOC abatement are adsorption, absorption, condensation, biofiltration, thermal and catalytic oxidation as well as membrane separation (Khan & Ghoshal, 2000; Moretti, 2001).

Catalytic oxidation is an economic and environmentally friendly abatement method, because it is an effective way to destroy volatile organic compounds (VOCs) as well as chlorinated volatile organic compounds (CVOCs) at a low temperature range (200–500 °C). It is also capable of treating diluted emission streams (Azalim, 2011; Carole, 2012; Juan R. González-Velasco, Aranzabal, Gutiérrez-Ortiz, López-Fonseca, & Gutiérrez-Ortiz, 1998; Khan & Ghoshal, 2000; Lambert, Cellier, Gaigneaux, Pirard, & Heinrichs, 2007; Ojala, 2005). Furthermore, CVOC oxidation in the presence of an efficient catalyst leads selectively to the desired reaction products, i.e. CO₂, H₂O and HCl, and the formation of harmful and toxic by-products such as dioxins can be avoided (González-Velasco et al., 2000).
1.3 Properties and catalytic oxidation of dichloromethane

In this work, dichloromethane (methyl chloride, DCM, CH₂Cl₂) was selected as the representative molecule of CVOCs. DCM is produced by two methods, the first method consists of the chlorination of methane by chlorine and the second is the chlorination of methanol by hydrogen chloride followed by the chlorination of methyl chloride (ATSDR, 2000; IARC, 2016). 100 000 to 1 000 000 tonnes per year of DCM was produced or imported by the European countries in the 2010’s (ECHA, 2017). It is an extensively used chemical in several industrial processes, and almost the whole quantity is emitted to the environment. DCM is a colourless liquid compound, having an ether-like smell. The physical and chemical properties of DCM are summarized in Table 1.

Table 1. Physical and chemical properties of dichloromethane (ECSA, 1999).

<table>
<thead>
<tr>
<th>compound</th>
<th>Molecular weight (g mol⁻¹)</th>
<th>Boiling point (°C)</th>
<th>Density (g mL⁻¹)</th>
<th>Water solubility</th>
<th>Other solubility</th>
<th>Hazards identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCM</td>
<td>84.9</td>
<td>39.8-40</td>
<td>1.325</td>
<td>13 (g L⁻¹) at 25°C</td>
<td>ethanol, ether, dimethyl formamide</td>
<td>H315, H319, H335, H336, H351, H373, R40, Xn</td>
</tr>
</tbody>
</table>

The use of DCM depends on the industrial area and purpose of use, e.g. 30% by pharmaceutical industry, 19% for paint stripping, 9% in aerosols, 10% for adhesives and 32% in different applications as foam blowing, chemical processing, metal degreasing, etc. (ATSDR, 2000; CEPA, 1993; ECSA, 1999; EPA, 2011; Krausova et al., 2006; Manahan, 1991; WHO, 2000). Long-term contact with DCM may cause dermatitis and harm to the central nervous system and liver (CDC, 2015). Additionally, the contact with DCM can cause headache, nausea, weakness, unconsciousness, drying of the skin, redness of eyes, death, etc. (CDC, 2015). The exposure limit determined by the European Union for DCM is 100 ppm for 8 h and 200 ppm for 15 min (European Commission, 2009). In the US, it has been reported that at least 14 persons have died since 2000 due to the use of DCM in bathtub refinishing with stripping agents (OSHA-NIOSH, 2013). The carcinogenicity of DCM is under discussion and recently the European Chlorinated Solvent Association (ECSA) declined re-classification of DCM from possibly carcinogenic to humans (Group 2B) to probably carcinogenic to humans (Group 2A) by the International Agency for Research on Cancer (IARC, 2016), since there are no scientific proof for its carcinogenicity. In addition, the ECSA supported a study related to DCM, which stated that there is no cancer risk to humans (ECSA, 2017). These indications show the danger of the exposure to DCM, even though...
carcinogenicity is still debated. For those reasons, the emissions of DCM should be decreased or eliminated.

During the past 20 years, increasing efforts have been taken to develop catalysts for the total oxidation of CVOCs. The following table presents some examples of previous studies related to CVOC abatement.

Table 2. Example of CVOC oxidation by catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CVOC used</th>
<th>Catalyst performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt, Pd supported on alumina</td>
<td>DCE</td>
<td>$T_{100}=325^\circ C$</td>
<td>(Juan R. González-Velasco et al., 1998)</td>
</tr>
<tr>
<td></td>
<td>TCE</td>
<td>$550^\circ C$ (99.8 and 99.9% conversion over Pt and Pd catalysts, respectively)</td>
<td></td>
</tr>
<tr>
<td>VO_{x} supported on TiO_{2}</td>
<td>O-DCB</td>
<td>$T_{100}=60^\circ C$ over 3% and 8% V/TiO_{2}</td>
<td>(Gallastegi-Villa et al., 2015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_{90}=480^\circ C$ over 1% V/TiO_{2}</td>
<td></td>
</tr>
<tr>
<td>Manganese-zirconia, Mn_{x}Zr_{1-x}O_{2}</td>
<td>DCE</td>
<td>450</td>
<td>(Jose I Gutiérrez-Ortiz et al., 2007)</td>
</tr>
<tr>
<td></td>
<td>TCE</td>
<td>$T_{100}=500-650^\circ C$; depending on the catalyst</td>
<td></td>
</tr>
<tr>
<td>Pt, Pd, Rh, V_{2}O_{5}, supported on Al_{2}O_{3}, Al_{2}O_{3}-TiO_{2} and Al_{2}O_{3}-CeO_{2} coated monoliths</td>
<td>PCE</td>
<td>72–99% conversion at around 700 °C; depending on the catalyst</td>
<td></td>
</tr>
<tr>
<td>CeO_{2} supported on alumina</td>
<td>DCM</td>
<td>$T_{100}=420-440^\circ C$</td>
<td>(Pitkäaho, Matejova, Ojala, Gaalova, &amp; Keiski, 2012)</td>
</tr>
<tr>
<td>Pt or Au supported on Ce_{0.5}Zr_{0.5}O_{2}</td>
<td>DCM</td>
<td>91–98% conversion at 500 °C</td>
<td>(Matějová et al., 2013)</td>
</tr>
<tr>
<td>HFAU containing Pt</td>
<td>DCM</td>
<td>$T_{100}=450^\circ C$</td>
<td>(L. Pinard, Mijoin, Ayrault, Canaff, &amp; Magnoux, 2004)</td>
</tr>
<tr>
<td>Pt/Al_{2}O_{3}, Al_{2}O_{3}</td>
<td>DCM</td>
<td>$T_{100}=380^\circ C$</td>
<td>(I. Maupin, Pinard, Mijoin, &amp; Magnoux, 2012)</td>
</tr>
<tr>
<td>Al_{2}O_{3}</td>
<td>DCM</td>
<td>$T_{100}=327^\circ C$</td>
<td>(Van Den Brink et al. 1998a)</td>
</tr>
<tr>
<td>Pt/Al_{2}O_{3}</td>
<td>CB</td>
<td>$T_{100}=440/270^\circ C$ in presence of heptane</td>
<td>(Van Den Brink, Mulder, &amp; Louw, 1999)</td>
</tr>
<tr>
<td>Pt/Al_{2}O_{3}</td>
<td>CB</td>
<td>$T_{100}=440/550^\circ C$ over Al_{2}O_{3}</td>
<td>(Van Den Brink et al. 1998b)</td>
</tr>
<tr>
<td>MgO/study at fixed temperature</td>
<td>TCM</td>
<td>88% conversion at 500 °C, reached 88% after 24h</td>
<td>(Weiss, Rosynek, &amp; Lunsford, 2000)</td>
</tr>
<tr>
<td>MgO, CaO, BaO, SrO, La_{2}O_{3}, CeO_{2}, PrO_{2} and NbdO_{3}</td>
<td>TCM, DCM</td>
<td>depending on the catalysts</td>
<td>(Van Der Avert &amp; Weckhuysen, 2004)</td>
</tr>
</tbody>
</table>

*) 1. The conversion did not reach 90%, Lanthanide more active than alkaline oxide after 7h of testing at 350 °C. 2. Supported oxide on Al_{2}O_{3} increase their activity but a lanthanide-based catalyst is still more active. 3. La_{2}O_{3} supported catalyst oxidize 100% of TCM, 68% of Chloroform (CHCl_{3}, CF) and 53% of DCM but the unsupported one oxidize 62, 37 and 16% of TCM, CF and DCM, respectively.
In this work, powders and monolith forms of catalysts were used. Ten catalyst supports, (Al₂O₃, TiO₂, CeO₂, MgO and (Al₂O₃)₁₋ₓ(SiO₂)ₓ (x = 5, 10, 15 mol-%)) and four active phases (Pt and V, Mn as well as Cu oxides) were used in a powder form. In addition, 200 and 600 cpsi monoliths were used. The monoliths were washcoated by (Al₂O₃)₁₋ₓ(SiO₂)ₓ (x = 5, 10, 15 mol-%) followed by wet impregnation of Pt. These materials represent different types of textural, structural and surface properties. Even though similar materials have been studied earlier, we aim to find out the effect of selected properties on DCM total oxidation to find a more optimal catalyst composition using a systematic approach. The next section will describe the aims of the current work in more detail.

### 1.4 Aims and scope

The general aim of this work is to study in detail the effect of certain physico-chemical properties of the selected catalytic materials in DCM oxidation. This study was done to find out the best catalyst compositions having industrial relevance for DCM abatement. In order to achieve the aim, the following stages were executed:

1. **Study on the effect of support properties**: preparation and characterization of oxide supports with different physico-chemical properties;
2. **Study on the effect of active phases**: wet impregnation of prepared support oxides by four different active phases, their testing and detailed characterization; and
3. **Application towards industrial scale**: washcoating and wet impregnation of ceramic monoliths by the best catalytic materials followed by testing and physico-chemical characterization.

The scope of the thesis is shown in Figure 1.
The study has been reported in three peer-reviewed articles and one submitted manuscript. In Paper I, the results related to the studies on the effect of support properties in the total oxidation of DCM are reported. For this purpose, several oxides, i.e. Al$_2$O$_3$, TiO$_2$, CeO$_2$, MgO, were prepared, followed by wet impregnation of Pt. In this paper, also the results related to the influence of Pt impregnation as well as the influence of Pt amount on the total oxidation of DCM are discussed. In the second paper (Paper II), the effect of impregnation of transition metal oxides (Cu, V and Mn) on TiO$_2$, CeO$_2$, and MgO used as supports of the studied catalysts in DCM oxidation is shown. In Paper III, the research related to Cu, V and Mn oxides continues, and the results are reported when the transition metals are supported by alumina. Paper IV focuses on the development of monolithic catalysts. In this study, ceramic monoliths are coated by (Al$_2$O$_3$)$_{1-x}$(SiO$_2$)$_x$ oxides ($x=5, 10, 15$ mol-%) followed by Pt impregnation. The study of a variety of physico-chemical properties allows understanding of the phenomena involved in the total oxidation of DCM, in particular, and reveals certain vital aspects about catalytic CVOC oxidation in general.
2 Theoretical aspect of catalyst preparation and properties of the selected materials

In general, a variety of methods exist that can be used in catalyst preparation. Industrially, the most relevant catalyst preparation methods are precipitation, sol-gel method, impregnation and washcoating of ceramic and metallic monoliths. (Hutchings & Vedrine, 2004) In laboratory-scale research, new catalyst preparation methods are constantly developed aiming to prepare more specified catalyst compositions. The catalyst preparation method affects the final catalyst properties. By selecting a suitable method, chemicals and precursors, the catalyst composition and performance can be optimized towards the wanted direction. In the preparation of materials used in this research, the mostly employed methods contain sol-gel, precipitation, impregnation and washcoating of monoliths. For this work, the sol-gel method was selected, and it is described in more detail.

2.1 Preparation of catalysts by sol-gel method

The sol-gel method, or fine chemistry, is a technique consisting of two consecutive reactions: hydrolysis and condensation (Audebert & Miomandre, 2005; C. Jeffrey Brinker & Scherer, 1990; C J Brinker et al., 1994; Campanati, Fornasari, & Vaccari, 2003; Gonzalez, Lopez, & Gomez, 1997; Narendar & Messing, 1997; Ratanakam, 2005; Yoldas, 1993). In 1846, Ebelen observed the formation of silicon dioxide from silicon alkoxide under humid atmosphere (Audebert & Miomandre, 2005; Baccile, Babonneau, Thomas, & Coradin, 2009; Pierre & Riggaci, 2011; Sachse, 2011). This was the first synthesis of silica by a method later called sol-gel. However, the first industrial use began with Schott industry (Germany) in 1930. Then, in 1939 the company submitted the first patent for manufacturing of rear view mirrors made by the sol-gel method (Collignon, 2008; Sachse, 2011). Currently, the sol-gel method is widely used due to its specific advantages. The advantages of the sol-gel method are: purity of the product, homogeneity, and controlled porosity and the ability to form a large surface area to the prepared material at low temperatures of preparation.

