Structured microreactors for the heterogeneously catalyzed gas-phase dehydration and partial oxidation of 1-butanol

Yaseen Khan
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Abstract

Structured microreactors are considered as a tool to study catalytic activity and intrinsic kinetics because of their characteristic mass and heat transfer advantages. In this thesis, microreactor structures coated with catalysts (γ-Al2O3, Au/TiO2, Pd/TiO2 and Au-Pd/TiO2) were applied to study the activity and to investigate the kinetics of the heterogeneously catalyzed gas-phase reactions in dehydration and partial oxidation of 1-butanol. In addition, the morphology and durability of the prepared noble metal catalyst coatings (Au/TiO2, Pd/TiO2 and Au-Pd/TiO2) were studied.

A structured microreactor coated with γ-Al2O3 catalyst having a layer thickness of 15-30 μm was used for the heterogeneously catalyzed gas-phase dehydration of 1-butanol. The kinetic parameters were estimated from the produced experimental data. A dynamic 2D plug flow reactor type model with diffusion-reaction in the catalyst layer confirmed insignificant internal mass transfer resistances and prevalence of the kinetic regime. A computational fluid dynamics study using 3D and 2D-axisymmetric models incorporating fluid flow non-idealities, revealed the presence of axial and radial concentration gradients. The insights from the simulations revealed the catalyst layer thickness and the microchannel dimensions as key parameters to improve the performance of microreactors applied for the heterogeneously catalyzed gas-phase reactions.

New heterogeneous catalyst coatings of titania-supported mono- and bimetallic gold and palladium were prepared and tested for the 1-butanol partial oxidation. A sol-immobilization method was used for catalyst preparation and coatings were prepared via a suspension method. A layer thickness of 17±7 μm with an average metal nanoparticle size of 3.6 nm was achieved. The Au/TiO2 catalyst coatings were most selective towards n-butyaldehyde, whereas Pd/TiO2 and Au-Pd/TiO2 catalysts were more selective towards propene, CO and CO2. The kinetic experiments were performed using Au/TiO2 coated catalyst. Kinetic modeling was performed by applying 1D-pseudohomogeneous plug flow reactor type model and dynamic 2D model incorporating axial dispersion effects in gas-phase. The model simulations reproduced the experimental data.

In this thesis, preparation of active, selective and durable Au/TiO2 coated catalysts was demonstrated. The activity of the prepared Au/TiO2 coated catalyst was reproducible for 57 tested runs that is reported, in the author's knowledge, for the first time for the nanogold catalyst. In addition, kinetic modeling and reactor simulations were performed successfully to describe the system dynamics of both the dehydration and partial oxidation reactions of 1-butanol.

Keywords microreactor, coated catalyst, 1-butanol, gamma-alumina, dehydration, nanogold, partial oxidation, butyraldehyde, kinetic modeling, reactor simulations, CFD

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Espoo, 17 July 2020
Muhammad Yaseen Ahmed Khan
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# Abbreviations and symbols

## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ABE</td>
<td>Acetone-butanol-ethanol</td>
</tr>
<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>ASA</td>
<td>Amorphous silica-alumina</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller (surface area)</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett–Joyner–Halenda (pore size)</td>
</tr>
<tr>
<td>BuO/Buald</td>
<td>n-Butyraldehyde</td>
</tr>
<tr>
<td>BuOH</td>
<td>1-Butanol</td>
</tr>
<tr>
<td>CTMR</td>
<td>Catalyst testing microreactor</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational fluid dynamics</td>
</tr>
<tr>
<td>DBE</td>
<td>Dibutyl ether</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>FEG</td>
<td>Field emission gun (microscopy)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared (spectroscopy)</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-performance liquid chromatograph (pump)</td>
</tr>
<tr>
<td>IMM</td>
<td>Institut für Mikrotechnik Mainz GmbH</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared (spectroscopy)</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>LPO</td>
<td>Low pressure oxo-process</td>
</tr>
<tr>
<td>MCR</td>
<td>Microchannel reactor</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>NTP</td>
<td>Normal temperature and pressure</td>
</tr>
</tbody>
</table>
ODE  Ordinary differential equation
ODH  Oxidative dehydrogenation
PBR  Packed-bed reactor
PDE  Partial differential equation
PFR  Plug flow reactor
PVA  Polyvinyl alcohol
Rh-TPP Rhodium tri-phenylphosphine (complex)
RSS  Residual sum of squares
SEM  Scanning electron microscopy
SMSI Strong metal-support interaction
STEM Scanning transmission electron microscopy
TGA  Thermogravimetric analysis
XRF  X-ray fluorescence

Symbols

\(A\)  Pre-exponential factor \([1/s]\)
\(c_i\)  Concentration of component \(i\), in Matlab and COMSOL \([\text{mol/m}^3]\)
\(c_i^b\)  Concentration of component \(i\) in free channel domain, in Matlab and COMSOL \([\text{mol/m}^3]\)
\(c_i^c\)  Concentration of component \(i\) in catalyst layer, in Matlab and COMSOL \([\text{mol/m}^3]\)
\(C_{i,G}\)  Concentration of component \(i\) in gas, in gPROMS \([\text{mol/m}^3]\)
\(C_{i,S}\)  Concentration of component \(i\) in catalyst, in gPROMS \([\text{mol/m}^3]\)
\(D_{ei}\)  Effective diffusivity of component \(i\), in Matlab and COMSOL \([\text{m}^2/\text{s}]\)
\(D_{eff,i}\)  Effective diffusivity of component \(i\), in gPROMS \([\text{m}^2/\text{s}]\)
\(D_i\)  Molecular diffusion coefficient of component \(i\) \([\text{m}^2/\text{s}]\)
\(D_{ik}\)  Binary diffusion coefficient of component \(i\) and \(k\) \([\text{m}^2/\text{s}]\)
\(D_x\)  Axial dispersion coefficient, in gPROMS \([\text{m}^2/\text{s}]\)
\(E\)  Activation energy \([\text{kJ/mol}]\)
\( F \) Volume force vector in Navier–Stokes equation [N/m\(^2\)]

\( F_i \) Molar flow of component \( i \) [mol/s]

\( \Delta H^\circ_r \) Heat of reaction at \( T_0 \) (298 K) [J/mol]

\( I \) Identity tensor in Navier–Stokes equation

\( i \) Component \( i \)

\( k \) Component \( k \)

\( j \) Reaction \( j \)

\( \bar{k} \) Kinetic constant of reaction \( j \) at average temperature, in Matlab

\( k_j \) Kinetic constant of reaction \( j \)

\( k_{j,\text{ref}} \) Kinetic constant of reaction \( j \) at average temperature, in gPROMS

\( K \) Adsorption constant

\( K_{eq} \) Equilibrium constant at temperature \( T \)

\( K_{eq_0} \) Equilibrium constant at temperature \( T_0 \) (298 K)

\( l \) Reactor length varying from 0 to \( L \) [m]

\( L \) Total reactor length [m]

\( M_i \) Molar mass of component \( i \) [g/mol]

\( m \) Reaction \( m \)

\( n \) Component \( n \) or reaction order

\( \dot{n}_i \) Molar flow of the component \( i \) [mol/s]

\( \dot{n}_{i,\text{C,atoms, in}} \) Molar flow of total carbon atoms going in the reactor [mol/s]

\( \dot{n}_{i,\text{C,atoms, out}} \) Molar flow of total carbon atoms out of the reactor [mol/s]

\( P \) Pressure [Pa]

\( Pe \) Peclet number [-]

\( Q_0 \) Gas flow at NTP [ml/s]

\( Q_p \) Objective function

\( r \) Radial location, in gPROMS [m]

\( r_p \) Radial location within the layer, in gPROMS [m]

\( r_j \) Reaction rate of reaction \( j \) [mol/(m\(^3\cdot\text{s})] \)