Two types of raw materials can be used in the sol-gel method. When the starting precursors used are alkoxides (M(OR)$_n$), the method is called organometallic preparation. In the case of using metallic salts, the method is referred to as inorganic preparation. (Azalim, 2011; Bellifa, 2009; C J Brinker et al., 1994)
As mentioned, sol-gel preparation consists of two steps. The hydrolysis step is initiated when water is added to dissolve the reactant. This step produces acidic oligomers (monomers) corresponding to the used alkoxide and the nonhomogeneous crystalline microstructure, which consist of replacing an alkoxide ligand by a hydroxyl ligand (Collignon, 2008).

\[
\text{H}_2\text{O} + \text{M(OR)}_n \rightarrow \text{H}_2\text{O-M-(OR)}_{n-1} \rightarrow \text{ROH} + \text{M(OR)}_{n-1}\text{OH} \quad (1)
\]

This step can be accelerated by adding an acidic catalyst or slowed by adding a basic catalyst during the reaction (Collignon, 2008; Gonzalez et al., 1997). The condensation step depends on the hydrolysis step. The oxolation reaction occurs if two hydroxyl (\(\text{M(OR)}_{n-1}\text{OH}\)) groups react or between hydroxyl (\(\text{M(OR)}_{n-1}\text{OH}\)) and alkoxide (\(\text{M(OR)}_n\)) groups (alcoxolation). That provides the formation of a polymer. (C J Brinker et al., 1994; Gonzalez et al., 1997; Niederberger & Pinna, 2009; Rechberger & Niederberger, 2017). The Oxolation reaction produces water as follows:

\[
\text{M(OR)}_{n-1}\text{OH} + \text{M(OR)}_{n-1}\text{OH} \rightarrow (\text{OR})_{n-1}\text{M-O-M(OR)}_{n-1} + \text{H}_2\text{O} \quad (2)
\]

The Alcoxolation reaction, on the other hand, produces alcohol as follows:

\[
\text{M(OR)}_{n-1}\text{OH} + \text{OR-M(OR)}_n \rightarrow (\text{OR})_{n-1}\text{M-O-M(OR)}_{n-1} + \text{ROH} \quad (3)
\]

The sol is produced during the hydrolysis step and partial condensation, and the gel is obtained when the condensation is progressed by the formation of a three-dimensional network of sol particles (polymers network). (Rattanakam, 2005)

The sol-gel preparation steps are influenced by pH, gelation temperature, the used alkoxide ligand, reactant stoichiometries, solvent removal and conditions during the pre-treatment step. (Gonzalez et al., 1997)

### 2.2 Shaping of the catalysts

In industrial application, the use of powder-form catalysts is not practical. For this reason, the catalysts need to be shaped. Different alternatives for the immobilization or shaping of the catalysts exist. The catalysts may appear in the form of pellets, spheres, monoliths and foams. A typical way of dispersing of a catalytically active material on a larger surface area to improve the contact with reactants and minimize the pressure drop is to coat the shaped substrates. (Tomašić & Jović, 2006, Campanati et al., 2003) In catalysis, the monolith is one solid piece with different channels (shapes and densities), which is called a support, substrate or honeycomb structure. There are two types of monoliths: metallic and ceramic.
For this study, we chose ceramic cordierite monolith \((2\text{MgO})_2\text{Al}_2\text{O}_3\text{SiO}_2\)). Ceramic monoliths are often used in industrial applications due to their numerous advantages, such as low pressure drop (large open frontal area; OFA) (Heck, Gulati, & Farrauto, 2001), insensitivity to temperature changes due to almost zero thermal expansion coefficient (Cybulski & Moulijn, 1998), lower price than that of metallic monoliths and their greater resistance in aggressive reaction medium. Cordierite allows high bonding between the substrate and coating materials. (Giroux, Hwang, Liu, Ruettinger, & Shore, 2005) Furthermore, precious metals present in the coating materials do not migrate to the cordierite substrate and the monolith material cannot migrate to the coating phase, even in severe conditions such as reducing atmosphere or in the presence of sulphur compounds. The low thermal expansion coefficient of the cordierite substrate offers a resistance to thermal shock and good stability of the washcoat. In addition, cordierite substrate has good thermal stability and it has a melting point higher than 1450 °C. (Avila, Montes, & Miró, 2005; Williams, 2001)

The geometric parameters used in connection with monoliths are:

- **Geometric Surface Area**: \[\text{GSA} \ [\text{mm}^{-1}] = 4\pi(n(d_{ch} - e_{ch}))\]  

- **Open Fraction Area**: \[\text{OFA} = n(d_{ch} - e_{ch})^2\]  

- **Thermal Integrity Factor**: \[\text{TIF} = \frac{d_{ch}}{e_{ch}}\]  

- **Mechanical Integrity Factor**: \[\text{MIF} = \frac{e_{ch}^2}{d_{ch}(d_{ch} - e_{ch})}\]

where \(d_{ch}\), \(e_{ch}\) and \(n\) are the channel size, wall thickness and channel density (number of channels per surface), respectively.

### 2.3 Properties of the used materials

For this thesis work, ten support materials and four active phases were selected based on their different physico-chemical properties. The support-oxides were initially selected due to their different acido-basic characters (aluminium, cerium, magnesium, titanium, aluminium-silicate based oxides). Platinum, as an active metal, has shown already its good activity in DCM oxidation (I. Maupin et al., 2012; Ludovic Pinard, Mijoin, Magnoux, & Guisnet, 2003, 2005, Pitkäaho et al., 2011, 2013; Wang, Sakurai, & Kameyama, 2008) (Paper I). However, Pt is an expensive noble metal, whilst active and selective, other alternatives should be found. For this purpose, copper-, manganese- and vanadium-based oxides were selected (Gu, Yang, Qiu, Sun, & Xu, 2010; J.I. Gutiérrez-Ortiz, López-Fonseca, Aurrekoetxea, &
In this section, the properties of the used materials are described in more detail.

Aluminium oxide (Al₂O₃), or alumina, is an amphoteric oxide. This means that alumina has both acidic and basic properties. Alumina appears in different phases depending on the preparation method, and especially on the calcination temperature used. The preparation of alumina can be done by thermal decomposition of boehmite (γ-AlOOH), gibbsite (γ-Al(OH)₃), bayerite (α-Al(OH)₃) and nordstrandite (Al(OH)₃), that leads to a crystalline phase of alumina (Busca, 2014; Demichelis, Noël, Ugliengo, Zicovich-Wilson, & Dovesi, 2011; Digne, Sautet, Raybaud, Toulhoat, & Artacho, 2002). The quality of the crystallinity of alumina depends on the starting materials and the decomposition temperature. Alumina appears on seven crystalline phases: chi (χ), kappa (κ), alpha (α), gamma (γ), delta (δ), theta (θ) and eta (η). The most-used crystalline phases in catalysis are γ- and η-alumina (Deutschmann, Knözinger, Kochloeff, & Turek, 2009). The objective of this work is to prepare γ-alumina with high surface area and acidic properties.

Titanium oxide (TiO₂), or titania, has two metastable crystalline phases, namely anatase (tetragonal) and brookite (rhombohedral) and they can be transformed with heating to a stable phase named rutile (tetragonal) (Deutschmann et al., 2009; Diebold, 2003). The anatase form of titania is widely used as photocatalysts, pigments, and catalysts, etc., due to its high dielectric constant, humidity and oxygen sensitivities (Rattanakam, 2005), but when it is heated it transforms to rutile, which affects critically the activity of the support. Zhang et al. (H. Zhang & Banfield, 1998) reported that the anatase phase is more stable than the rutile phase when the particle sizes of material are less than 14 nm. Thus, the anatase phase with high stability was selected to be the titania-based support material in this study.

Cerium oxide (CeO₂), or ceria, has a fluorite structure. It is a non-stoichiometric oxide due to its oxygen storage capacity (Sohlberg, Pantelides, & Pennycook, 2001). The oxygen storage capacity of ceria is caused by an easy transformation of Ce⁴⁺ to Ce³⁺ and vice-versa. It is highly used in three-way catalysis in vehicle exhaust gas treatment (Deutschmann et al., 2009) and also in the water-gas shift reaction (Rattanakam, 2005). CeO₂ presents basic properties (Deutschmann et al., 2009).

Magnesium oxide (MgO), or magnesia, is known as a basic solid with octahedral coordination between Mg and O. The ab-initio method used for orbital calculation of magnesia indicates an electronic structure of the following oxide Mg²⁺O²⁻. Deutschmann et al. (2009) reported that the existence of hydroxyl groups...
and the oxygen anion (O\(^{2-}\)) on the surface of MgO are responsible for the basic properties of magnesia. (Deutschmann et al., 2009)

Silica (SiO\(_2\)) has weak acid properties. SiO\(_2\) has a variety of crystalline structures such as quartz, tridymite, and cristobalite. Generally, the amorphous structure of silica is used in catalysis. (Deutschmann et al., 2009) In this study, the silica is used in doping of a simple oxide to optimise the physico-chemical properties of the support.

Platinum (Pt) is a noble metal and one of the platinum group metals. It presents aesthetic qualities and a permanent lustre, which makes it more interesting from a jewellery manufacturing perspective. In addition, it is receiving more interest also in catalysis applications. Most platinum used in the world is extracted by South Africa. (Gunn, 2014; Rao & Reddi, 2000; Suoranta, 2016) In catalytic reactions, it may be present in a metallic form (Pt (0)) or an oxide form in two states (PtO (+2) and PtO\(_2\) (+4)) (Rao & Reddi, 2000).

Copper (Cu) is a transition metal. Copper and copper oxides-containing catalysts are used for polymerization, isomerization and cracking reactions. It is used as mordant and oxidant in textile colouring and printing, as pigment in glass, ceramics, porcelains and varnishes. Copper exists in different oxidation states such as metallic copper (0), +1, +2 and +3. Of these, Cu\(^{+1}\)- and Cu\(^{+2}\)- based oxides are the most important ones from the commercial point of view. Cu\(^{+1}\) exists as Cu\(_2\)O with red/red-brown colour in cubic or octahedral crystal morphology and Cu\(^{+2}\) occurs as CuO with black colour in a triclinic form of crystals. (Wayne Richardson, 2012)

Vanadium (V) is a transition metal discovered by mineralogist A. M. Del Rio in Mexico in the year 1801. Vanadium is present in different oxidation states; the most widely used oxides are V\(_2\)O\(_5\) (+5), VO\(_2\) (+4), V\(_2\)O\(_3\) (+3) and VO (+2) (Weckhuysen & Keller, 2003). V\(_2\)O\(_5\) has an orange-red colour and it represents acidic properties. The crystalline form of V\(_2\)O\(_5\) is a distorted octahedron. The slight reduction of V\(_2\)O\(_5\) leads to a dark-blue oxide that is VO\(_2\). This compound has a rutile-like crystal structure. It presents amphoteric properties. V\(_2\)O\(_3\) is formed by the reduction of V\(_2\)O\(_5\) by H\(_2\) and CO. It is black, has a corundum structure and presents basic properties. The fifth oxide is a grey-coloured VO, and it possesses a deficiency rock-salt crystalline structure.

Manganese (Mn) is a transition metal existing in different oxide forms such as MnO\(_2\), Mn\(_2\)O\(_3\) and Mn\(_3\)O\(_4\). MnO\(_2\) and Mn\(_3\)O\(_4\) are metastable in air at atmospheric pressure in the temperature range between 100–900 °C and they can easily be
transformed to $\alpha$-Mn$_2$O$_3$ (Baldi, Sanchez Escribano, Amores, Milella, & Busca, 1998).
3 Experimental

Chapter 3 of this thesis will present the preparation methods of the supports and catalysts used in this study. It also gives information on the characterization methods used and explains to what purposes the revealed information was used.

3.1 Preparation of supports

Preparation of aluminium oxide (γ-Al₂O₃)

The γ-Al₂O₃ support was prepared using the sol-gel method according to Yoldas procedures (Yoldas, 1975) by using aluminium-tri-sec-butoxide (Al(O-C₄H₉)₃, Sigma-Aldrich, 97 wt-%) as a precursor. The molar ratio of Al(O-C₄H₉)₃: H₂O: HCl used for the preparation of γ-Al₂O₃ was 1:100:0.1. During the preparation, the mixture of aluminium-tri-sec-butoxide and ultrapure water was kept under stirring at 60 °C for 60 min followed by the addition of HCl in order to catalyse the condensation process. Then, the alumina sol was kept at 80 °C under vigorous stirring for 2 h after which a white gel was obtained. During preparation, the beaker was covered to minimize the evaporation of water. (Paper I and Paper III)

Preparation of titanium oxide (TiO₂)

TiO₂ gel synthesis was started by mixing titanium butoxide (Ti(OC₄H₉)₄, Sigma Aldrich, 97%) with 1-butanol and HCl. After this, the solution was hydrolysed with ultrapure water. At the end of water addition, a white gel was obtained. The molar ratio of Ti(OC₄H₉)₄:1-butanol:HCl:H₂O was 1:15:0.3:4. (Paper II)

Preparation of cerium oxide (CeO₂)

For the preparation of CeO₂, a mixture of cerium (III) nitrate hexahydrate (Ce(NO₃)₃.6H₂O, Sigma Aldrich, 99%) and absolute ethanol was maintained under stirring at 85 °C. After 15 min, the ultrapure water was added dropwise during 10 min, while continuing the stirring. Then, the sol was dried in a sand bath and during drying, the formation of a ceria gel was observed. The molar ratio used in the preparation for Ce(NO₃)₃:C₂H₅OH:H₂O was 1:14:20. (Paper II)
Preparation of Magnesium oxide (MgO)

MgO preparation was done by mixing magnesium ethoxide (Mg(C\(_2\)H\(_5\)O\(_2\)), Sigma Aldrich, 98%), absolute ethanol and water followed by the addition of oxalic acid solution (H\(_2\)C\(_2\)O\(_4\)) as a hydrolysis catalyst. The mixture was refluxed at 80 °C during 3h after which the ultrapure water was added to form the gel of MgO. The molar ratio of Mg(C\(_2\)H\(_5\)O\(_2\)):C\(_2\)H\(_6\)O:H\(_2\)O:H\(_2\)C\(_2\)O\(_4\) was 1:17:5:0.4. (Paper II)

Preparation of Alumina-silica support

(Al\(_2\)O\(_3\))\(_{1-x}\)(SiO\(_2\))\(_x\) (Al\(_{6x}\), x= 0, 5, 10, 15) supports were prepared by modifying the procedure described by Nijhuis et al. (Nijhuis, Kreutzer, Romijn, Kapteijn, & Moulijn, 2001). The starting materials were Dispersal P2 (AlOOH, 260 m\(^2\) g\(^{-1}\), Sasol Germany), urea (NH\(_2\)CONH\(_2\), Sigma Aldrich), 0.3M of nitric acid (HNO\(_3\), 65%, Merck) with the molar ratio of 2:1:5 and tetraethylorthosilicate (Si(OCH\(_2\)CH\(_3\))\(_4\), TEOS). Urea was dissolved in HNO\(_3\) (0.3 M) under high-speed stirring (1600 rpm) at room temperature. After that, the corresponding amount of TEOS, in order to obtain the desired amount of SiO\(_2\), was added followed by the addition of Dispersal P2. A white gel was obtained after vigorous stirring. (Paper IV)

Thermal treatment of the supports

The obtained sols were dried at 60 °C on a sand bath overnight followed by drying at 120 °C in a ventilated oven. After that, the dried materials were calcined at 500 °C for 6 h with 5 °C min\(^{-1}\) as the heating rate. This profile was used for all the prepared supports except Al\(_{6x}\) supports that were calcined first at 120 °C for 1 h and then at 500 °C for 2 h with 1 °C min\(^{-1}\) as the heating rate.

3.2 Impregnation of active materials

The aim was to prepare the catalysts (1 g of each) with 30 wt-% of transition metal oxides, i.e. CuO (also 10 wt-%) and MnO\(_x\), 30 and 10 wt-% of V\(_2\)O\(_5\) and 0.5 as well as 1 wt-% of platinum. The preparation of catalysts was done by wet impregnation of the active phase on the supports. Cu(NO\(_3\))\(_2\)·3H\(_2\)O (sigma Aldrich, 99.9%), NaMnO\(_4\)·H\(_2\)O (sigma Aldrich, > 97%), V(C\(_{10}\)H\(_{11}\)O\(_5\)) (Merck, > 98%) and
H$_2$PtCl$_6$·xH$_2$O (Johnson-Matthey, 99.9%) were the used precursors for wet impregnation.

The corresponding amount of the active material precursor (copper, manganese, vanadium and platinum) was dissolved in a minimum amount of ultrapure water, except the vanadium precursor, which was dissolved in methanol. Then, the calcined supports were plunged in the precursor solutions. The mixtures were kept under mechanical stirring overnight. Then, the liquid phase was evaporated on a sand bath at 60 °C followed by final drying in a ventilated oven at 120 °C. Finally, the obtained materials were calcined at 500 °C for 6 h, except the Pt-based catalysts, which were calcined for 2 h. The Pt-based catalysts were reduced after calcination in two steps. First, at 250 °C for 1 h and then at 500 °C for 2 h in a diluted stream of hydrogen (H$_2$, 1/3) in nitrogen (N$_2$, 2/3). The heating rate during the calcination and reduction steps of the catalysts was 5 °C min$^{-1}$.

3.3 Preparation of monoliths-form catalysts

Two types of monoliths were used. The first type with a channel density of 200 cpsi, is denoted by 200M in this study. The second type with a channel density of 600 cpsi is denoted by 600M. The following paragraphs describe the preparation of the monolith form catalysts.

3.3.1 Chemical treatment of monoliths

Ceramic monoliths were used as a support for the selected catalysts. At the beginning before the coating of the monoliths, they were immersed in concentrated nitric acid (65%) for 1 h in order to clean and eliminate the impurities from the channels, monolith surface and pores, to increase the specific surface area of monoliths and also to decrease the thermal expansion (TE) (Avila et al., 2005; Jiahai & Lucun, 2006). After the acid treatment, the monoliths were washed carefully with ultrapure water followed by drying in a ventilated oven at 100 °C. The dried monoliths were calcined at 300 °C for 1h. These uncoated monoliths are later called substrates.

3.3.2 Washcoating of monoliths

The cleaned substrates were coated by the AlSix (x= 5, 10, 15) sol during 1 h. Then, the coated monoliths were flushed carefully with N$_2$. This step aims to remove the
excess of sol on the surface and inside the channels of monoliths. After that, the monoliths were left at room temperature overnight for maturing. In order to avoid cracks in the washcoated phase of the monoliths, the washcoated monoliths were calcined at 120 °C for 1 h followed by increasing the temperature to 500 °C with a heating rate of 1 °C min⁻¹. The calcination was further continued at 500 °C for 2 h. These coated and calcined monoliths are denoted later as 200Mx (x= 5, 10, 15).

### 3.3.3 Addition of the active phase

In the monolith-form catalysts, Pt was used as an active phase. The target amount of the active phase was 1 wt-% of Pt per 1 g of washcoat mass (AlSix) on the monoliths. Firstly, the corresponding mass of hexachloroplatinic acid to achieve the target composition was dissolved in a minimum amount of distilled water followed by immersion of Mx in the solution. Then, the wet impregnation continued under mechanical stirring overnight at room temperature. Finally, the excess solvent was evaporated in a sand bath at 60 °C. The coated and impregnated monoliths (denoted later by PtMx) were calcined similarly than the powder form Pt-catalysts.

### 3.4 Characterization

The prepared catalysts are different from each other by their physico-chemical properties. Those properties influence catalytic activity, selectivity and stability. To find out information on the properties of the catalysts, several techniques were used to characterise the prepared materials. The used techniques are TGA-DTA, XRD, N₂ physisorption, ICP-OES, XRF, SEM, TEM, XPS, TPR, NH₃-TPD, pyridine and lutidine thermodesorption followed by FTIR analysis and Raman analysis. In addition, X-ray computed tomography (CT) was used in imaging of monolith catalysts in collaboration with GTK, Espoo, Finland.

#### 3.4.1 Thermal gravimetric and differential thermal analysis (TGA-DTA)

TGA and DTA methods give information on the variation of the physico-chemical states of samples when increasing temperature. During sample treatment, it is possible to observe exothermic and endothermic peaks, and if they are incorporated
with the loss of weight, the related phenomena are evaporation of compounds from the materials, crystallization and/or decomposition of samples. In absence of weight loss, the exotherms and endotherms are related to the phase changes in the material.

TGA and DTA curves of non-calcined support materials were drawn using SDT 2960 TA and STA 449-F3 analysers. Prior to the experiments, the samples were dried and packed into a Pt crucible. The weights of the samples were between 20 and 30 mg. Samples were analysed with a heating rate of 10 °C min⁻¹ from 25 to 1000 °C under air flow (100 mL min⁻¹).

The aim of the TGA-DTG analyses was to understand the behaviour of the prepared powder in air-atmosphere when the temperature rises. The most important information that needs to be drawn from this analysis, is to find out the adequate temperature of calcination to reach the desired oxide.

### 3.4.2 X-ray diffraction (XRD)

The XRD measurement is used to study structural properties of the catalytic materials by using monochromatic X-ray. The diffracted rays give information about different crystalline phases existing in the sample. The identification of the obtained phase is done utilizing the JCPDS (Joint Committee on Powder Diffraction Standards) library.

The XRD diffractograms were obtained with a BRUKER-5500 and Rigaku SmartLab 9 kW diffractometers using Cu and Co radiation with a wavelength of $\lambda_{\text{Cu}} = 0.15406$ nm and $\lambda_{\text{Co}} = 0.178901$ nm in addition to a graphite monochromator for eliminating $K_\beta$ radiation and fluorescence. The samples were scanned in a range of $2\theta$ from 5° to 90° with a rate of measurement of 0.04°/2 s. The diffraction patterns obtained were compared with the library data from JCPDS. Data handling was carried out using the software package HighScore plus. The size of the crystallites was determined from the full width at half-maximum (FWHM) $\beta$, (area/height) of the different peaks using the Scherrer equation:

$$D = \frac{K \lambda}{\beta \cos \theta}, \text{ with } \beta = (\beta_{\text{exp}}^2 - \beta_{\text{std}}^2)^{1/2}$$

where $K$ is constant, $\theta$ (°) is the Bragg angle, $D$ (nm) is the mean size of the crystallites, $\beta$ (°) is the corrected integral for FWHM, $\beta_{\text{exp}}$ (°) is the experimental value measured for a peak with high intensity and $\beta_{\text{std}}$ (°) is the standard value measured for LaB₆ (error of the apparatus).
The XRD analysis was used in this study to identify the crystalline phases present in the used materials and to get an estimation of the crystal sizes.

3.4.3 Nitrogen physisorption

Nitrogen physisorption is a technique that allows determining the specific surface area and certain information on the porous structure of the high surface area materials, such as catalysts and adsorbents. In this study, the specific surface areas and pore volumes were determined by nitrogen adsorption–desorption isotherms at -196 °C using Micromeritics TriStar 3000 and ASAP 2020 instruments. The BET theory (Brunauer, Emmett, & Teller, 1938) was used to determine the surface area ($S_{BET}$) and the BJH equation was used to determine the pore size distribution. The volume of a pore is calculated based on a high value of P/P$_0$ with the assumption that the pore geometry is cylindrical. Prior to N$_2$ adsorption, the samples were degassed under a vacuum at 250 and 350 °C during 2 h.

Nitrogen physisorption was used to define the specific surface areas, pore size and pore volume of the materials. This information is relevant, since high surface area of the material allows high dispersion of active phase when the active material is added to the supports. This can allow as well more active sites for the reaction. The differences in the porous structure and the surface area may explain the differences in catalyst performance in the DCM oxidation reaction.

3.4.4 Elemental analysis (ICP-OES, XRF)

The elemental analysis permits determination of the amounts of different elements existing in the materials. A Perkin Elmer Optima 2000 DV was used in inductive coupled plasma optical emission spectroscopy (ICP-OES) analyses. The mineralization was done as follows: at first, nitric acid (HNO$_3$, 65%), hydrochloride acid (HCl, 37%) and hydrofluoric acid (HF, 70%) were mixed with the catalyst to form a suspension. The mineralization was carried out in a microwave oven of 1000 W for 1h. After that, boric acid (H$_3$BO$_3$ 40 g L$^{-1}$) was added to form a complex with the excess of hydrofluoric acid. The complexing took place at the microwave oven operating at 1000 W for 30 min.

The XRF analyses were done with a PANalytical Axios-MAX apparatus equipped with a rhodium anode as a standard. In order to enhance the sensitivity, the power was fixed at 3 kW (60 kV, 50 mA). Prior to the analysis, the samples were diluted in an x-ray flux 66:34 (Lithium Tetraborate/Lithium Metaborate:...
66%/34%, PANalytical) followed by melting this mixture at 1150 °C in a PANalytical-Eagon 2 device to obtain a glass disc. The results of elemental analysis were used in the evaluation of the real amount of different oxides/elements in the prepared catalysts.

3.4.5 Temperature programmed reduction with hydrogen (H2-TPR)

Temperature programmed reduction by H2 gives information about the reducibility of the material at different temperatures. The characterization of the samples was done using an AutoChemII 2920 device. The samples (about 0.2 g) were placed in a U-shaped reactor and oxidized with O2 in order to clean the sample surface and ensure the oxide-form of the materials. The oxidation was realized from room temperature (RT) to 500 °C at 5 °C min⁻¹ under a flow of 50 mL min⁻¹ of pure O2. Then, the samples were cooled to RT under the flow of O2 followed by flushing with Ar before the actual TPR experiment. The H2-TPR was carried out with 1% H2 in Ar using the same heating profile as in the oxidation. During the experiment, the H2 consumption was analysed by a TCD detector.

The results of H2-TPR experiments were used to evaluate the reducibility of materials and the temperature needed for material reduction. This analysis gives information on the oxidation state of the sample.

3.4.6 Scanning and Transmission Electron Microscopes (SEM-TEM)

Electron microscopy, in general, gives information on the morphology of materials. SEM and TEM methods were used to determine morphology as well as sizes and shapes of the particles in the powder and shaped forms of catalysts. This information is relevant in the determination of the ability of gas molecules to be in contact with the active sites. SEM was used to also to verify the quality of the coating on the monoliths.

Field Emission Scanning Electron Microscopy (FESEM) was used in the surveying of the monolith-form catalysts. The FESEM images were obtained by a ZEISS ULTRA PLUS device equipped with an Energy-Dispersive X-ray Spectrometer (EDS) at an accelerating voltage of 15.0 kV. Prior to taking the images, the monoliths were cut to fit in the FESEM chamber and coated to avoid sample charging. This analysis was done to verify the morphology of the coated phase AlSix on the monolith and its composition.
The TEM images were obtained by a JEOL 2100 UHR electron microscope, equipped with an Energy dispersive X-ray spectrometer (EDS). The catalyst was ultrasonically dispersed in ethanol, and the suspension was deposited on an aluminium grid coated with a porous carbon film. The particle size distribution of the active phase (Pt) on the support was obtained from the TEM images, and the average particle diameter \( (d_p) \) was calculated by using the following equation:

\[
d_p = \frac{\sum n_id_i^3}{\sum n_id_i^2}
\]

(9)

where \( n_i \) is the number of particles with the size \( d_i \).

### 3.4.7 Raman spectroscopy

The Raman spectra were obtained by using a Timegated® 532 Raman Spectrometer equipped with 532 nm pulsed laser and CMOS SPAD avalanche detector. The advantage of this device is that it allows suppression of the possible fluorescence interference. The spectra were collected in the window from 200 to 1200 cm\(^{-1}\) with a spectral resolution of 10 cm\(^{-1}\). Raman analysis was used to check the presence of chlorine in the case of Cu- and Mn-based catalysts.

### 3.4.8 X-ray photoelectron spectroscopy analysis

The X-ray photoelectron spectroscopy (XPS) analysis can be used in the determination of chemical composition and oxidation state of elements on the surface of the samples (ESCA, 2017). The XPS study was done for the catalysts before and after the activity tests. The analysis was performed with a Thermo Fisher Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy system equipped with Al Ka X-ray source = 1486.7 eV. The X-ray source operated at 10 mA and 12 kV. The spectral regions corresponding to Cl 2p, Pt 4f, Ti 2p, Ce 3d and O 1s core levels were recorded for each studied sample. The static charge of the samples was corrected by referencing all binding energies (BE) of TiO\(_2\)-based catalysts to the C1s peak (285 eV). Ce 3d3/2 peak at 916.8 eV was used by Qui et al. (Qiu, Liu, Zhao, Ma, & Yao, 2006) as a reference for the CeO\(_2\) sample since the C1s peak (285 eV) is weak for the sample due to contamination. Therefore, the Ce 3d3/2 peak at 916.8 eV was used for the calibration of the charging shifts of the spectra of the CeO\(_2\)-based catalysts.
The XPS analysis gave information for the current research about the oxidation state and the existence/absence of chlorine on the surface of catalysts after testing the catalysts in DCM oxidation.