7
\( R \) General gas constant \([J/(mol.K)]\)
\( R \) Inner reactor radius, in gPROMS and COMSOL \([m]\)
\( R_1 \) Inner reactor radius, in Matlab \([m]\)
\( R_2 \) Reactor radius, in Matlab \([m]\)
Re Reynolds number \([-\] \]
\( R_p \) Catalyst particle radius or layer thickness, in Matlab \([m]\)
\( R_w \) Reactor radius, in gPROMS \([m]\)
s Catalyst shape factor \([-\] \]
\( S_i \) Selectivity of product component \(i\) \([\%]\)
\( T \) Temperature \([°C\ or\ K]\)
\( \bar{T} \) Average temperature \([°C\ or\ K]\)
\( t \) Time \([s]\)
\( u_G \) Superficial velocity of the gas \([m/s]\)
\( v_{ij} \) Stoichiometric coefficient of \(i\) in reaction \(j\)
\( v \) Volume contribution of molecules
\( x_i \) Mole fraction of component \(i\)
\( x \) Non-dimensionalized axial coordinate, in Matlab \([-\] \]
\( X \) Conversion of 1-butanol \([\%]\)
\( y_{\text{cal}} \) Model value of component \(i\)
\( y_{\text{exp}} \) Experimental value of component \(i\)
\( Y_i \) Yield of product component \(i\) \([\%]\)
\( y_i \) Volume fraction of component \(i\)
\( z \) Axial location, in gPROMS \([m]\)
\( z \) Non-dimensionalized radial coordinate, in Matlab \([-\] \]
\( \varepsilon_p \) Porosity of the catalyst layer or particle \([-\] \]
\( \varepsilon_b \) Reactor channel or catalyst bed void fraction \([-\] \]
\( \eta_i \) Effectiveness factor \([-\] \]
\( \rho \) Fluid density \([kg/m^3]\)
\( \rho_b \) Catalyst bulk density, 1D-pseudohomogenous model \([kg/m^3]\)
\( \rho_p \)  
Catalyst particle or layer density, dynamic 2D model [kg/m^3]

\( \tau \)  
Residence time, in Matlab [s]

\( \tau \)  
Tortuosity in catalyst layer or particle [ - ]

\( \tau \)  
Viscous stress tensor in Navier–Stokes equation [Pa]

\( \theta \)  
Used in Arrhenius equation for difference (as inverse) between reaction and average temperature [°C or K]

\( \theta \)  
Surface coverage of species in mechanistic kinetic models for 1-butanol dehydration [0 ≤ θ ≤ 1]

\( \varphi_i \)  
Thiele modulus [ - ]

\( \delta_s \)  
Catalyst layer thickness [µm]

\( \zeta \)  
Dimensionless washcoat layer, in gPROMS [ - ]
List of Publications

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


*Shared first authorship.
Author’s Contribution

Publication I: 1-Butanol dehydration in microchannel reactor: kinetics and reactor modeling.

Yaseen Khan, Minna Marin and Reetta Karinen interpreted the experimental data from the microreactor experiments performed by Minna Marin. Yaseen Khan performed kinetic parameter estimation and the microreactor simulations. Juha Lehtonen and Jaana Kanervo assisted with the kinetic modeling. Yaseen Khan and Jaana Kanervo developed the dynamic 2D diffusion-reaction model and surface reaction expressions. Yaseen Khan wrote the first draft of the manuscript with support from Minna Marin and co-authors. The manuscript was reviewed and commented by Reetta Karinen, Juha Lehtonen and Jaana Kanervo.

Publication II: 3D simulations of a microchannel reactor with diffusion inside the catalyst layer for 1-butanol dehydration reaction in gas phase.

Yaseen Khan developed the Computational Fluid Dynamics (CFD) model, performed the simulations, interpreted the results and wrote the first draft of the manuscript. The model was based on the reactor experiments performed by Minna Marin reported in Publication I. Juha Lehtonen and Reetta Karinen reviewed and commented the manuscript.

Publication III: Structured microreactor with gold and palladium on titania: active, regenerable and durable catalyst coatings for the gas-phase partial oxidation of 1-butanol

Yaseen Khan and Minna Marin share the first authorship of the manuscript. Yaseen Khan, Minna Marin, Reetta Karinen and Juha Lehtonen planned customization of the catalyst testing microreactor (CTMR) system. Minna Marin and Yaseen Khan co-operated in the catalyst preparation, coating process and
catalyst characterizations. Yaseen Khan performed the startup and troubleshooting of CTMR. Yaseen Khan, Minna Marin, Tiia Viinikainen and Reetta Karinen developed the FTIR analysis method. Yaseen Khan designed, performed and supervised the catalyst-screening experiments. Yaseen Khan interpreted and wrote the catalyst-screening results and discussions. Minna Marin and Tiia Viinikainen interpreted and wrote the catalyst characterization results and discussions. Yaseen Khan, Minna Marin and Tiia Viinikainen wrote the first draft of the manuscript. Reetta Karinen and Riikka L. Puurunen took part in the interpretation of the results and reviewed and commented the manuscript. Juha Lehtonen reviewed and commented the manuscript.

**Publication IV:** Modelling of a microreactor for the partial oxidation of 1-butanol on a titania supported gold catalyst.

Yaseen Khan and Teuvo Kilpiö share the first authorship of the manuscript. Yaseen Khan and Minna Marin co-operated in the catalyst preparation process. Yaseen Khan planned, performed and supervised the kinetic experiments. Yaseen Khan designed and simulated the mixer unit. Yaseen Khan performed the kinetic modeling and reactor simulations in Matlab. Teuvo Kilpiö and Vincenzo Russo performed the kinetic modeling and reactor simulations in gPROMS. Juha Lehtonen prepared the mechanistic kinetic model. Yaseen Khan and Teuvo Kilpiö interpreted the experimental and simulation results and wrote the first draft of the manuscript. Tapio Salmi, Vincenzo Russo, Minna Marin, Reetta Karinen and Juha Lehtonen took part in the interpretation of the results, reviewed, and commented on the manuscript.
1. Introduction

Climate change, due to effect of greenhouse gases, has made it evident that alternative energy resources are inevitably needed [1]. The dependency of fuel, primary energy and fine chemicals on the fossil-based sources, which are a major source of greenhouse gases, has prompted a shift in policy from the European Union (EU). The EU has adopted the 2020 climate & energy package, the 2030 climate & energy framework and the 2050 roadmap for low-carbon economy [2]. Clean energy from renewable resources, such as solar, wind, geo-thermal and biomass, all present different options to add to the primary energy mix. To reduce dependencies from fossil fuel resources and avail incentives from future carbon tax on chemical industries, the research on chemical synthesis from biomass and carbon capture has received an increased focus [1].

Biomass represents a huge possibility for biofuels and platform chemicals, which can be further synthesized to fine and value-added chemicals [3–5]. Finland has an abundance of biomass resources [6]. Biomass conversion to fuels and chemicals proceeds by various processes, such as thermochemical and biochemical routes [4,5]. Thermochemical routes include gasification, pyrolysis and torrefaction [5], whereas biochemical route includes fermentation [3–5]. Fermentation process can be applied to separated cellulose fraction and sometimes to hemicellulose fraction from biomass, which can be converted to different platform and value-added chemicals [3,4,6].

1.1 Catalysis

Catalysis is a phenomenon that refers to the use of the catalysts to accelerate chemical reactions [7]. Catalysts decrease the activation energy of a reaction (increase speed/rate of a reaction) without being consumed. The lower activation energy, because of the change in reaction pathway and mechanism, in turn allows to optimize the energy and materials consumption [8]. Homogeneous and heterogeneous catalysts are the two broader categories for the catalysts. Homogeneous catalysts are applied to systems where the reactants and the catalyst are in same phase, such as strong H₂SO₄ used for alcohol dehydration to respective alkenes [9]. In heterogeneous catalysts, the reactant and the catalyst are in different phases, such as zeolites used for cracking of gas-oil [7].
The focus of this work is on heterogeneous catalysis for fluid-solid systems, in particular in the systems where the reactant and the products are in the gas phase, whereas the catalyst is in the solid phase coated on walls of a structured microreactor plate, referred to as coated catalysts [10].