### 3.4.9 Acidity measurement

Acidity of a catalyst is an important characteristic that affects catalyst activity. Different types of acid sites exist, which are called Lewis and Brønsted acid sites. For the determination of the total acidity and quality of the acid sites, several approaches are available. In this study, NH$_3$-TPD was used for the determination of total amount of acid sites and acid strength. However, this method cannot reveal information about the type of acid sites (Lewis and Brønsted). In order to obtain the nature of surface acidity, additional characterization was done by using pyridine and lutidine as the probe molecules. Pyridine is more sensitive to Lewis acid sites (LAS) and lutidine to Brønsted acid sites (BAS). Pyridine and lutidine thermal desorption followed by FTIR can give an idea about the nature, amount and strength of the acid sites of the used materials.

#### Temperature programmed desorption of ammonia (NH$_3$-TPD)

NH$_3$-TPD was done with an AutoChemII 2920 device. Prior to the analysis, the sample (0.05–0.2 g) was heated in a He flow from RT to 500 °C with a 5 °C min$^{-1}$ temperature rise and kept at maximum temperature for 30 min. Then, the sample was cooled down to RT under a flow of He followed by ammonia (15% NH$_3$ in He) adsorption for 60 min. After the adsorption, the sample was flushed with He for 30 min to remove the physisorbed ammonia. The NH$_3$ desorption took place from RT to 500 °C using the heating rate of 5 °C min$^{-1}$. The concentration of the desorbed NH$_3$ was analysed with a TCD detector.

The information from the NH$_3$-TPD analysis was used in the quantification of the total acid sites and the strength of acid sites of the samples.

#### Thermodesorption of pyridine and lutidine followed by Fourier transform infrared (FTIR) spectroscopy

Lutidine and pyridine desorption were done for the powder-form catalysts. Prior to the experiments, the samples were compressed (2 tons) to obtain a self-supporting wafer (16 mm of diameter), which was then placed in an IR cell coupled to a
vacuum system. The IR cell was then evacuated at 450 °C overnight to clean the sample surface. At the beginning of the experiment, the reference spectrum was recorded before introduction of 2 mbar of the probe molecule (pyridine or lutidine for 10 and 5 min, respectively) to the IR cell at room temperature. Then the IR cell was evacuated to eliminate the physisorbed molecules. The IR spectra were recorded in-situ during desorption of the probe molecule at different temperatures. Before recording the spectra, samples were evacuated (pyridine and lutidine for 20 and 30 min, respectively) at each temperature (at room temperature, 50 °C and then with 50 °C steps to 450 °C). The spectrometer used was a Thermo Nicolet-Nexus FTIR instrument and the data was analysed using OMNIC software.

### 3.5 Activity tests

The DCM oxidation experiments were carried out in a vertical fixed-bed continuous flow reactor operating under atmospheric pressure. Due to corrosive reaction products, all the materials used in the experimental set-up (Pitkäaho et al., 2012) are corrosion resistant: quartz glass, heated Teflon piping (T=180 °C) and Teflon connectors. In the vaporizer unit, liquid DCM and water were fed with syringe pumps equipped with gas tight syringes to the heater, where the DCM vapour was mixed with air coming from a mass flow controller. The preheating oven was set to 150 °C to ensure the mixing and evaporation of gases.

The gas analysis during the experiments was done with a Gasmet DX-4000N FTIR analyser (Figure 2), which is able to measure almost all gas phase compounds excluding noble gases and diatomic mononuclear compounds such as O$_2$, N$_2$ and Cl$_2$. The analyser was calibrated to detect the following chlorinated hydrocarbons: C$_2$Cl$_4$, C$_2$HCl$_3$, CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, COCl$_2$ and HCl. The analyser consists of a high temperature sample cell, a temperature controlled MCT-detector, and signal processing electronics. Calcmet for Windows analysis software was used to analyse the spectra.

The DCM (Sigma Aldrich, Algol) concentration was 500 ppm in all the activity tests performed in the presence of 1.5 vol-% of water to ensure the sufficient selectivity towards HCl (Pitkäaho et al., 2012, 2013). The total flow of the reaction mixture (DCM, H₂O and air) was set to be 1.02 L min⁻¹ through the catalyst bed of 0.1 and 0.4 g giving a GHSV 704 867 and 143 790 h⁻¹, respectively.

The temperature range during the light-off test was from 100 to 500 °C with 5 °C min⁻¹ as the heating rate. The tests were always repeated with the same sample at least once to verify the results. Prior to the experiment, the samples were sieved in order to have the particle diameter between 0.25 and 0.5 mm.

Prior to the activity tests over the prepared samples, a thermal oxidation test was done without a catalyst and a diffusion study was done to verify the effect of catalyst particle size during the DCM conversion. The diffusion tests were carried
out over three different types of samples of $\gamma$-Al$_2$O$_3$. The change in the particle size between two samples was related to the determination of the internal diffusion effects, and the study on the external diffusion was done with two samples having different masses, but the same particle size. For these tests, the GHSV was kept constant and it was equal to 264 325 h$^{-1}$. The constant GHSV was obtained by changing the flow rate only for a sample with a higher weight to 1250 L min$^{-1}$.

In order to study the durability of the most active catalyst, an extended test was done. This test started with a light-off test in the temperature range from 100 to 500 °C, after which the temperature was fixed at 400 °C. At the end of each testing day, the feed and oven were switched off and the next day the test was continued at 400 °C. After 55 h of testing, a light-off test was done again from 100 until 500 °C, in order to make comparison between the initial and final state of the catalyst.

### 3.6 Modelling

The modelling was done using HSC Chemistry 6 software to check the stability of the metal oxides in presence of chlorine compounds. The Gibbs energy minimization method was used for calculation of the equilibrium composition as a function of temperature. The modelling conditions were adjusted to represent the experimental conditions of DCM oxidation. The used feed concentrations were 500 ppm of DCM, 1.5 vol-% of H$_2$O, which corresponded to 0.48 and 15 mol, respectively. In addition, 200 mol of O$_2$ was used as an oxidant and the mixture was adjusted with N$_2$ to reach 1000 mol (total feed). The simulation was done in the presence and absence of water in the feed. In the absence of water N$_2$ was added to adjust the total feed. In the second case, also the observed reaction by-products were taken into account. The amounts of by-products used in the modelling were: 4.8 mmol CH$_2$O, 4.8 mmol CH$_3$Cl and 7.7 mmol CO. The amounts were calculated based on the maximum production of the by-products and 60% conversion of DCM (192.0 mmol). In this case, also HCl was considered to be present in the feed. The amount of HCl used in the modelling was 270.7 mmol. In all the modelling cases the products were: H$_2$O, CO$_2$, HCl, Cl$_2$ in addition to feed compounds. The studied oxides were MgO (1.8 mol; 70 wt-%), CuO (1.50, 0.50 and 0.25 mol), MnO$_2$ (1.3, 0.46 and 0.23 mol) and V$_2$O$_5$ (0.66, 0.22 and 0.11 mol); the molar amounts of CuO, MnO$_2$ and V$_2$O$_5$ corresponded to 30, 10 and 5 wt-% loadings.

In the following chapters of the thesis, the results presented in publications I – IV are summarized and discussed. Some new supporting results are as well presented to clarify the already published results.
4 Effect of supports properties in the total oxidation of DCM

The results represented in this chapter are related to Papers I, II and III. Later in this chapter $\gamma$-Al$_2$O$_3$, CeO$_2$, TiO$_2$ and MgO are denoted as Al, Ce, Ti and Mg, when convenient.

4.1 Characterization of supports

Structural and textural characterization

The TGA-DTA profiles of the supports show different stages in the weight loss, which correspond to evaporation of H$_2$O and organic substances (coming from the precursor). These losses were observed as endothermic peaks. With TiO$_2$, the weight loss between 100 and 400 °C was indicated by an exothermic peak at around 240 °C. This phenomenon was related to the loss of crystalline water and formation of amorphous TiO$_2$. Above 500 °C, the weight loss was only about 1% or less. This temperature was, thus, chosen for the support calcination in order to obtain the desired oxides.

The XRD diffractograms of simple supports (Al$_2$O$_3$, TiO$_2$, CeO$_2$ and MgO) reveal the formation of $\gamma$-Al$_2$O$_3$, anatase for TiO$_2$, cerianite for CeO$_2$ and periclase for MgO (Figure 3). These oxides crystallize in cubic face centred structures except anatase, which is present in a tetragonal structure. Additionally, an amorphous phase was observed in high amounts in $\gamma$-Al$_2$O$_3$. The approximate crystalline size of different supports calculated by the Scherrer relation was less than 20 nm. The increase in the crystalline size follows the order: Al < Ce < Ti < Mg (Table 3).

Table 3. Physico-chemical properties of prepared materials.

<table>
<thead>
<tr>
<th>Support</th>
<th>$N_2$-Physisorption</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_{BET}$ (m$^2$ g$^{-1}$)</td>
<td>$D_p$ (nm)</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>255</td>
<td>6</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>89</td>
<td>13</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>75</td>
<td>9</td>
</tr>
<tr>
<td>MgO</td>
<td>64</td>
<td>11</td>
</tr>
</tbody>
</table>

$S_{BET}$: specific surface area, $D_p$: average pores size and $D$: approximate average size of crystallites determined by XRD.
Fig. 3. Diffractograms of simple supports analysed by XRD technique: (a) MgO, (b) CeO$_2$, (c) Al$_2$O$_3$ and (d) TiO$_2$.

The isotherms of physisorption of nitrogen at -196 °C are of the Type IV according to the IUPAC classification. The Type IV isotherm shows that the used supports are mesoporous. This is confirmed by the size of the pore diameter, which is in the range of mesoporous materials (2-50 nm). In addition, the low consumption of nitrogen at low relative pressures ($0 < P/P_0 < 0.1$) indicates the absence of microporous materials. However, there are some visible differences between the adsorption-desorption isotherms of the studied supports related to the shape of the hysteresis loops. The TiO$_2$ and $\gamma$-Al$_2$O$_3$ samples exhibit a H2 type shape indicating that these materials contain a more complex pore structure (e.g., pore blocking/percolation). The Type H1 that is generally associated with porous materials exhibiting a homogenous distribution of relatively uniform (cylindrical-like) pores is obtained for CeO$_2$. The hysteresis loop for the MgO sample is of the
Type H3 that denotes the absence of an adsorption limit value at high P/P₀ (Figure 4). This can, for instance, be caused by assemblages of the slit-shaped pores, and in principle, should not be expected to provide a reliable pore size distribution. (Sing et al., 1985; Thommes, 2004) (Paper I)

As can be seen in Table 3, the specific surface area (calculated by the BET method) is the highest for γ-Al₂O₃ followed by that observed for CeO₂, then TiO₂ and finally MgO. These results are in accordance with the results obtained from the XRD analysis. The higher surface area corresponds to a smaller crystalline size of materials.

Fig. 4. Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms at -196 °C of simple supports.

Temperature programmed reduction (H₂-TPR) of supports did not show clear reduction peaks except for ceria with a maximum at around 430 °C. This peak is related to the surface reduction of Ce⁴⁺ to Ce³⁺, which is in agreement with the previous findings (Barrabès et al., 2009; H.-H. Liu et al., 2014; Watanabe, Ma, & Song, 2009; Zhu, Qin, Shan, Shen, & Wang, 2004). A small broad peak was observed in the case of TiO₂ at around 450°C, which is in agreement with the finding of Zhu et al. (2004) where they observed two small peaks of reduction of the TiO₂ support appearing at 575 and 615 °C.
Fig. 5. H₂-TPR profiles of the prepared supports, where Al, Ti, Ce and Mg are Al₂O₃, TiO₂, CeO₂ and MgO, respectively (Paper I, Published by permission of Elsevier).

Acidity determination

NH₃-TPD thermodesorption analysis was done for all the prepared simple oxides. The obtained results are displayed in the next figure and they reveal that the total amount of acid sites on γ-Al₂O₃ is much higher than that of other oxides and the order of the obtained amount is as follows: Al > Ti > Ce > Mg. The total acidity has no correlation with the specific surface area. To evaluate the nature of the acid sites, pyridine and lutidine thermodesorptions were done and the results are discussed hereafter.
Pyridine thermodesorption followed by FTIR analysis was used to quantify and qualify the acid sites present on the studied single oxide supports. Pyridine coordinated to acid sites is observed in the range of wavenumbers between 1700 and 1400 cm\(^{-1}\). Pyridine coordinated to Lewis acid sites is revealed with bands in the range of 1445–1460 (\(\nu_{19b}\) ), 1478–1490 (\(\nu_{19a}\) ), 1575–1585 (\(\nu_{8b}\) ), 1602–1632 (\(\nu_{8a}\) ) cm\(^{-1}\) and when it is coordinated to Bronsted acid sites, the bands at 1530–1550 (\(\nu_{19b}\) ), 1470–1490 (\(\nu_{19a}\) ), 1600–1613 (\(\nu_{8b}\) ), 1631–1640 (\(\nu_{8a}\) ) cm\(^{-1}\) are observed. The Al\(_2\)O\(_3\) support showed bands at 1448 (\(\nu_{19b}\) ), 1493 (\(\nu_{19a}\) ), 1577 (\(\nu_{8b}\) ), 1614 and 1621 (\(\nu_{8a}\) ) cm\(^{-1}\). These bands were attributed to pyridine coordinated to Lewis acid sites on the surface (Can et al., 2007; Ellassal et al., 2011; Poupin, Maache, Pirault-Roy, Brahmi, & Williams, 2014; Prescott et al., 2005; Sadiq et al., 2011; Scire, Crisafulli, Maggiore, Mimicò, & Galvagno, 1998; Zaki, Hasan, Al-sagheer, & Pasupulety, 2001). The \(\nu_{8a}\) bands were assigned to pyridine coordinated to tetrahedral Al\(^{3+}\) (1621 cm\(^{-1}\), strong LAS) and to both tetrahedral and octahedral Al\(^{3+}\) (1614 cm\(^{-1}\), both medium and weak LAS) (Can et al., 2007; Poupin et al., 2014; Prescott et al., 2005). Those bands (\(\nu_{19b}, \nu_{19a}, \nu_{8b}, \nu_{8a}\) ) were also observed for other supports at around 1444, 1475, 1490 and 1600 cm\(^{-1}\), indicating the presence of LAS on the surface of the supports. In addition, thermal desorption of pyridine from TiO\(_2\).
presented another band at 1640 cm\(^{-1}\), which may also be attributed to pyridine coordinated to LAS due to the absence of another band in the range between 1540 and 1530 cm\(^{-1}\) (Zaki et al., 2001).

The vibration band \(\nu_{19b}\) is used to calculate the amount of acidity of LAS by using molar adsorption coefficient values \((\varepsilon = 1.28 \text{ cm mol}^{-1})\) (Guisnet, Ayrault, & Datka, 1997). The amount of LAS calculated as a function of temperature is drawn in Figure 7.

![Fig. 7. Evolution of support Lewis acid sites as a function of temperature measured by pyridine thermodesorption.](image)

As can be seen from the presented results, only Lewis acid sites were observed and the pyridine molecule is known to be more sensitive to Lewis acid sites than to Brønsted acid sites. In order to reveal the existence of Brønsted acid sites, an additional acidity measurement was done with lutidine (Figure 8). When lutidine is coordinated to Lewis acid sites on the surface, the bands appear in the wavenumbers at 1410 (\(\nu_{19b}\), 1477 (\(\nu_{19a}\), 1580 (\(\nu_{8b}\), 1595–1620 (\(\nu_{8a}\) cm\(^{-1}\) and coordination to Brønsted acid sites releases bands at 1415 (\(\nu_{19b}\), 1473 (\(\nu_{19a}\), 1625–
1630 ($v_{8b}$), 1640–1655 ($v_{8a}$) cm$^{-1}$. The lutidine thermodesorption revealed the presence of LAS and BAS for Al$_2$O$_3$ and TiO$_2$. The LAS amount is the highest over Al$_2$O$_3$ and BAS is the highest on TiO$_2$. CeO$_2$ has LAS only up to 200 °C. A small amount of weak BAS was observed on MgO up to 150 °C.

![Graph showing the amount and nature of acid sites at different temperatures determined by thermodesorption of lutidine.](image)

**Fig. 8.** Amount and nature of acid sites at different temperatures determined by thermodesorption of lutidine.

### 4.2 Performance of the supports in the oxidation of DCM

In this section, the activity tests over the prepared single supports will be discussed. In the beginning, certain preliminary tests were done to verify the effect of diffusion, GHSV and water, and a homogeneous test to verify the thermal decomposition of DCM in the absence of a catalyst.

**Effect of water**

Two tests were done with and without water to check the effect of water addition to the reagent mixture. The first remark was that water does not influence the DCM
conversion. The second one was the decrease in the amount of CO and CH$_3$Cl after the introduction of water vapor. The final remark was that the presence of water increases the formation of HCl and CH$_2$O. As reported earlier, the H$_2$-rich reaction medium (water, toluene...) (Pitkäaho et al., 2012, 2013; Wang et al., 2008) directs the Deacon’s reaction towards the formation of HCl instead of the formation of Cl$_2$ via the Deacon reaction:

$$\text{HCl} + \text{O}_2 \leftrightarrow \text{Cl}_2 + \text{H}_2\text{O}$$

(10)

Internal and external diffusion

The effect of internal and external diffusion was evaluated by activity tests. In the experiments, Al$_1$ has the particle size of 0.25–0.5 mm and Al$_2$ has the particle size of 0.5–1.19 mm. The mass of the sample was the same, i.e. 200 mg. The Al$_3$ sample has the same particle size than Al-1, but the mass of the sample used in the experiment was 244 mg. The activity test results (DCM conversion and HCl yield) are different between Al-1 and Al-2 (Figure 9), which means that internal diffusion influenced the DCM oxidation results. On the contrary, the test results over Al-1 and Al-3 are almost similar, which means that the external diffusion did not affect the DCM oxidation. To avoid the influence of internal diffusion on the test results, the particle size between 0.25 and 0.5 mm was used in all the experiments.
DCM oxidation over simple support oxides

In the DCM oxidation over simple oxides, thermal conversion (blank test, test without catalysts, HT) was first studied. As can be seen in Figure 10, a low conversion, less than 10%, is reached at high temperatures (500 °C). MgO presents also a low DCM conversion of around 16%. The highest conversion was reached over \( \gamma \)-Al\(_2\)O\(_3\) followed by TiO\(_2\) and CeO\(_2\) and the T\(_{50}\) temperatures (the temperature of 50% DCM conversion) were at around 345 °C, 375 °C, and 400 °C, respectively. From the characterization results, it is known that CeO\(_2\) has better reduction properties (H\(_2\)-TPR) compared to the other supports. In the case of specific surface area, it is the second best after \( \gamma \)-Al\(_2\)O\(_3\). The acidity order is as follows: Al > Ti > Ce, which suggests that one of the key parameters affecting DCM oxidation is the presence of acid sites on the surface of the materials. (Paper I) The following subchapter will focus on the discussion of the HCl yield and by-products formation as a function of DCM conversion.
Fig. 10. DCM conversion over the prepared supports where HT is the thermal test, DCM 500 ppm, H₂O 1.5 vol-%, and GHSV 143793 h⁻¹ where Al, Ti, Ce and Mg are γ-Al₂O₃, TiO₂, CeO₂ and MgO, respectively; temperatures correspond to 90% of DCM conversion (Modified from Paper I).

Selectivity

The DCM conversion over γ-Al₂O₃ and TiO₂ gives a higher HCl yield than over CeO₂ and MgO (Figure 11). The homogenous reaction shows a very low HCl formation, i.e. 3%, which was maximum at 500 °C. The HCl yield at high temperatures (> 440°C) increases more significantly over TiO₂ than over γ-Al₂O₃. This can be due to the desorption of chlorine from the surface, which further reacts to HCl in the presence of water (Deacon reaction).

In the case of MgO, a low DCM conversion leads to a very low HCl yield. Interestingly, Fenelonov et al. (Fenelonov et al., 2001) observed earlier a high conversion of 1-chlorobutane over MgO and they concluded that the conversion occurs via two mechanisms, i.e. simultaneous dehydrochlorination of 1-chlorobutane and formation of MgCl₂ from MgO in the presence of HCl originating from dehydrogenation:

\[
\text{MgO} + 2\text{HCl} \leftrightarrow \text{MgCl}_2 + \text{H}_2\text{O} \quad (11)
\]
Fenelonov et al. (2001) reported that MgCl$_2$ is an active catalyst for the dehydrochlorination reaction in their experimental conditions. In order to verify this observation, thermodynamic modelling related to MgCl$_2$ formation was done by the HSC software using our experimental conditions (Paper II) and by considering that DCM is converted completely to HCl. The total decomposition of MgCl$_2$ and the formation of MgO were observed at temperatures below 220 °C. In our case, HCl was produced at a temperature of around 280 °C, which means that the MgCl$_2$ formation is not thermodynamically possible at that temperature. If MgCl$_2$ is the active phase for CVOC oxidation, the absence of chloride in our case might explain the low activity.

To understand the effect of surface area, a commercial $\alpha$-Al$_2$O$_3$ (2.5 m$^2$g$^{-1}$) and prepared $\theta$-Al$_2$O$_3$ (118.5 m$^2$g$^{-1}$) by calcination of $\gamma$-Al$_2$O$_3$ were tested in the DCM oxidation and the results were compared to those obtained by $\gamma$-Al$_2$O$_3$ (255 m$^2$g$^{-1}$). The first remark was the large difference in the DCM conversion and the HCl yield between $\alpha$-Al$_2$O$_3$ and other samples. The second remark was that $\gamma$- and $\theta$-Al$_2$O$_3$ have a small difference in the DCM conversion and HCl yield. Accordingly, in our study, the difference in the surface areas of the studied supports does not affect markedly the DCM conversion and the HCl formation (Paper I).

![Figure 11](image-url)  
*Fig. 11. HCl yield over the prepared supports. The same experimental conditions were used as in Fig. 10 (Modified from Paper I).*
The main by-products observed in the DCM oxidation were CO, CH$_3$Cl and CH$_2$O (Figure 12). CeO$_2$ produces less by-products than the other supports probably due to its good redox properties. In practice, only CO is observed in significant amounts. It has been demonstrated in Paper I, that CH$_3$Cl is observed when DCM reacts on the Lewis acid sites. In contrast, CH$_2$O is produced on the Brønsted acid sites. This finding was in accordance with the previous research showing that the nature of acid sites determines the nature of by-products formed. (L. Pinard et al., 2004) In our case, $\gamma$-Al$_2$O$_3$ contained more Lewis acid sites than Brønsted acid sites, and it produced higher amounts of CH$_3$Cl than CH$_2$O. The situation was opposite in the case of TiO$_2$.

![Fig. 12. By-product formation over the prepared supports. The same experimental conditions were used as in Fig. 10.](image)

4.3 Conclusion

The desired support oxides, *i.e.* the gamma phase of Al$_2$O$_3$, the anatase phase of TiO$_2$, the cerianite phase of ceria and the periclase phase of magnesia, were obtained at 500 °C as the calcination temperature verified by XRD. $\gamma$-Al$_2$O$_3$ had very high specific surface area (255 m$^2$/g) compared with other single oxides,
which had surface areas less than 100 m$^2$/g. The order of specific surface area is the following: Al > Ce > Ti > Mg. All the prepared supports were mesoporous. The acidity analyses done by the thermal desorption of NH$_3$, pyridine and lutidine revealed that all oxides have acid sites and the order from the highest amount to the lowest is Al > Ti > Ce > Mg. $\gamma$-Al$_2$O$_3$ and TiO$_2$ had both acid sites (Lewis acid site, LAS and Brønsted acid sites, BAS), however, $\gamma$-Al$_2$O$_3$ had more LAS and TiO$_2$ had more BAS when they were compared to each other. A low amount of weak BAS was observed for MgO. CeO$_2$ had only LAS sites. The order of single oxides based on the total acidity is independent of the specific surface area of the oxides.

The results of activity experiments showed that the highest conversion of DCM, i.e. higher than 90%, was reached over $\gamma$-Al$_2$O$_3$, TiO$_2$ and CeO$_2$, but over the MgO support and the homogenous test, low conversion values were obtained (the maximum was less than 20% at 500 °C). The ranking of the activity of the supports follows the same order as the classification of supports’ acidity. This remark is valid also for the selectivity towards HCl formation. CO, CH$_2$O and CH$_3$Cl were the major by-products observed during the DCM oxidation and their amounts depended on the support properties. The most abundantly existing by-product was CO. CH$_2$O was obtained when the Brønsted acid sites were present on the surface while CH$_3$Cl was obtained in the presence of Lewis acid sites. The high reducibility of ceria might be beneficial for the selectivity as this support led to the formation of insignificant amounts of CH$_2$O and CH$_3$Cl.

Due to the formation of high amounts of by-products, it is evident that using single oxides as the catalysts in DCM oxidation is not enough, even though rather high DCM conversions can be achieved. In this case, we can also observe that materials used as catalyst supports are not inert but play an important role in DCM oxidation.
5  Effect of active phases on total oxidation of DCM

In the previous chapter, the effects of physico-chemical properties of different supports on the total oxidation of DCM was studied. Rather good DCM conversions and HCl yields were obtained over some of the studied supports. The good results were, however, accompanied by the formation of undesired products such as CO, CH\textsubscript{3}Cl and CH\textsubscript{2}O with significant amounts. In order to minimize their formation and orientating DCM conversion towards the most desired compounds, i.e. HCl and CO\textsubscript{2}, the studied supports were wet impregnated by noble and transition metals. The related results on the effect of impregnation of different active phases on the supports in the oxidation of DCM are reported hereafter. Firstly, the results of physico-chemical characterization are shown followed by the study on the catalyst performance in DCM oxidation (Papers I, II and III).

5.1  Platinum

Noble metals are well known as active catalysts in CVOCs’ oxidation and particularly in the oxidation of DCM. Furthermore, their ability to minimize by-product formation has been noted. The earlier results show that platinum-based catalysts are more active and more extensively used catalysts compared to other noble metals (Padilla et al. 1999; Corella et al. 2000; Pinard et al. 2003; Pinard et al. 2004; Maupin et al. 2012; Pitkäaho et al. 2013). In the current work, the prepared supports were impregnated by Pt and their performance was studied in the DCM conversion. The abbreviations PtAl, PtTi, PtCe and PtMg are used as notations of Pt/Al\textsubscript{2}O\textsubscript{3}, Pt/TiO\textsubscript{2}, Pt/CeO\textsubscript{2} and Pt/MgO, respectively, in the following chapters.

5.1.1  Characterization

In the characterization of Pt catalysts, several methods were used. The Pt amount on impregnated catalysts was verified by ICP, and it was quite similar to the target loading (0.5 wt-% per gram of catalyst), except on Al\textsubscript{2}O\textsubscript{3} that had a Pt loading of 0.7 wt-% (Paper I). Due to the low loading of Pt, it was not observed in the XRD analysis and the diffractograms achieved for the Pt-containing catalysts were similar to those of the supports. Similarly, N\textsubscript{2}-physisorption showed the same kind of isotherms and hysteresis loops as the corresponding supports. The surface areas
were decreased after Pt impregnation, which is due to the coverage of pores of the original supports by Pt particles. The total acidity of the catalysts, analysed by NH3-TPD, was increased after the impregnation compared to the corresponding supports. This was somewhat expected due to the used acidic Pt precursor. Table 4 summarizes the results of the characterization of the Pt-containing catalysts.