The ‘coated catalysts’ are considered as classification of the heterogeneous catalysts, where the catalysts are applied as catalytically active layers on inert structured surfaces, such as ceramic monolith structures or structured stainless-steel plates [10]. These catalyst materials for the active layers consist of bulk catalysts (e.g. γ-Al2O3, TiO2 and ZrO2) and supported noble metals (Au, Pd, Pt, Ru etc.). The typical examples for the application of coated catalysts are monoliths in the engine exhaust gas cleaning of automobiles as well as industrial applications for the flue gas treatment and structured milli-micro reactors for the synthesis of fuels and value-added chemicals [11–13]. The reported main advantages with the application of coated catalysts compared to typical packed bed reactors are the optimal use of the active mass, rapid mass transfer due to shorter diffusion lengths from fluid phases to the solid catalyst layer, efficient heat transfer and low pressure drop [10,12].

1.2 Bio 1-butanol to value-added chemicals

In this work, 1-butanol was selected as a model component. 1-Butanol can be obtained, for example, from cellulosic feedstock by acetone-butanol-ethanol (ABE) fermentation [3,4]. Typical ABE ratio is 3:6:1 using solvent-producing Clostridium species [3,4]. ABE fermentation involves two phases: acidogenic phase and solventogenic phase. In acidogenic phase, which is the initial growth phase, acetic acid and butyric acid are produced, which lower the pH of the growth medium. The lowered pH leads to the solventogenic phase where the culture is in stationary growth phase and some acids are transformed into ABE [3,14]. Compatible profits could arise in the future for fine chemicals obtained from renewable resources because of tax incentives and subsidies aiming to reduce dependencies on fossil-based resources. This has shifted focus on the bio-butanol production from ABE fermentation [15].
1-Butanol (from here onwards bio 1-butanol to be referred as 1-butanol) can be converted into different products, such as butenes, ethers, esters, aldehydes and carboxylic acids. These value-added chemicals (Fig. 1) have applications in different chemical, pharmaceutical, food, cosmetics and other industries (Table 1).

Table 1. Derivatives for 1-butanol and their applications [13].

<table>
<thead>
<tr>
<th>Derivatives from 1-butanol</th>
<th>Structure</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td><img src="image1" alt="structure" /></td>
<td>Fuels and chemicals</td>
</tr>
<tr>
<td>Iso-butene</td>
<td><img src="image2" alt="structure" /></td>
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<tr>
<td>Trans-2-butene</td>
<td><img src="image3" alt="structure" /></td>
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<tr>
<td>Cis-2-butene</td>
<td><img src="image4" alt="structure" /></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td><img src="image5" alt="structure" /></td>
<td></td>
</tr>
<tr>
<td>Dibutyl ether</td>
<td><img src="image6" alt="structure" /></td>
<td>Solvents and additives</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td><img src="image7" alt="structure" /></td>
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<tr>
<td>Butyraldehyde</td>
<td><img src="image8" alt="structure" /></td>
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<tr>
<td>Butanoic acid</td>
<td><img src="image9" alt="structure" /></td>
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<tr>
<td>2-Butoxyethanol</td>
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<td>Butyl propionate</td>
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<tr>
<td>Compound</td>
<td>Structure</td>
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<tr>
<td>Butadiene</td>
<td><img src="image" alt="Butadiene" /></td>
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<tr>
<td>Butyl acrylate</td>
<td><img src="image" alt="Butyl acrylate" /></td>
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<tr>
<td>Butyl methacrylate</td>
<td><img src="image" alt="Butyl methacrylate" /></td>
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<tr>
<td>Butyl vinyl ether</td>
<td><img src="image" alt="Butyl vinyl ether" /></td>
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<tr>
<td>Butyl phthalates</td>
<td><img src="image" alt="Butyl phthalates" /></td>
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<td>Tributyl citrate</td>
<td><img src="image" alt="Tributyl citrate" /></td>
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<td>Butylparaben</td>
<td><img src="image" alt="Butylparaben" /></td>
<td></td>
</tr>
<tr>
<td>Butyl amines</td>
<td><img src="image" alt="Butyl amines" /></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Category</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers</td>
<td></td>
</tr>
<tr>
<td>Plasticizers and</td>
<td></td>
</tr>
<tr>
<td>Miscellaneous</td>
<td></td>
</tr>
</tbody>
</table>

There are various reaction routes to convert 1-butanol into value-added chemicals, such as dehydration, dehydrogenation and oxidative dehydrogenation [15]. In this thesis, the dehydration and the partial oxidation routes are discussed with context to coated catalysts [19–25] and microreactors for heterogeneously catalyzed gas phase operation (Section 1.3).
1.2.1 Dehydration of 1-butanol: reactions and catalysts

Dehydration of 1-butanol via direct route produces butenes, which are important chemicals for organic synthesis (Fig. 2). The most important application is in hydrocarbon fuel and synthetic elastomer markets [15,26]. The lighter hydrocarbon fractions, such as butenes are typically fossil-based. Thus, the synthesis of butenes from biomass-based resources would provide a sustainable route.

![Fig. 2. Main products from dehydration of 1-butanol.](image)

Typical reactions for 1-butanol dehydration are [27]: direct dehydration to butenes (1), formation of dibutyl ether (2) and subsequent dehydration of dibutyl ether to form butenes (3). The dehydration of 1-butanol produces different butene isomers (1-butene, cis-2-butene, iso-butene and trans-2-butene), and depending upon the reaction conditions and catalyst, the ratio of the isomers can vary [27].

\[
\begin{align*}
C_4H_9OH &\rightarrow C_4H_8 + H_2O \quad (1) \\
2C_4H_9OH &\rightleftharpoons C_4H_9OC_4H_9 + H_2O \quad (2) \\
C_4H_9OC_4H_9 &\rightarrow 2C_4H_8 + H_2O \quad (3)
\end{align*}
\]

Dehydration of an alcohol is a catalyzed elimination reaction, which removes H₂O to form alkene. Typical acid catalyst for dehydration is H₂SO₄. In case of heterogeneous catalysts, metal oxides are commonly used due to their acid-base properties [28,29]. The dehydration of 1-butanol has been studied extensively in the literature by applying different catalysts, such as γ-Al₂O₃, H-ZSM-5, aluminosilicate and aluminophosphate [26,27,29–43].

γ-Al₂O₃, among other catalysts reported in the literature, has been studied for dehydration of 1-butanol owing to its Lewis acidity and acido-basicity [27–29,44]. The γ-Al₂O₃ is considered an irreducible oxide [45]. The main advantage
is its stable nature within alcohol dehydration reaction and acidity in acid-catalyzed reactions. Knözinger and Köhne [37] suggested that formation of alkenes and ethers from alcohol dehydration occurred with unknown yet the same mechanism. Knözinger et al. [46] later suggested that alkenes are formed via alkoxide species. The classical review from Knözinger and Ratnasamy [47] provides detailed information about the complicated alumina surface and presence of different types of hydroxyl surfaces due to defective spinel lattices. Bertau et al. [27] found that on γ-Al₂O₃, the intermolecular dehydration of two butanol molecules led to dibutyl ether formation, whereas intramolecular dehydration of butanol led to direct dehydration to butene. Decanio et al. [28] proposed formation of two types of alkoxides from the Lewis acid site and the nucleophilic surface base site, which were intermediates to ethene and ether. Through infrared (IR) spectroscopic insights on ethanol dehydration to ethene, Busca et al. [45] and Phung et al. [48] have further reviewed the γ-Al₂O₃ surface sites. Phung et al. [48] have reported ethoxy surface species as the intermediate species for the ethanol dehydration to ethene and diethyl ether. Phung et al. [48] proposed that the ethoxy species were formed on Lewis acid-base sites and surface hydroxyl sites.