### Table 4. Characterization results of Pt-based catalysts. The ‘support’ indicates the result for a single support and ‘catalyst’ indicates the related value after Pt impregnation.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pt (wt-%; ICP)</th>
<th>SBET support ( (\text{m}^2\text{g}^{-1}) )</th>
<th>SBET catalyst ( (\text{m}^2\text{g}^{-1}) )</th>
<th>Pore size catalyst ( (\text{nm}) )</th>
<th>Total acidity catalyst ( (\mu\text{mol g}^{-1}) )</th>
<th>( d_p ) ( (\text{nm}, \text{TEM}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtAl</td>
<td>0.7</td>
<td>255</td>
<td>227</td>
<td>7</td>
<td>189</td>
<td>1.2</td>
</tr>
<tr>
<td>PtCe</td>
<td>0.6</td>
<td>89</td>
<td>82</td>
<td>14</td>
<td>60</td>
<td>2.4</td>
</tr>
<tr>
<td>PtTi</td>
<td>0.5</td>
<td>75</td>
<td>53</td>
<td>11</td>
<td>79</td>
<td>3.6</td>
</tr>
<tr>
<td>PtMg</td>
<td>0.5</td>
<td>64</td>
<td>33</td>
<td>16</td>
<td>21</td>
<td>3.7</td>
</tr>
</tbody>
</table>

The TEM imaging revealed a high dispersion of Pt on the surface of the supports (Figure 13). The dispersion was especially high over \( \gamma\)-Al\(_2\)O\(_3\) where very small particle size was observed. The particle size distribution of Pt was calculated using the ImageJ software. The histograms show that the particle sizes were centred at 0.8, 3, 1.25 and 3 nm over \( \gamma\)-Al\(_2\)O\(_3\), TiO\(_2\), CeO\(_2\) and MgO, respectively. The average sizes of Pt particles calculated by Equation (9) are given in Table 2. The impregnated catalysts, except PtAl, contain also some larger particles of Pt, i.e. higher than 5.5 nm.
Fig. 13. Histograms for Pt particle size distribution calculated using ImageJ software based on the TEM analysis: a) PtAl, b) PtTi, c) PtCe and d) PtMg (modified from Paper I).

The H₂-TPR analysis of impregnated catalysts is shown in Figure 14. At low temperatures, *i.e.* below 100 °C, a small peak with a low consumption of H₂ was observed for all the catalysts. This was most probably due to the reduction of PtOₓ particles to Pt that has low interaction with the surface of the supports (Kuhaudomlap et al., 2018; Merlen et al., 1996; Reyes, Pecchi, Morales, & Fierro, 1997; C. Zhang, He, & Tanaka, 2006). In the case of PtTi, two weaker peaks were observed between 250–310 °C and 350–470 °C. The last peak can be related to the reduction of TiO₂ that was observed in the case of the Ti support at around 450 °C. The second peak can be due to the reduction of PtOₓ that is interacting with the support or the PtTi interface site (Kuhaudomlap *et al.* 2018). In the case of PtCe,
Pt metal is shifting the reduction of Ce$^{4+}$ to lower temperatures, which was observed as a small peak in the range of 310–500 °C with a maximum at around 380 °C (not visible due to high intensity of the strong peak at around 210 °C). (Barrabés et al., 2009; H.-H. Liu et al., 2014) In addition, PtCe shows a very strong peak which is related to the reduction of Pt (Yao & Yao 1984; Liu et al. 2014). This peak is related also to ceria reduction, since $\text{H}_2$ consumption higher than the theoretical amount is observed when considering only Pt reduction.

A strong peak (190–240°C) was observed for PtMg at around 210 °C. Two smaller peaks with the maxima at 280 °C and 350 °C accompany this peak. These smaller peaks may be related to the Pt$^{4+}$ reduction to Pt$^{2+}$, and also the reduction of Pt$^{2+}$ interacting with the support (Aramendia et al., 1999; Larimi, Kazemeini, & Khorasheh, 2016). The results achieved with the TEM analyses can explain the different temperatures of Pt reduction, namely, the differences in Pt particle sizes in agreement with Merlen et al. (1996).

![H$_2$-TPR profiles of impregnated catalysts: PtAl, PtTi, PtCe and PtMg](image)

Fig. 14. H$_2$-TPR profiles of impregnated catalysts: PtAl, PtTi, PtCe and PtMg (Paper I, published by permission of Elsevier).
5.1.2 Activity

The impregnation of Pt did not change the activity order of the single oxide supports. The DCM conversion reached 100% over PtAl as well as PtTi, and about 95% over PtCe (Figure 15). In another study, an insignificant effect of Pt addition on the supports (Al₂O₃, HFAU faujasite zeolite) related to DCM conversion was observed. However, the effect was seen with the distribution of products (Pinard et al. 2005; Maupin et al. 2012). In our case, an exception with the TiO₂-supported catalysts was observed, since an increase in the DCM conversion after Pt impregnation was observed. This improvement in the DCM conversion was also observed earlier when TiO₂ was impregnated by RuO₂ (Ran et al. 2013) and CeO₂ (Cao et al., 2016). To explain the improved activity better, a hypothesis was drawn. We expected that in the presence of DCM the TiO₂ support was slightly deactivated due to the adsorption of chlorine. After impregnation of Pt, the adsorption of chlorine was avoided. To study this assumption more, XPS analyses were made for fresh and used catalysts with and without platinum. The results showed that Pt impregnation, indeed, decreases the chlorine adsorption on the TiO₂ surface by 50%. A similar phenomenon was not observed with other used single oxides.
5.1.3 Selectivity

The PtMg catalyst showed a low HCl yield due to the low DCM conversion. The other impregnated catalysts showed a higher yield of HCl, and it reaches about 80% over PtTi and PtAl (Figure 16). These catalysts present a similar evolution of HCl production at the studied temperature. The PtCe catalyst produces about 65% of HCl. When studying the impregnated catalysts with the corresponding supports, it was observed that Pt impregnation improves the HCl formation, except in the case of PtCe. The XPS analysis was done for fresh and used CeO$_2$ and PtCe to explain the negligible improvement of HCl formation after Pt impregnation. For the fresh catalyst (PtCe), a small peak appeared related to metal chloride with atomic percentage of 0.51% that was due to the used Pt precursor. The presence of Cl was not observed on the fresh CeO$_2$. In the case of used catalysts, a high amount of Cl compared to the fresh catalyst was observed. The detected amount of chlorine on the surface of the used CeO$_2$ was higher than on PtCe. Consequently, Pt impregnation can inhibit Cl adsorption on the ceria surface, as in the case of
TiO₂. Even though some chlorine was adsorbed on the used PtCe, it cannot completely explain the low production of HCl. Low formation of HCl can be also due to Cl₂ formation, which we cannot directly prove, since Cl₂ cannot be detected by an FTIR. Cl₂ might be formed via the Deacon reaction or by desorption from the surface.

![Graph showing HCl yields observed for different catalytic tests.](image)

**Fig. 16.** HCl yields observed for different catalytic tests. The test conditions were the following: DCM 500 ppm, H₂O 1.5 vol-% and GHSV 143793 h⁻¹ (Modified from Paper I).

CO, CH₂O and CH₃Cl were the main by-products observed over the studied supports. The amounts of these products are significantly decreased after Pt impregnation (See Figure 17). The by-product formation was the highest over PtAl. At high temperatures, PtCe had higher formation of CO than the other two catalysts. In the case of Pt catalysts, the quality of the acid sites was not determined. However, it was proven earlier that the type of the acid sites has a direct connection to the quality of the by-products. It is clear also, that the total acidity of the catalysts increased due to the used acidic precursor. Based on the by-products formed, it can be suggested that the quality of acid sites on γ-Al₂O₃ were affected after Pt impregnation. This is noted based on the increased formation of CH₂O compared
to the formation of CH₃Cl, which was more pronounced on γ-Al₂O₃. A similar change cannot be observed for TiO₂ or CeO₂.

Fig. 17. By-product formation over different catalysts. The test conditions are the following: DCM 500 ppm, H₂O 1.5 vol-% and GHSV 143793 h⁻¹.

5.1.4 Stability

The desired properties of catalysts are high conversion and selectivity to desired products and a long lifetime or stability in reaction conditions. Since the DCM oxidation conditions are very harsh for the catalysts, a stability study is required. In the current work, a short stability test of 55 hours was made with a PtAl sample (Paper I). The temperature of the stability test was selected based on T₉₀, and it was 400 °C. The results shown in Figure 18 present the light-off curves before and after the 55 hours stability test. During the 55 hours of testing, no decrease in the DCM formation or HCl yield was observed. Similarly, Figure 18 does not show any significant deactivation.
Fig. 18. DCM conversion and HCl formation over the PtAl catalyst before (Be) and after (Af) the 55 hours durability test. The used experimental conditions were: DCM 500 ppm, H₂O 1.5 vol-% and GHSV 143 793 h⁻¹ (Paper I, Published by permission of Elsevier).

The by-products of the reaction were CO, CH₂Cl and CH₂O with the concentration maxima at around 350 °C. The comparison of by-products formation in both cases showed a slight increase in the formation of CH₂O and CH₂Cl (less than 10 ppm) and no difference in CO production was observed. The XRD analysis did not show any change in the structural properties of the used catalysts. The comparison between the TEM images before and after the 55 hours test showed an increase in the Pt particle size (Paper I), which indicates slight sintering of Pt. However, the activity remained the same, which showed also that a change in the Pt particle size from around 1 nm to about 10 nm does not affect the DCM conversion nor HCl formation. However, the sintering of Pt particles might affect the formation of by-products and indicate a tendency towards deactivation after a longer time period of use.
5.2 Transition metal oxides (Cu, V and Mn)

Noble metals such as Pt show good performance in DCM oxidation. However, they present some disadvantages, e.g. possible deactivation by Cl and high costs (Liu et al., 2001; Vu et al., 2009; Saleh & Rahman, 2009; Tseng et al., 2010). Therefore, the following research focuses on alternative metals to replace the noble metals. The alternative metals should be resistant to poisoning and less costly than the noble metals (Gutiérrez-Ortiz et al., 2003; Tseng et al., 2010; Saqer et al., 2011).

In our study, three transition metal oxides (Cu, Mn and V) were chosen for further research. In this part of the work, a comparison is made between these three transition metals. This study is related to Papers II and III.

5.2.1 Characterization

In this section, characterization of catalysts, prepared by impregnation of copper, vanadium, manganese in the oxide form, done by ICP, XRF, XRD, Raman, FESEM, NH3-TPD and N2-physisorption are presented.

The elemental analysis carried out with XRF and ICP analyses of impregnated supports show that the desired amounts of active metals were reached (Papers II and III). Diffractograms, obtained by XRD for 30 wt-% of copper-based catalysts, shows the existence of only the crystalline phase of copper, CuO, in addition to the earlier detected phase of different used supports. The XRD patterns of 30 wt-% of manganese catalysts were difficult to relate to the exact phase based on the data from JPCD, but it was observed that Na0.7MnO2.05 was the most probable phase for the manganese compound present on the supports. This result was confirmed by dissolving the same Mn precursor in distilled water at room temperature, after which the same drying and calcination procedure was done as in the case of preparation of impregnated catalysts. After this treatment of the Mn precursor, the same phase (Na0.7MnO2.05) was observed. The similar phase was found also by Kappenstein (Kappenstein et al. 2002).

A shcherbinate phase of V2O5 (30 wt-%) was observed on all the supports, except on MgO. In the case of MgO support, Mg3(VO4)2 was observed in addition to the MgO phase, the result of which is in accordance with the results of Mishakov et al. (Mishakov, Vedyagin, Bedilo, Zaikovskii, & Klabunde, 2009). An additional phase was also observed on ceria, which was CeVO4. Also, this phase was observed in previous studies (Cousin et al., 1997; Radhika & Sugunan, 2006; Opara Krašovec et al., 1999; Martinez-huerta & Coronado, 2004; Mouammine et al., 2002).
In addition to the observed phases, an amorphous phase was seen in the case of all the catalysts, and its amount was most significant in the case of γ-Al₂O₃.

In the case of 10 wt-% Cu and V supported on γ-Al₂O₃, an amorphous phase was also observed for γ-Al₂O₃. In these analyses, a diffractrogram was observed for V₂O₅, but not for CuO. This might be due to the high distribution of Cu on γ-Al₂O₃ surface, which is in agreement with the result of Li et al. (Li et al., 2011).

The N₂-physisorption of impregnated supports shows the mesoporosity of the materials. The catalysts have rather large pores with smaller openings based on the hysteresis loops observed (Type H2). The specific surface areas of the supports decreased after impregnation of the transition metal oxides (Paper III). This is normal, and due to the coverage of part of the pores by deposition of the active phases on the surface. The FESEM analysis was done for 10CuAl and 10VAI (Figure 19). The EDS mapping of the analysed samples showed good distribution of Cu and V on the surface of the catalysts. The average amount of Cu and V determined by the EDS mapping is quite similar to the results obtained by XRF (Paper III).
Fig. 19. EDS mapping of the prepared catalysts by FESEM (modified from Paper III).
5.2.2 Performance of the catalysts in DCM oxidation conditions

30 wt-% copper-containing catalysts

A rather high conversion of DCM was obtained over the 30 wt-% Cu oxide catalysts. The conversion was around 60% over CuAl followed by CuTi with 45% conversion. Lower conversions were observed for the other catalysts (CuMg and CuCe), i.e. less than 25% (Figure 20). The order of the activity of single oxides remains the same after copper impregnation, as in the case of Pt. In addition, the 30CuAl and 30CuTi catalysts produce more HCl than the other two catalysts. The highest HCl yield was observed over CuAl (30%).

![Figure 20. DCM conversion and HCl yield of copper-containing catalysts. Test conditions were the following: DCM 500 PPM, H₂O 1.5 vol-%, m 0.1g, GHSV 704 867 h⁻¹.](image)

As the reaction by-products, CO, CH₂O and CH₃Cl were observed. At 500°C, the maximum production for CO was observed and it was less than 10 ppm with all the used supports containing copper. The amounts of by-products were slightly higher with CuAl and about 5 ppm of CH₂O and CH₃Cl was measured at 500 °C. In the cases of CuTi, CuCe and CuMg, no formation of CH₂O and CH₃Cl was observed. However, the difference in organic by-product formation is very small, and the detection limit of FTIR measurement is 2 ppm, which should be kept in mind when evaluating the results. Better activity (based on DCM conversion) of CuAl and CuTi might be due to their higher total acidity compared to CuCe and CuMg. To summarize, CuAl seems to be an interesting catalyst for DCM oxidation due to the rather high DCM conversion, HCl yield and low production of by-products.
30 wt-% of V-containing catalysts

30 wt-% vanadia-containing catalysts showed the highest DCM conversions of about 60% over Al₂O₃ followed by the MgO support with about 30% conversion. A conversion of around 20% was observed with the other two catalysts (Figure 21). In the case of vanadia, the same order of activity of the supports shown earlier was not observed. Actually, vanadia-impregnated MgO was more active than copper-impregnated MgO. It was observed (by XRD) that the VMg catalyst had an additional phase, i.e. Mg₃VO₄. It might be that this new phase is responsible for the improvement of activity.

The catalysts’ order based on the DCM conversion was the same for the HCl yield. The yield of HCl was 25 and 15% over VAl and VMg, respectively. The lowest HCl yields (5%) were obtained over VCe and VTi.

Fig. 21. DCM conversion and HCl yield of V-containing catalysts. The experimental conditions were the following: DCM 500 PPM, H₂O 1.5 vol-%, m 0.1g, GHSV 784 867 h⁻¹.

With vanadia-containing catalysts, the same by-products were observed as earlier. All the catalysts produced the same by-products, which was not the case with copper-containing catalysts. CO was produced at the highest amounts of 185, 45, 15, 10 ppm over 30VAl, 30VTi, 30VCe and 30VMg, respectively. The 30VAl catalyst produced significantly more CH₂O (~25 ppm at 500 °C) than the other catalysts. The amounts of formed CH₃Cl stayed low, below 5 ppm. Since we know that formaldehyde is produced on BAS, we can also conclude that vanadia impregnation affects the quality of acid sites on the Al₂O₃ support. It has been earlier noted that V₂O₅ contains BAS sites (Lin & Bai, 2003), and actually vanadia catalysts are also used in the production of formaldehyde (Mouammine et al., 2013;
Koivikko et al., 2018). Thus, it was expected that Brønsted acidity of the supports increases after vanadia impregnation. To conclude the results related to vanadia catalysts, 30VAl presents the best performance in DCM oxidation (Papers II and III).

30 wt-% Mn-containing catalysts

The DCM conversions over Mn-containing catalysts were low and the maximum conversion was reached (about 25%) over 30MnMg followed by 30MnCe. The lowest conversion, less than 15%, was observed over both 30MnAl and 30MnTi (Figure 22). The HCl production was less than 5% over all the Mn catalysts. This is less than expected based on the DCM conversion values. The low HCl yield might be due to several reasons, such as formation of Cl₂ by the Deacon reaction or decomposition of surface chlorides at high temperatures as follows (Bertinchamps et al., 2008; Gu et al., 2010; Vu et al., 2009):

\[
\text{MnCl}_2 + \text{O}_2 \leftrightarrow \text{MnO}_2 + \text{Cl}_2
\] (12)

Due to the low conversions of DCM over the Mn-containing catalysts, also the by-product formation was very low. The concentrations were slightly increasing with the temperature (for CO, CH₃Cl and CH₂O), but never reached significant levels. Opposite to our results, Gutierrez-Ortiz et al. (2003) obtained high conversions of DCM and TCE over Mn₂O₃ supported on H-ZSM-5. In our case, the XRD diffractograms of Mn-based catalysts revealed the presence of Na₀.₇MnO₂.₀₅ that formed due to the used precursor. This phase might be the reason for the low performance of the Mn-based catalysts.
Stability of metal chlorides in the experimental conditions

Gu et al. (2010) studied the combination of CuMnO_x supported on pure TiO_2-Al_2O_3 (Ti-Al) (20% of Ti) or TiO_2-Al_2O_3 modified by zirconium (Zr-Ti-Al). They obtained a total oxidation of DCM over CuMnO_x/Zr-Ti-Al at 470 °C and it was achieved at temperatures 40–60 °C lower than over the CuMnO_x/Ti-Al catalyst. They also observed an important decrease in the conversion during the first hour when they studied the stability of CuMnO_x/Zr-Ti-Al. They related the deactivation to the partial chlorination of CuMnO_x and the formation of CuCl_2 and MnCl_2. Since copper and manganese oxides were the used active phases in the current study, the stabilities of Mn and Cu oxides in the presence of Cl-based compounds (HCl, Cl_2) were evaluated by modelling with HSC Chemistry.

The conditions for the modelling were selected to represent the complete conversion of DCM simulating the used experimental conditions. Modelling was done in the presence and in the absence of steam (1st case). In addition, by-products such as CH_2O, CH_3Cl as well as CO and Cl_2 were included in the modelling study in the 2nd case. In both cases, the product stream included CO_2, HCl and H_2O in addition to the feed compounds. The amounts of Cu and Mn oxides were considered to correspond 30, 10 and 5 wt-% of oxides.

The results of thermodynamic modelling showed that in presence of H_2O in the feed, the CuCl_2 is decomposed at a lower temperature (300°C) than without
H₂O. The presence of water did not have any impact on the MnCl₂, and it was still present at 800°C. VCl₂ and VCl₃ were not thermodynamically stable forms of vanadium between room temperature to 850°C. The presence of by-products in the feed did not change the results of the modelling. It seems that the manganese oxide catalyst might not be stable in the experimental conditions used in this study. However, copper should be more stable at high temperature (high conversion of DCM) in the presence of steam. Most probably, vanadia should not deactivate significantly in the presence of chlorine compounds. To verify the modelling results, a Raman analysis was done for the fresh and used MnAl and CuAl catalysts as well as the γ-Al₂O₃ support. From the time-gated Raman spectra, chlorine compounds were observed for the used catalysts and the support. It seems that after two repeated DCM oxidation experiments, chlorine compounds are already present on the support and the catalysts. In addition, the XRF analysis was done for the fresh and used catalysts. The results reveal that 30MnAl contain a higher amount of chlorine than Cu- and V-containing catalysts.

10 wt-% V- and Cu-containing catalysts

During the activity tests, the Mn-containing catalysts showed low conversion of DCM accompanied with an insignificant HCl yield. Thus, the Cl-balance was not fulfilled, probably due to the formation of MnCl₂. MnCl₂ might be then oxidized at higher reaction temperatures leading to the formation of Cl₂. The Time-gated Raman and XRF analyses confirmed the existence of Cl on the used Mn catalysts that supports the formation of MnCl₂. Due to the low activity, selectivity and sensitivity to deactivation by chlorine compounds, the Mn catalysts were not included in further studies. In the further studies, 10 wt-% of CuO and vanadia supported on Al₂O₃ were considered, since they were more active and selective than the other alternatives. The aim of the study was to discover the performance of these two catalysts when smaller loading of active transition metal oxide was used. All the characterization results of 10 wt-% catalysts are presented in Section 5.2.1 in detail.

The 10 wt-% catalysts showed high conversion of DCM (about 100% at 500 °C) accompanied with high selectivity to HCl, i.e. more than 90% at 500 °C (See Figure 23). The 10VAl catalyst is slightly more active and selective (towards HCl formation) than 10CuAl. When other by-products were taken into account, it was observed that 10CuAl produces less CO, CH₂O and CH₃Cl than 10VAl. The total amount of formed by-products at 500 °C over 10CuAl is only 15 ppm of which 13 ppm is CO.
The comparison between the 10 wt-% CuAl catalysts and 0.7 wt-% PtAl revealed that they show rather comparable results in the view of DCM conversion and HCl yield. In addition, 10CuAl forms less by-products at a lower temperature range compared to PtAl. Above 450 °C, the formation of CO and CH₃Cl is increased in the case of 10CuAl. In general, especially CuAl catalysts could be good alternatives for the Pt-based catalysts.

### 5.3 Conclusion

The aim of the addition of different active materials on the studied metal oxide supports was to increase the selectivity of the studied materials towards HCl formation and to minimize the by-product formation. At first, Pt impregnation was considered. Secondly, Cu-, V- and Mn- containing transition metal oxides were considered as an alternative for the noble metal catalyst.

According to XRF and ICP-OES, the target amounts of the active phases (Pt and transition metal oxides) were closely reached in the cases of all the studied support oxides. The specific surface areas were decreased after impregnation due to the blockage of pores by active phases. The desired oxides were obtained for CuO and V₂O₅ based on the XRD measurements for the 30 wt-% loaded catalysts. However, for the Mn-containing catalyst, Na₀.₇MnO₂₀₅ was observed due to the used precursor. XRD showed also the presence of the same phases for the support oxides as observed without impregnation of active phase. The FESEM-EDS mapping demonstrated a good dispersion of the active oxide in the 10 wt-% of V₂O₅.
and CuO. HR-TEM was used in the case of Pt, and it showed a good dispersion of less than 4 nm particles over the supports used in the study. The total acidities of the materials were increased after the Pt, CuO and V₂O₅ impregnations. It was also possible to propose, based on the relative amounts of the by-products, that in the case of γ-Al₂O₃ support, also the quality of acid sites was modified after the impregnation Pt and V₂O₅.

Earlier, we observed that Al₂O₃ was the best support among the metal oxides studied. After impregnation of Pt, CuO and V₂O₅, it still kept the highest position. The most probable explanation for the good performance of Al₂O₃ is the beneficial acidic character of the material that remained also after impregnation. The quality of the acid sites on the catalyst affects the formation of by-products. CH₃Cl is formed on Lewis acid sites and CH₂O on Brønsted sites. The influence of acidity is also visible in the improved DCM conversion. In contrast, the characteristics of the active phase are related to the total oxidation activity and HCl selectivity. Of the tested active phases, 0.7 wt-% Pt and 10 wt-% CuO showed the best performance. The addition of Pt on the supports, except TiO₂, did not change the DCM conversion. The effect of Pt was visible in the improved HCl yields and reduced by-product amounts. The addition of only 0.7 wt-% Pt seems to be enough to make this change. The DCM conversion was improved after Pt impregnation in the case of TiO₂. This was observed to be due to the inhibition of chlorine-induced poisoning by Pt. The 10 wt-% of copper on γ-Al₂O₃ support was not equally active compared to 0.7 wt-% of Pt, based on the DCM conversion. However, the formation of CH₂O and CH₃Cl was significantly lower. This makes the copper–containing catalyst a good alternative for platinum in the DCM oxidation.

It is known that copper catalysts are easily deactivated in the presence of chlorine. Therefore, a modelling study was done with HSC Chemistry 6. The study was done to simulate the experimental conditions used and four different cases were considered. At first, DCM oxidation was considered in the presence and absence of water in the feed. Then, similar modelling cases were realized in the presence of by-products in the feed. The results show that the presence of water inhibits the formation of metal chloride. Based on thermodynamics, CuCl₂ was decomposed at around 300 °C, and after that the thermodynamically favoured form of copper was CuO. The presence of by-products did not have an influence on the modelling results. Therefore, rapid deactivation of CuO is not expected in the used experimental conditions and at the level of temperature required for the total DCM oxidation.
A short stability test of 55 hours was done for the 0.7 wt-% Pt on γ-Al₂O₃ catalyst. Light-off tests done before and after the long-term test did not demonstrate any deactivation of the catalyst. The HR-TEM analysis showed, however, an increase in the Pt particle size from ~1 nm to ~10 nm.

To continue the research towards more industrially relevant forms of catalysts, a study with monoliths was done. Based on the earlier results, Pt supported on Al₂O₃ was a justified choice for this study. Since acidity affects DCM conversion, SiO₂ was added to the support. Another benefit of SiO₂ is the improved thermal stability of the material (Saber & Gobara, 2014).
6 Approach to industrial application level: Pt supported on washcoated monoliths

The results shown in this part of the thesis are related to the monolith-form catalysts. The following chapter presents the characterization results obtained by physico-chemical techniques and the results obtained from the DCM oxidation tests. In the beginning, the effect of coating and impregnation was studied after which the effect of substrate type is discussed.

The used monoliths (substrate) were made of cordierite with the formulae of 2(MgO)2(Al2O3)5(SiO2) manufactured in the Corning Company (Germany). Two types of substrates were used, one with 200 cpsi (cells per square inch) and another with 600 cpsi. In Chapter 6, the monoliths are denoted with 200M or 600M showing the channel density of the monolith. The monoliths were washcoated with Al2O3 modified by SiO2 and denoted as AlSix (x=5, 10, 15) when they exist in a powder form and as Mx when supported on the monoliths.

The substrates used in this study are in a cylindrical form 1cm in diameter and 3 cm in length (Figure 24). The substrates are known by their geometric parameters, that can be measured directly from the substrates, such as channel size (dch) and wall thickness (ech), as shown in Figure 24. In addition, other parameters can be measured indirectly by calculation from dch and ech as geometric surface area (GSA), open frontal area (OFA), thermal integrity factor (TIF), mechanical integrity factor (MIF) and channel density (n) (Paper IV). The measured and calculated parameters are shown in Table 5.

![Figure 24. X-ray tomography image of a monolith used in this study: (a) the channel view and (b) the outside view of the monolith (Image taken at Geological Survey of Finland GTK, ESPOO).](image-url)
Table 5. Geometric parameters of the used substrates.