The findings from reported works on dehydration of 1-butanol [27,29] and ethanol [28,29,45,48,49] on γ-Al₂O₃ provide an opportunity to develop surface reaction mechanism for the kinetics of 1-butanol dehydration from the microreactor data in this work [I]. To author’s best knowledge, the application of γ-Al₂O₃ as coated catalyst in a structured microreactor for 1-butanol dehydration kinetics had not be reported before this work [I]. The kinetic studies of 1-butanol dehydration on pure γ-Al₂O₃ has been reported by Clayborne et al. [29] in temperature programmed desorption studies. Makarova et al. [32] used H-ZSM-5 and amorphous aluminosilicate in the liquid phase. The activation energies for 1-butanol dehydration studies reported in the literature are summarized in Table 2.

Table 2. Activation energies reported in the literature for 1-butanol dehydration reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Makarova et al. [32], E (kJ/mol)</th>
<th>Clayborne et al. [29], E (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butanol dehydration to butenes</td>
<td>134</td>
<td>132 ± 10</td>
</tr>
<tr>
<td>1-Butanol dehydration to dibutyl ether</td>
<td>92</td>
<td>100 ± 10</td>
</tr>
<tr>
<td>Dibutyl ether dehydration to butenes</td>
<td>134</td>
<td>-</td>
</tr>
</tbody>
</table>
1.2.2 Partial oxidation of 1-butanol: reactions and catalysts

Oxidation reactions play an important role in industry in the synthesis of base and specialty chemicals, such as aldehydes, ketones and carboxylic acids from corresponding primary and secondary alcohols [15,16,50,51]. Oxidation reactions of alcohols can be carried out in both liquid and gas phase. However, typically liquid phase oxidation is used to promote selectivity towards aldehydes [16,50,51]. The process uses air and pure oxygen as a clean reagent [16,51], although air is a cheaper and safer option. The molar ratio of alcohol to oxygen vary for the reaction to avoid total oxidation products and to perform selective partial oxidation [16,51–53].

Aldehydes in general are important intermediates for synthesis of fine chemicals and pharmaceuticals. Opposite to the traditional oxo-synthesis process [54], n-butyraldehyde can be produced from the partial oxidation of 1-butanol according to the following reaction equation [15,16]:

\[
2\text{C}_4\text{H}_9\text{OH} + \text{O}_2 \rightarrow 2\text{C}_4\text{H}_8\text{O} + 2\text{H}_2\text{O}
\]  \hspace{1cm} (4)

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\]  \hspace{1cm} (4)

Fig. 3. Derivatives from the partial oxidation of 1-butanol [15–17].

Typical applications for n-butyraldehyde (Fig. 3) are as an intermediate for the production of various chemicals and fuel components, such as acetal, 2-ethylhexanol, 2-ethylhexanoic acid, polyvinyl butyral and trimethylolpropane [15,16]. Currently in industrial scale, butyraldehyde synthesis is mainly performed by oxo-synthesis via propylene hydroformylation using homogeneous catalysts. The main technologies are the original cobalt catalyzed high pressure process and low pressure oxo-process (LPO) process catalyzed by triphenylphosphine (Rh-TPP) complexes [10]. However, both processes take place at relatively high pressures (2–35 MPa) and the raw materials are mainly coming from fossil resources [54]. The renewable resources as raw materials and subsequent development of synthesis routes with milder conditions will lead to more environmentally friendly and sustainable manufacturing process [15].

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1-Butanol partial oxidation has been reported in the literature in both the liquid and gas-phase by applying noble metal nanoparticles, such as Au, Pd, Pt, Ru as well as Cu on different supports, such as ZrO$_2$, CeO$_2$, TiO$_2$, activated carbon (AC), Al$_2$O$_3$, AC and SiO$_2$ [17,50–52]. In the liquid phase, however, further oxidation of n-butyraldehyde can lead to butyric acid [51]. The n-butyraldehyde over-oxidation has been reported to take place at 100 °C even in the absence of a catalyst, which is related to the presence of water in the system that leads to the production of geminal diol, which rapidly reacts to form acid [52,55]. This may be solved by developing a catalyst that is selective towards n-butyraldehyde but does not enhance over-oxidation [52]. Gandarias et al. [52] developed Pt catalysts on different supports, such as TiO$_2$, amorphous silica-alumina (ASA), Al$_2$O$_3$, AC and CeO$_2$ and applied these catalysts in the aqueous phase partial oxidation of n-butanol. Gandarias and co-workers reported that the high selectivities towards n-butyraldehyde were only possible at intermediate conversions i.e. the presence of n-butanol in the aqueous medium was necessary to avoid over-oxidation products. The higher selectivity towards n-butyraldehyde than butanoic acid can be also tuned by using a solvent that usually enhances the desired reactions towards corresponding aldehydes. The solvent effect to the reaction selectivity has been attributed towards the solubility of oxygen and the interaction of the noble metal centers [56]. Nevertheless, the solvent used in the liquid phase leads to additional challenges in obtaining a pure final product [16].

To overcome these challenges and to find other promising routes for the selective alcohol catalytic oxidation, different heterogeneous catalysts, such as Au/SiO$_2$, Ru/ZrO$_2$, Ru-Cu/TiO$_2$, Ru/CeO$_2$ have been studied in the gas phase as well [16,50].

Gold as catalyst has been reported as early as in 1913 by Fokin [57,58] for oxidation of methanol to formaldehyde. Sabatier referred in his book "La Catalyse en Chimie Organique" (translated into English version "Catalysis in Organic Synthesis") [59,60] that finely divided gold had activity resembling silver. The interest to use Au nanoparticles for alcohol selective oxidation and to achieve better activity and selectivity to corresponding aldehydes has been discussed in detail in a review by Sharma et al. [61]. The ability of the Au nanoparticles to dissociate molecular oxygen [51,62,63], the nontoxicity and the recyclability [64] add to the advantages of using the gold nanoparticles in heterogeneous catalysis application. Au and bimetallic gold-palladium supported on TiO$_2$ have been tested for different primary alcohols and were found to be active for the selective oxidation towards aldehyde and carboxylic acid [51,53]. The gold nanoparticles are most active in a size range of 2-6 nm [63]. Gandarias and coworkers [51,52] have used gold, palladium and platinum nanoparticles under moderate conditions (P= 3 bar, T=80-120 °C) in a solvent and base free environment, which demonstrated that the noble metal nanoparticles were appealing for applications in 1-butanol partial oxidation.
The choice of catalyst support material for oxidation reactions in relation to the interaction with the noble metals is essential for final product distribution [65–69]. For the partial oxidation of 1-butanol, different catalyst support materials, such as ZrO$_2$, CeO$_2$, TiO$_2$, AC, Al$_2$O$_3$, SiO$_2$, ASA and perovskites have been employed in both the gas and liquid phases [17,50–52,70]. The TiO$_2$ applied in this work, has shown strong metal-support interaction (SMSI), it is stable at high temperatures and it has a mesoporous structure [61,71]. Adding or depositing the metal nano-particles on TiO$_2$ have shown to result in active catalysts in the oxidation reactions of alcohols and sugars [67]. A direct correlation between catalytic activity and electron transfer from the Au particles (particle size less than 5 nm) to the TiO$_2$ support was discovered by Okazaki et al. [72]. Simakova et al. [73] and Holz et al. [62] tested Au/TiO$_2$ in ethanol oxidation in the gas phase and reported that the Au nanoparticles were active and selective towards acetaldehyde.

To prepare supported metal catalyst with good metal dispersion and narrow metal particle size distribution, the most common synthesis methods are impregnation, deposition-precipitation and sol-immobilization [53,61,69]. For the supported bimetallic Au-Pd catalysts, the metals can be incorporated either simultaneously or successively using aforementioned synthesis methods [74]. Gandarias et al. [51] and Lopez-Sanchez et al. [75] compared these different preparation methods and reported that the sol-immobilization method, i.e. the colloidal method, was advantageous to synthesize Au nanoparticles with a narrow particle size distribution and with a specific morphology. The reason was that the colloidal method uses organic ligands or polymers to stabilize the nanoparticles in the colloid [69]. The typically used stabilizer for supported Au-Pd nanoparticles is polyvinyl alcohol (PVA) [76].