<table>
<thead>
<tr>
<th>Monoliths channel density* (cpsi)</th>
<th>(d_{ch}) (mm)</th>
<th>(e_{ch}) (mm)</th>
<th>(n^{**}) (cpsi)</th>
<th>GSA (mm(^{-1}))</th>
<th>OFA</th>
<th>TIF</th>
<th>MIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.92</td>
<td>0.30</td>
<td>175</td>
<td>1.76</td>
<td>0.71</td>
<td>6.40</td>
<td>0.03</td>
</tr>
<tr>
<td>600</td>
<td>1.03</td>
<td>0.24</td>
<td>628</td>
<td>2.97</td>
<td>0.59</td>
<td>4.29</td>
<td>0.07</td>
</tr>
</tbody>
</table>

*Values of channel density given by the manufacturer and **calculated by ourselves.

6.1 Characterization of catalysts

The elemental analysis by XRF for the AlSix samples are summarized in Table 6. The analysis revealed that the wanted silica loading on Al\(_2\)O\(_3\) was achieved. The weighing of the substrate after pre-treatment and after calcination of the coated monoliths showed that the coating was successful, resulting in 10 wt-% of washcoat on the monolith, which is in the optimal range of washcoating (Tsou et al. 2006). The \(N_2\)-physisorption of the coated monoliths showed the existence of mesoporous material with large pores with small openings (isotherms of Type IV and hysteresis Type H2) (Sing, 1982). The comparison between the values of specific surface area obtained for the coated monoliths and corresponding powders showed the values to be quite similar. The slight difference can be due to heterogeneity of the washcoated film and/or loss of washcoat when the coated monoliths were broken for the analysis (Paper IV).

Table 6. Chemical composition of the prepared materials.

<table>
<thead>
<tr>
<th></th>
<th>200M</th>
<th>200M5</th>
<th>200M10</th>
<th>200M15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of SiO(_2) in</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>the coated phase by</td>
<td>-</td>
<td>6</td>
<td>12</td>
<td>18</td>
</tr>
<tr>
<td>XRF (mol-%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amount of AlSix</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>washcoated on monolith</td>
<td>-</td>
<td>12</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>(wt-%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S_{BET}/ m^2 g^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monolith</td>
<td>10</td>
<td>35</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Coating</td>
<td>-</td>
<td>290 (300*)</td>
<td>215 (320*)</td>
<td>230 (350*)</td>
</tr>
<tr>
<td>Pore volume cm(^3)g(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monolith</td>
<td>0.01</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Coating</td>
<td>-</td>
<td>0.34 (0.49*)</td>
<td>0.22 (0.42*)</td>
<td>0.23 (0.42*)</td>
</tr>
<tr>
<td>Pore size / nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monolith</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Coating</td>
<td>-</td>
<td>0.34 (0.49*)</td>
<td>0.22 (0.42*)</td>
<td>0.23 (0.42*)</td>
</tr>
</tbody>
</table>

* Value obtained for powders used for coating.

The FESEM analysis of substrate and coated monoliths revealed that the thickness of the coating was about 4 \(\mu\)m (calculated using ImageJ software). The EDS mapping of coated monoliths displayed a good distribution of Al and Si on the surface with some cracks on the coating layer (Figure 25). The comparison of the EDS results (Table 7) showed an increase in the Al amount and a decrease in the Si...
amount and especially in the Mg amount. The three techniques used for characterization of the washcoated monolith all demonstrate a successful coating, and in addition it can be observed that the most important properties of the powders were successfully transferred to the coated monoliths.

Table 7. Elemental composition of uncoated and 200M10 samples determined by EDS analysis (adapted from Paper IV).

<table>
<thead>
<tr>
<th>Monoliths</th>
<th>Al (wt-%)</th>
<th>Si (wt-%)</th>
<th>O (wt-%)</th>
<th>Mg (wt-%)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>18</td>
<td>25</td>
<td>49</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>Coated substrate</td>
<td>42</td>
<td>11</td>
<td>46</td>
<td>1</td>
<td>100</td>
</tr>
</tbody>
</table>
Fig. 25. Images taken by FESEM: (a) the washcoated monoliths (b) the position area of EDS mapping and (c) the EDS mapping image of elements in coated monolith from (b).
6.2 Activity and selectivity

6.2.1 Studies with the 200 cpsi monolith

The DCM conversions over different monolith catalysts with 200 cpsi are presented in Figure 26. As can be seen, the substrate alone is showing a low conversion of DCM, \textit{i.e.} less than 20%. The coating of substrate increases the DCM conversion significantly and it reached a value higher than 80% over all the coated monoliths. T_{50} (temperature needed for 50% of DCM conversion) is the lowest for 200M10 (420 °C) followed by 200M5 (425 °C). For the other catalysts, the T_{50} temperature was 430 °C, except for Pt200M10 (440 °C) (Paper IV). The varying silica amounts and Pt impregnation had only a minor effect on the DCM conversion.

![Fig. 26. DCM conversion over impregnated and coated monolith with 200 cpsi; DCM 500 ppm, GHSV 30556 h^{-1} (1.2 L min^{-1}), H_2O 1.5 vol.-%. In the figure, 200M is the substrate alone and 200Mx (x=5, 10, 15) is the coated monolith where x is the loading of silica on alumina (adapted from Paper IV).](image)

The HCl yield reached 70% for 200M5, 60% for 200M10 and 200M15 and about 5% over the 200M cordierite substrate (Figure 27). The effect of substrate (cordierite monolith) on DCM oxidation and HCl formation was found to be very
small. After Pt impregnation, an increase in the HCl formation was observed for 200M10 around 500 °C. The HCl yields of 75 and 65% were observed for Pt200M10 and Pt200M15 at 500 °C, respectively, and the yields were higher than for the corresponding washcoated monoliths. On the contrary, Pt impregnation had a negative effect on the HCl formation in the case of 200M5. This might be due to the formation of Cl2 by the Deacon reaction (L. Pinard et al., 2004; Pitkäaho et al., 2011) and the poisoning of the surface of Pt200M5 by Cl2. From the point of view of by-products, the formation of CO, CH2O and CH3Cl was observed, as earlier. CO was produced in the highest amounts with all the coated monoliths and its amount was decreased after Pt impregnation. CH3Cl formation was smaller than that of CH2O over the tested monoliths, and their amounts were significantly decreased after Pt impregnation (Paper IV). These results are in accordance with previous studies, where the effect of Pt impregnation was more pronounced in the case of products and by-products. (Chen et al., 2008; Pinard et al., 2004; Pinard et al., 2005; Pinard et al., 2003). The 200M10 catalysts showed the best performance in the view of DCM conversion and HCl yield. For that reason, it was selected for the comparative study with another substrate, i.e. the cordierite substrate with 600 cpsi.

![Graph showing HCl formation over the studied monoliths. The same experimental conditions were used as in Fig. 26 (adapted from Paper IV).](image-url)
6.2.2 Comparison of 200 and 600 cpsi monoliths

The results of the catalytic oxidation of DCM over the catalysts supported on two types of substrates (200M10 and 600M10) are presented hereafter. The light-off curves for the DCM oxidation are shown in Figure 28. This reveals that the increase in the channel density from 200 to 600 cpsi improves the DCM conversion. This is due to a more efficient contact of DCM with the active sites in the case of 600 cpsi, which has the highest GSA. After Pt impregnation, the activities of the catalysts are slightly decreased. This could be due to the changes occurring in the coated monoliths during impregnation, such as blocking of active sites or changes in the coating quality (homogeneity, cracks, etc.).

Fig. 28. Effect of substrate type on DCM oxidation. 200M and 600M are monoliths with 200 and 600 cpsi, respectively. The same experimental conditions were used as in Fig. 26 (adapted from Paper IV).

The HCl yields over the 600M10 catalysts are higher than the yields obtained for the 200M10 catalysts (Figure 29). No remarkable increase in the DCM conversion at higher temperatures was observed in the case of 600M10 after Pt impregnation. The main by-products, CO, CH₂O and CH₃Cl, were observed in both cases, and with less amounts for 600M10 (Paper IV). After Pt impregnation, the amount of
by-products was decreased, and the decrease was slightly more significant for Pt600M10 than for Pt200M10, since there was 90% less by-products for Pt200M10 and 95% for Pt600M10. As a conclusion, the increase in the channel density improved the performance of the catalysts, which was due to the increase in the GSA and MIF values and a decrease in the OFA, and TIF values (Paper IV).

![Fig. 29. Effect of substrate type on the HCl formation. 200M and 600M are monoliths with 200 and 600 cpsi, respectively. The same experimental conditions were used as in Fig. 26 (adapted from Paper IV).](image)

### 6.3 Conclusion

The cordierite monoliths were successfully coated with 10–18 wt-% of (Al₂O₃)ₓ(SiO₂)ₙ, which is in the optimal range of washcoating in order to have a high dispersion of the active phase. The high specific surface area of the (Al₂O₃)ₓ(SiO₂)ₙ powder was also preserved after washcoating on the monolith. The FESEM images showed a rather good quality of the thin layer (4µm) of (Al₂O₃)ₓ(SiO₂)ₙ coated on the monoliths, with EDS results showing the expected elemental composition. These analyses demonstrated the success of the coating.
The light-off curves of DCM oxidation showed that the coated monoliths (200M) convert more than 80% of DCM and lead to higher than 50% yields in HCl production. The by-products formation over the coated monoliths were decreased considerably after Pt impregnation. The results showed that the increase in the channel density improved the catalyst performance and it was due to the better contact of DCM with the active sites on the catalysts. It can also be concluded that in the used experimental conditions of DCM oxidation, a high value of GSA and MIF and low value of OFA and TIF are beneficial for good catalyst performance.
7 Summary and future perspectives

The wide use of DCM in several applications in the production of goods has given rise to increased DCM emissions in the atmosphere. In addition, DCM is a threat to human health. In the worst case, contact with DCM can be lethal to humans. Many countries have adopted legislation and directives in order to limit the emissions and uses of DCM. For this reason, effective techniques to decrease DCM releases into the outdoor environment, as well as indoors, are needed. For this purpose, catalytic oxidation is a promising technique, being a feasible, economic and environmentally friendly method.

In this thesis, several catalysts were developed starting from the preparation, followed by characterization, of the catalysts by physico-chemical techniques. Finally, the catalysts were tested in the catalytic oxidation of DCM. The aim was to understand the effect of material properties influencing DCM oxidation, and use this information further in developing a monolith-shaped heterogeneous catalyst for DCM oxidation and CVOC abatement in general. To reach the aim, the work was divided in three stages: 1. Study of support properties, 2. Study related to the active phase and 3. Development of the monolith form catalyst.

The main result of the first stage of the work was that acidity of the support influences DCM conversion and quality of the formed by-products. A more-acidic support (Al₂O₃) results in better DCM conversion than a less acidic support (MgO). Brønsted acidity of the support leads to the formation of formaldehyde (CH₂O) and Lewis acidity leads to methyl chloride (CH₃Cl). (Paper I)

In the second stage, the influence of active compounds was considered (Papers I–III). Metallic Pt, V₂O₅, CuO and Na₀.7MnO₂.05 were the observed forms of the impregnated phases. Na₀.7MnO₂.05 was not an active form of manganese in the oxidation of DCM, and therefore it was not considered in detail. The other three active phases improved the selectivity towards the complete oxidation products, which was the main observation of this stage. Pt seems to inhibit chlorine poisoning of the support. Of the transition metal oxides, CuO is shown to be a promising alternative to Pt, since only minor amounts of by-products are formed during DCM oxidation. Since it is known that CuO is poisoned by chlorine, a modelling study was done where the experimental conditions were simulated and the stability of CuCl₂ was evaluated. It was found that CuO is the thermodynamically favoured form of copper at above 300 °C in the presence of water. Stability of Pt/γ-Al₂O₃ was also checked, but in this case, experimentally. The 55 hours stability test did
not show any changes in the catalyst activity, and only the Pt particle size increase was observed.

In the third stage (Paper IV), cordierite monolith was used as a substrate for the Pt(Al₂O₃)ₓ(SiO₂)ₙ (x = 5, 10 and 15) catalysts. The properties of the coating were studied in both powder and in monolith forms when possible. Similar structural and textural characteristics were found for both forms of the catalyst. Furthermore, the quality of the coating was observed to be rather good. The performance of the monolith catalyst in DCM oxidation was excellent, and 10 mol-% of SiO₂ was found to be optimal in terms of activity and selectivity. The increase in the channel density from 200 to 600 cpsι improved DCM oxidation, which was due to the increase in GSA and MIF and the decrease in OFA and TIF.

The results summarized here and presented in detail in the related publications (Papers I-IV) prove that the initial aims set for the thesis were achieved. However, as always during the research, certain interesting details were found during the work that would merit further investigation. For example, further detailed study is needed focusing on the relation between the type of acid sites and by-product distribution. The observation that Brønsted acidic sites in the case of alumina support lead to formaldehyde and Lewis acid sites to methyl chloride formation should be studied with other supports. Another interesting study would be to further examine the observed inhibition of the chlorine poisoning of CeO₂ and TiO₂ after Pt impregnation. A more comprehensive study should be done related to the redox properties of the studied catalysts and their connections to DCM oxidation. Furthermore, more studies are required related to the durability and long-term use of the catalysts in the presence of DCM. To gain better perspectives on the applicability of the materials in CVOC oxidation, in general, several other model compounds should be studied, such as perchloroethylene (PCE). These examples show that further research is needed in the field of catalytic CVOC oxidation.
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98


Suoranta, T. (2016). *Advanced analytical methods for platinum group elements:*


http://doi.org/10.1039/a909552g


Original publications

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


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Original publications are not included in the electronic version of the dissertation.
671. Porambage, Pawani (2018) Lightweight authentication and key management of wireless sensor networks for Internet of things
672. Bibikova, Olga (2018) Plasmon-resonant gold nanoparticles for bioimaging and sensing applications
674. Isokangas, Elina (2018) Quantifying the groundwater dependence of boreal ecosystems using environmental tracers
676. Leinonen, Markus (2018) Distributed compressed data gathering in wireless sensor networks
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