Kinetics for 1-butanol partial oxidation to n-butyraldehyde on nanoparticle gold catalyst supported over TiO$_2$ have not been reported in the literature before this work [IV]. The reaction system is exothermic with heat of reaction ca. -500 and -2300 kJ/mol for partial oxidation and total oxidation reactions, respectively. Therefore, using microreactor as a tool to conduct kinetic studies isothermally within the kinetic regime (thin catalyst layer on channel walls <40-50 µm) is beneficial [49,77].

### 1.3 Microreactors

Microreactors, as considered in this work, are miniaturized reactors, which consist of multiple channel structured stainless-steel plates (Fig. 4 and Fig. 5) with at least one dimension in the microscale <1 mm [20,21,49,78,79]. The catalyst is coated on the walls of the microchannels [21,78]. Examples of different terminologies used for microreactors, the respective dimensions of the channels and thickness of the coated catalyst layer, are summarized in Table 3.
Microreactor structure can differ depending upon the final application [12,19–22]. Microreactors have emerged over the last decade as an alternative to conventional reactors, where exploiting microreactors’ advantages related to good heat and mass transfer properties as well as safe application in hazardous chemical synthesis are necessary, in process applications [12,80]. These advantages for the microreactors, applied for heterogeneously catalyzed gas phase reactions, arise from small-scale dimensions where diameter or depth of the flow channel is usually in micrometer-scale. The different length scales involved in the use of microreactors are depicted in Fig. 4. High heat transfer area-to-volume ratios, typically 10,000-50,000 m²/m³ [79] and high heat transfer coefficients typically up to 25,000 W/m²K [79], lead to nearly isothermal conditions in both the endothermic and exothermic reactions. Furthermore, lower material hold-up provides inherent safety for highly exothermic and hazardous reactions [12,21,49].
Table 3. Examples of terminology to refer to stainless-steel structured reactors with dimensions in microscales and in a similar range as in this work used in the heterogeneously catalyzed gas-phase reactions

<table>
<thead>
<tr>
<th>Terminologies</th>
<th>Dimensions of channels</th>
<th>Coating/ washcoat</th>
<th>Reaction systems</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length (mm)</td>
<td>Height/ depth (µm)</td>
<td>Width/ diameter (µm)</td>
<td>Layer thickness (µm)</td>
</tr>
<tr>
<td>Microchannels/ Microreactor plates</td>
<td>50</td>
<td>300/300/70</td>
<td>500/750/70</td>
<td>20-70/20-70/10-20</td>
</tr>
<tr>
<td>Microchannels/ Microreactor plates</td>
<td>25</td>
<td>250</td>
<td>500</td>
<td>15-40</td>
</tr>
<tr>
<td>Microchannel reactor</td>
<td>20</td>
<td>-</td>
<td>280</td>
<td>5-20</td>
</tr>
<tr>
<td>Microreactor/Microstructured reactor</td>
<td>9.5*10 stacks</td>
<td>75</td>
<td>460</td>
<td>15-20</td>
</tr>
<tr>
<td>Microreactor</td>
<td>9.5*10 stacks</td>
<td>90</td>
<td>460</td>
<td>30</td>
</tr>
<tr>
<td>Microchannel reactor</td>
<td>70</td>
<td>550</td>
<td>550</td>
<td>25</td>
</tr>
<tr>
<td>Microchannel reactor</td>
<td>25</td>
<td>250</td>
<td>500</td>
<td>15-30</td>
</tr>
<tr>
<td>Microstructured reactor/Microreactor</td>
<td>75</td>
<td>150</td>
<td>1000</td>
<td>10-24</td>
</tr>
</tbody>
</table>
Catalytic microreactors obeying isothermal conditions are excellent tools for investigation of intrinsic kinetics with a thin catalyst layer (<40-50 µm) coated on the walls of the channels [79,88]. Compared to conventional reactor types with the decrease of specific length scale and short diffusion paths (in micrometers), the external and internal mass transfer limitations could be suppressed [12,79]. Mass transfer is efficient and local mixing is rapid because of high local energy dissipation rate [19,21]. The diameter of the channels being in microscale (usually below 1 mm) only requires up to 50 ms of characteristic time for radial diffusion distances in the gas phase operation [11]. Thus, in the gas phase operation, the usual laminar flow profile (Re<100) does not hinder the diffusion of the molecules to the coated catalyst where characteristic time considerations are met [11].
Modified forms of Mears criterion [89] for external and Weisz-Prater criterion [90] for internal mass transfer considerations for wall coated microreactors have been discussed by various authors [21,23,24]. The thickness of the porous catalyst layer coated on the walls of the microreactor channels is a key parameter to determine whether the internal mass transfer is limiting [88]. Schmidt et al. [77] demonstrated that the methyl chloride synthesis, from methanol and hydrochloric acid, was operated in the kinetic regime by applying a microreactor coated with a porous catalyst layer of 10-20 µm. In previous studies of the same reaction, packed-bed systems with catalyst particles having diameters of 250-350 µm were applied inducing internal mass transfer limitations, as discussed by Schmidt et al. [77]. In addition to the advantages related to the intrinsic kinetics, the amount of expensive catalyst needed for the coating is used efficiently in the active layers [10].

Coating γ-Al₂O₃ and TiO₂ catalyst powders on the stainless-steel microreactor plates has been reported in the literature mainly in the work of Zapf and co-workers [82,92,93]. Zapf et al. [82] reported that the adhesion of the catalyst powder on the surface of the stainless-steel plates depends on many factors, such as use of binder, catalyst particle size and the interaction of the catalyst material to the metal surface oxide layer. To improve catalyst adhesion, a pre-treatment step is necessary, which may be a thermal or chemical pretreatment of the stainless-steel plates [82].

Kinetic modeling for wall coated microreactors and gas phase reactions is typically performed assuming plug flow conditions – neglecting back mixing and
axial dispersion of laminar flow conditions – with pseudohomogeneous models using a single phase modeling approach [20,21,77,78,80,94]. In principle, owing to the fast heat transfer, neglecting the axial heat conduction resistances, microreactors operate at isothermal conditions. Advanced and dynamic 2D models accounting for both the gas (free channel) and solid phases (catalyst coating) have also been reported in the literature [84,95]. A simplified illustration for the application of 1D-pseudohomogeneous model and 2D model including diffusion-reaction is presented in Fig. 6. The dynamic 2D models may incorporate flow regimes, back mixing and pressure drops – considering non-ideal flow behavior effects – within the bulk flow and radial flux to and from the catalyst layer [95]. Computational resources are often a limiting factor in utilizing the dynamic 2D models to determine kinetics and parameter estimation [95]. In this work, both the single-phase (1D-pseudohomogeneous) model [I, IV] and dynamic 2D modeling [IV] approaches were used to perform kinetic parameter estimation.

Fig. 6. A simplified illustration for (a) 1D-pseudohomogeneous plug flow reactor model and (b) 2D model with flux to catalyst layer.
1.4 Scope of the research

The aim of this work was to apply coated microreactors for the heterogeneously catalyzed gas-phase dehydration [I, II] and partial oxidation [III, IV] of 1-butanol to synthesize value-added chemicals. Owing to different levels of scales involved in microreaction technology (from the nanometer scale to the millimeter scale), the reaction engineering and the catalysis have a strong coupling, which brings both the topics to the scope of this thesis work. In the used microreactors, nearly isothermal conditions and operation in the kinetic regime was targeted by selecting microscale dimensions (width and height) of the stainless-steel channels and heterogeneous catalyst coatings with thickness below 40-50 µm.

The kinetic investigations were targeted for 1-butanol dehydration in a microreactor coated with γ-Al₂O₃ catalyst using power-law and surface reaction mechanism based kinetic expressions [I]. In addition, the aim was to develop a dynamic 2D model with diffusion-reaction inside the catalyst layer to simulate and study the reactor performance [I]. The reaction kinetics coupled with flow behavior inside the microchannels was targeted to gain further insight on the effect of laminar flow field on the diffusion-reaction of the components [II].

In the study of 1-butanol partial oxidation, the main goal was to develop TiO₂ supported mono and bimetallic Au and Pd catalysts, with narrow particle size distribution (<5 nm), using colloidal method. In addition, the aim was to produce mechanically and catalytically stable catalyst coatings. The developed catalyst coatings were targeted to be screened in a catalyst testing microreactor (CTMR) purchased from IMM. The CTMR was customized to operate for 1-butanol partial oxidation with air in the gas phase. The activity, durability and regenerability (by in situ regeneration for numerous operation cycles) of the coatings was of interest and focus [III].

The kinetic investigations for the multicomponent reaction system of 1-butanol partial oxidation were performed for the most selective catalyst towards n-butyraldehyde. The kinetic and reactor modeling was carried out by using a 1D-pseudohomogeneous model and an advanced 2D reactor model incorporating fluid flow properties based on dynamic mass balances in the gas- and solid phases [IV].
2. Materials and Methods

2.1 γ-Al₂O₃ coated catalyst plates

Coated catalyst plates with γ-Al₂O₃ were obtained from IMM to study 1-butanol dehydration reaction. The coating method has been described by Zapf et al. [93]. The amount of catalyst coated on each plate was 9 mg. Thus, in total a microchannel reactor consisting of two plates contained 18 mg of coated catalyst. Each plate constituted of 14 channels with a width of 500 µm, depth of 250 µm and a length of 25 mm. The catalyst-coated plates were calcined at 600 °C for 2 h. The thickness of the catalyst layer was determined by using Scanning Electron Microscopy (SEM). The SEM studies showed that the catalyst layer thickness varied between 15 - 30 µm, therefore, this whole catalyst layer range was used for reactor simulations [I, II].

2.2 Au-Pd/TiO₂ catalyst preparation by sol-immobilization method

TiO₂ supported monometallic and bimetallic Au-Pd catalysts were prepared via sol-immobilization method [III, IV], adapted from literature [53]. Schematic illustration of the Au catalyst preparation is presented in Fig. 7. Aqueous solution of gold(III)chloride (HAuCl₄, Aldrich, Au conc. 30 wt.% in dilute HCl) and/or palladium(II)chloride (PdCl₂, Alfa Aesar, Pd 20 – 25% wt. / wt. in PdCl₂ solution), was rinsed to 800 ml water. Fresh 1 wt.% aqueous solution of polyvinyl alcohol (PVA) (80% hydrolyzed, weight average molecular weight $M_w = 9000$-10 000 g/mol, Aldrich) was added to the noble metal solution (targeted PVA/metal=2 on weight basis) to protect formed nanoparticles from coalescence. A freshly prepared solution of NaBH₄ (0.1 M) reducing agent (Aldrich, targeted $n$(NaBH₄)/$n$(metal)=6) was then added to generate a dark brown solution indicating complete reduction of the metal ions. After 30 min, the colloid was immobilized by adding TiO₂ (Titanium (IV) oxide, anatase, <25 nm, 99.7% purity, Aldrich), acidified to pH 2-3 by H₂SO₄, under vigorous stirring conditions (800 rpm) for 2 h. After settling, the slurry was filtered followed by washing with distilled water. The catalyst was then dried overnight at 110 °C.
The targeted active metal weight percentages of Au and Pd were 0.6 wt.% on TiO₂ (to be named as 0.6Au and 0.6Pd). The targeted active metal weight percentages of bimetallic catalysts were 0.3 wt.% of Au and Pd (to be named as 0.3Au0.3Pd) and 0.6 wt.% of Au and Pd (to be named as 0.6Au0.6Pd). The TiO₂ support, without the active metals, was treated in similar manner to obtain a dried catalyst powder.

### 2.2.1 Pretreatment and coating of microreactor plates

Before the coating, the plates were pretreated by acid and thermal pretreatment to create sufficient surface roughness and a surface oxide layer [82]. The plates were obtained from IMM. Each plate had 13 channels with dimensions of 1000 µm width, 150 µm depth and 75 mm length (Fig. 8). The plates were washed with distilled water and then rinsed in a 0.25 wt.% citric acid solution for 2 h in an ultrasonic bath. The dried plates were then thermally oxidized in a furnace with ambient air flow at 800 °C for 2 h (ramp 5 °C/min).

The walls of the channels were coated with the prepared catalyst using a suspension method adapted from the literature [92]. The method was varied to find a procedure to prepare most stable coatings [96]. The schematic illustration for...
preparation of the catalyst and suspension is presented in Fig. 7, in brief: (i) PVA solution was prepared by mixing PVA ($M_w = 195\,000\,\text{g/mol}$, Aldrich) in distilled water for 2 h at 90 °C; (ii) dried catalyst powder was added to the PVA solution and the temperature was lowered to 65 °C at ca. 1 °C/min; (iii) the mixing at 65 °C was continued for 2 h; and (iv) the suspension was mixed at room temperature for 3 days. The suspensions were prepared with mass proportions of 1:19:4 for PVA:water:catalyst. The freshly made suspension was applied to the plates to fill the channels and excess suspension was wiped off. The coated plates were dried overnight at room temperature and then were calcined at 450 °C for 2 h (ramp 2 °C/min) in ambient air flow. The final amount of catalyst coated on two plates (constituting a microchannel reactor) was 60±4 mg.

Fig. 8. Example of an uncoated as received (left), uncoated pretreated (center) and pretreated & coated plated [III, IV] (stainless-steel plates manufactured by IMM). Photo taken by Valeria Azovskaya, Aalto University.

2.2.2 Characterization of coating powders

To obtain catalyst powder for analysis with similar thermal history as of the coated plates, the catalyst suspension was coated on a flat plate (stainless steel) and was calcined in ambient air at 450 °C (ramp of 2 °C/min) for 2 h. The coating was then scratched off from the plates for analysis.

Nitrogen physisorption (Ultra Surfer, Thermo Fischer at 77 K) was used to determine the surface area, pore volume and pore size distribution of the coating powders. The powder samples were treated under vacuum for 3 h at 300 °C for degassing to remove any adsorbed impurity species as a pre-step for the measurement. The Brunauer–Emmett–Teller (BET) method [97] was used to calculate the surface areas and the Barrett–Joyner–Halenda (BJH) method [98] was used to calculate the pore volumes, pore diameters and pore size distribution from the nitrogen desorption isotherms.
X-ray fluorescence (XRF) and an inductively coupled plasma optical emission spectroscopy (ICP-OES) were used to determine the metal loadings of the catalyst coating powders; more details of the equipment can be found in Publication III.

The effect of the coating and calcination to the metal nanoparticles size and size distribution was characterized by a JEOL-2200FS field emission gun (FEG) scanning transmission electron microscope (STEM). Three different sample sets were used [III]: (i) uncoated and uncalcined catalyst powder, (ii) catalyst powder coated and calcined at 300 °C and (iii) catalyst powder coated and calcined at 450 °C. Energy dispersive X-ray spectroscopy (EDS) was used to analyze the elemental content of the plate coatings.

The effect of the calcination step on the removal of PVA was measured for the 0.6 wt.% Au/TiO₂ catalyst via thermogravimetric analysis (TGA) using Thermal Analysis (TA) instruments 500 equipment operated from 30 to 700 °C in a N₂ atmosphere.

2.2.3 Characterization of catalyst coatings and durability tests

The thickness of the catalytic coating on the structured plates was measured [III] using a SEM with an energy dispersive X-ray spectroscopy (SEM-EDS Hitachi S-4700). A cross-section was sawed for the measurement.

The durability of the coated plates was tested by using a pair of plates for multiple activity experiments for almost 60 times (each of 6 h duration), and storing the same pair of coated plates for 6 months (at ambient pressure and temperature) after which their activity was compared to that of the fresh catalyst.

2.3 1-Butanol dehydration experiments with γ-Al₂O₃

2.3.1 Experimental setup

The experimental set-up of the microreactor system is presented in Fig. 9. The microreactor plates were obtained from IMM. The plates (Fig. 5) coated with γ-Al₂O₃ catalyst were joined together to form the sandwich-type structured microchannel reactor. Each plate constituted of 14 channels with a width of 500 µm, depth of 250 µm and a length of 25 mm [I].
Fig. 9. Experimental set-up for the microchannel reactor for 1-butanol dehydration experiments [1].
1-Butanol (VWR, 99.9%) was fed to evaporator with a high-performance liquid chromatograph (HPLC) pump (Agilent Technologies 1100 Series Isocratic pump). The generated vapors were then mixed with inert argon (AGA, 99.99%) and fed to the reactor. The analyses of the gaseous reaction products (Section 2.5) were performed by an online Fourier transform infrared spectrometer (FTIR, Gasmet Cr-2000, Temet Instruments). Before the FTIR, the flow was further diluted with nitrogen (AGA 99.99%) to achieve the minimum flow of 1000 ml/min required by the FTIR.

1-Butanol/argon ratios were adjusted to vary the partial pressure of 1-butanol in the experiments (Table 4). The partial pressure of 1-butanol was varied between 7.5-20.4 kPa [1]. The experiments were performed between 346 to 397 °C. The catalyst was regenerated between the experiments at a constant synthetic air flow of 30 ml/min at 550 °C for an hour.

**Table 4. Experimental conditions for the 1-butanol dehydration experiments [1].**

<table>
<thead>
<tr>
<th>Variables</th>
<th>Ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{C}_4\text{H}_9\text{OH}}$ (mol/m$^3$)</td>
<td>1.3–3.7</td>
</tr>
<tr>
<td>Partial pressure of 1-butanol (kPa)</td>
<td>7.5-20.4</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>346-397</td>
</tr>
<tr>
<td>1-Butanol flow rate (ml/min)</td>
<td>18-47</td>
</tr>
<tr>
<td>Ar flow rate (ml/min)</td>
<td>100-420</td>
</tr>
</tbody>
</table>

### 2.3.2 Kinetic modeling

Parameter estimation for kinetic modeling of 1-butanol dehydration was performed by using MATLAB® software. The generated ordinary differential equations (ODEs) were solved by using ode15s solver suitable for stiff systems. Neldel-Mead Simplex method based fmin search algorithm was used to obtain the global minimum of the objective function (Eq. 5) by minimization of Residual Sum of Squares (RSS)

$$Q_p = \min \sum_{i=1}^{nm} \left(y_{\exp} - y_{\text{cal}}\right)^2.$$  \hspace{1cm} (5)

Here, $Q_p$ is the residual sum of squares, $y_{\exp}$ is the experimental value and $y_{\text{cal}}$ is the calculated value for component $n$ in reaction $m$. The kinetic parameter
estimation was performed with a steady state 1D-pseudo-homogeneous plug flow model. In 1D-pseudo-homogenous model (Fig. 6a), it was assumed that the concentration gradients occur only in axial direction and fluid and catalyst are in close contact and at the same temperature. The catalyst was assumed to be dispersed uniformly across the reactor dimensions. The model was chosen after identifying that the experiments were performed in kinetic regime (discussed in detail in Publication I)

\[ \frac{d c_i}{d x} = \tau \rho_b \sum v_{ij} R_j . \] (6)

Here, \( x \) is the dimensionless length coordinate \( (x=l/L; l=0 \rightarrow L) \), \( L \) is the length of the reactor (m), \( c_i \) is the concentration (mol/m\(^3\)) of component \( i \), \( \tau \) is the space time (s), \( \rho_b \) is the catalyst bulk density (kg/m\(^3\)) that was calculated as catalyst mass divided by the reactor volume, \( v_{ij} \) is the stoichiometric coefficient for component \( i \) in reaction \( j \) and \( R_j \) is the corresponding reaction rate for reaction \( j \).

The temperature mean centering was applied to suppress parametric correlations between Arrhenius parameters \([77, 99]\):

\[ k = \bar{k} \exp \frac{E_a}{R} \frac{1}{\theta} , \] (7)

where \( E_a \) is the activation energy (J/mol), \( R \) is the gas constant (J/mol.K) and \( \bar{k} \) is the rate constant at average temperature \( (T/\bar{K}) \) and \( \theta \) is defined as:

\[ \frac{1}{\theta} = \frac{1}{T} - \frac{1}{\bar{T}} . \] (8)

## 2.4 1-Butanol partial oxidation experiments with Au-Pd/TiO\(_2\)

### 2.4.1 Experimental setup

The partial oxidation of 1-butanol with air was studied in catalyst testing micro-reactor (CTMR), manufactured by IMM [100]. The experimental setup is presented in Fig. 10 and the reactor system (as installed) is shown in Fig. 11. The reactor consisted of two compartments and each compartment contained 5 pairs of plates. Only one pair of coated catalyst plates (creating flow channels) was placed inside the reactor to perform the catalytic activity tests. The remaining space in the compartments of the reactor was filled with uncoated plates to complete the reactor packing for efficient heat transfer. Each plate had 13 channels with dimensions of 1000 \( \mu \)m width, 150 \( \mu \)m depth and 75 mm length.

1-Butanol (VWR, 99.9\%) was fed with Gilson 307 pump and evaporated and mixed with nitrogen (AGA, 5.0) in various ratios in an in-house designed mixer
The product gas analysis (Section 2.5) was performed with online FTIR (Gasmet instruments CR 5000).

The catalytic activity was studied at a steady state at atmospheric pressure and reactor temperatures of 130, 165, 250, 300 or 350 °C. The input lines were heated to 130 °C and output lines were heated to 130 °C, and then to 165 °C as the reactor temperature was increased to 165 °C, where it was kept constant. The catalyst screening experiments were carried out at 1-butanol partial pressure of 13.5 kPa and residence time of 0.137 s [III], experimental point 4 in Table 5. The kinetic experiments (experimental conditions in Table 5) were carried out at 1-butanol partial pressure of 13.5 and 18 kPa and residence times ranging from 0.066 - 0.137 s [IV]. The inlet concentrations of 1-butanol \( [C_{\text{m}}(C_4H_9OH)] \) and air \( [C_{\text{in}}(O_2)] \) and the flow of inert nitrogen were varied to change the flow velocity, \( U_F \), inside the reactor. After an experiment, the catalyst was regenerated at constant air flow of 100 ml/min at 400 °C for an hour.

Table 5. Experimental conditions [IV] for 1-butanol partial oxidation reaction in CTMR at 130-350 °C, partial pressure of 1-butanol 13.5 kPa (Exp. 1-4) and 18 kPa (Exp. 5-8).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Partial pressure (C₄H₉OH) [kPa]</th>
<th>( C_{\text{m}}(C_4H_9OH) ) [mol/m³]</th>
<th>( C_{\text{in}}(O_2) ) [mol/m³]</th>
<th>( U_F ) [m/s]</th>
<th>( \tau ) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.5</td>
<td>4.19</td>
<td>2.09</td>
<td>1.14</td>
<td>0.066</td>
</tr>
<tr>
<td>2</td>
<td>13.5</td>
<td>4.19</td>
<td>2.09</td>
<td>0.95</td>
<td>0.080</td>
</tr>
<tr>
<td>3</td>
<td>13.5</td>
<td>4.19</td>
<td>2.09</td>
<td>0.72</td>
<td>0.104</td>
</tr>
<tr>
<td>4</td>
<td>13.5</td>
<td>4.19</td>
<td>2.09</td>
<td>0.55</td>
<td>0.137</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
<td>5.59</td>
<td>2.80</td>
<td>1.14</td>
<td>0.066</td>
</tr>
<tr>
<td>6</td>
<td>18</td>
<td>5.59</td>
<td>2.80</td>
<td>0.95</td>
<td>0.080</td>
</tr>
<tr>
<td>7</td>
<td>18</td>
<td>5.59</td>
<td>2.80</td>
<td>0.72</td>
<td>0.104</td>
</tr>
<tr>
<td>8</td>
<td>18</td>
<td>5.59</td>
<td>2.80</td>
<td>0.55</td>
<td>0.137</td>
</tr>
</tbody>
</table>
Fig. 10. Experimental set-up for the 1-butanol partial oxidation experiments. Reproduced from Publication III with permission from Elsevier.
Fig. 11. Microreactor system and main components with annotations. Photograph courtesy of Janne-Joonas Tiitinen.
A mixer was designed in-house to mix the reactants prior to entering to the reactor by creating a nozzle like effect [IV]. Computational Fluid Dynamics (CFD) studies in 2D were carried out to confirm that the designed configuration resulted in proper mixing [IV]. COMSOL Multiphysics® 5.2a was used for the simulations applying a simplified geometry. Carrier gas N\textsubscript{2} and air entered from point A, whereas, 1-butanol vapors entered in from point B as presented in Fig. 12. The outlet was taken from point C. The geometry was extended to include 8 bends in the lines. In the actual experimental system, there were even more such bends and turnings before the mixture entered into the reactor, so the simulation results show reasonable mixing of the reaction mixture and carrier gas [22].

![Diagram](image)

**Fig. 12.** Geometry for designed mixer with extended flow line. Dimensions are given in meters. The inlet for N\textsubscript{2} (carrier gas) and air (reactant) is represented by 'A', point 'B' represents the 1-butanol vapor inlet, and point 'C' represents the outlet for the mixture [IV].

### 2.4.2 Kinetic modeling

The kinetic modeling [IV] was performed in Matlab® with 1D-pseudohomogeneous plug flow reactor model (Eq. 5-8) and in gPROMS model builder software [101] using dynamic 2D model (Eq. 9-10). In gPROMS, dynamic mass balances were written for each component in both the gas and solid catalyst phases assuming hydraulic diameter of the rectangular channels (Fig. 13). The model consisted of two sets of partial differential equations (PDEs) given in Equations 9 and 10.
Dynamic mass balance used for the gas phase includes convective and dispersion fluxes (both axial and radial):

$$\frac{\partial C_{i,G}}{\partial t} = -u_G \frac{\partial C_{i,G}}{\partial z} + D_z \frac{\partial^2 C_{i,G}}{\partial z^2}.$$  (9)

Here, $C_{i,G}$ is the concentration of component ‘$i$’ in gas (mol/m$^3$), $u_G$ is the superficial velocity of the gas (m/s), $D_z$ is the axial dispersion coefficient (m$^2$/s) and ‘$z$’ is the axial coordinate (m). The axial dispersion coefficient was calculated as $u_G \cdot L/Pe$, where $Pe$ was taken as 100 [IV] and $L$ is the length of the reactor (m).

For the solid (catalyst phase), the dynamic mass balance includes reaction and internal diffusion in the catalyst layer:
\[
\frac{\partial C_{i,S}}{\partial t} = -\frac{D_{\text{eff},i}}{\varepsilon_p} \left( \frac{\partial^2 C_{i,S}}{\partial r_p^2} + \frac{s}{r_p} \frac{\partial C_{i,S}}{\partial r_p} \right) + \frac{1}{\varepsilon_p} \sum_j v_{ij} r_j .
\]  

(10)

Here, \( C_{i,S} \) is the concentration of component \( i \) in the catalyst (mol/m\(^3\)), \( D_{\text{eff},i} \) is the effective diffusivity of component \( i \) (m\(^2\)/s), \( \varepsilon \) is the catalyst layer porosity taken as 0.5, \( s \) is the catalyst shape factor taken as 1, \( r \) is the radial coordinate (m), \( v_{ij} \) is the stoichiometric coefficient for component \( i \) in reaction \( j \) and \( r_j \) is the corresponding reaction rate for reaction \( j \). The effective diffusivity calculation procedure is described in Section 3.3, Eq. 33-35.

The PDEs were solved numerically with an inbuilt numerical method of lines reducing the PDE system to an ODE system in the gPROMS Model Builder software. The radial derivatives were solved with central difference and axial derivatives were solved with backward difference scheme. The grid points for the calculation were \( z=50, r=10, r_p=10 \) points. The model assumed the reaction to progress within the coated catalyst layer on evenly distributed active sites of the catalyst (Au/TiO\(_2\)). Both the individual reactions of each component and their internal diffusion steps were incorporated in the model for the coated catalyst layer [49,102].

The least square equation was used as the target function (Eq. 5) between the experimental and the model results. The conversion of 1-butanol as well as the yield of the products were used as the performance parameters. The details for the solution strategy and numerical methods are provided in Publication IV.

### 2.5 Performance evaluations in the experiments

Online FTIR was used to perform multicomponent analyses of the product gases and vapors in the experiments. FTIR was calibrated for the reactant 1-butanol, and products, such as 1-butene, cis-2-butene, trans-2-butene, dibutyl ether, \( n \)-butyraldehyde, \( n \)-butanoic acid, propene, CO and CO\(_2\). The liquid components were vaporized and diluted with carrier gas (in different proportions) to quantitate each measured spectrum [103,104].

The gas flows at normal temperature and pressure (NTP) \( Q_0 \) (\( T = 0 \) °C, \( p = 100 \) 000 Pa) were calculated from the dry gas volume flows with Eq. (11),

\[
Q_0 = \frac{V}{t} \cdot \frac{273.15 K}{T} \cdot \frac{p}{100000 \text{ Pa}}
\]  

(11)

The liquid flow of the components was converted to vapor flow at NTP using ideal gas law:

\[
P \dot{V} = \dot{n} \cdot R \cdot T_0
\]  

(12)

\[
\dot{V} = \frac{p \dot{V}}{p_M} R \cdot T_0
\]  

(13)
Here, $\dot{V}$ is the calculated vapor flow (ml/s), $\rho$ is the density of the liquid component (g/ml), $M_i$ is the molar mass (g/mol), $v$ is the liquid flow (ml/s) obtained from the pump and $R$ is the ideal gas constant (cm$^3$·Pa/[(mol·K)]).

The molar flow $F_i$ (mol/s) of component $i$ was calculated from the normalized volume flow with Eq. (14),

$$F_i = Q_0 \frac{y_i P}{RT_0}.$$  \hfill (14)

Here, $y$ is the volume fraction of the component $i$. The quantitative calibrations of the gases, such as CO$_2$, C$_3$H$_6$ and CO were performed similarly.

The FTIR software integrates the fingerprint analyses areas of unique molecular structures present in components and quantifies the respective molar fractions $y_i$ using the calibrated spectra [104]. The molar fractions obtained from the FTIR were then used in Eq. (14) to calculate the molar flows ($F_i$) for each component. The conversion of 1-butanol ($X_{1\text{-Butanol}}$) and selectivity ($S_i$) and yield ($Y_i$) of product components $i$ can be calculated based on the molar flows as:

$$X_{1\text{-Butanol}} (%) = \frac{F_{1\text{-Butanol,in}} - F_{1\text{-Butanol,out}}}{F_{1\text{-Butanol,in}}} \cdot 100\%.$$  \hfill (15)

$$S_i (%) = \frac{F_{i,\text{out}}}{F_{1\text{-Butanol,in}} - F_{1\text{-Butanol,out}}} \cdot 100\%.$$  \hfill (16)

$$Y_i (%) = \frac{F_{i,\text{out}}}{F_{1\text{-Butanol,in}}} \cdot 100\%.$$  \hfill (17)

The carbon balance was calculated with Eq. (18), as the ratio of the total molar flows in ($\dot{n}_{i,\text{C,atoms,in}}$) and out ($\dot{n}_{i,\text{C,atoms,out}}$) from the reactor by taking into account the total number of carbon atoms present in the components.

$$\text{Carbon balance} (%) = \frac{\sum_i \dot{n}_{i,\text{C,atoms,out}}}{\sum_i \dot{n}_{i,\text{C,atoms,in}}} \cdot 100\%.$$  \hfill (18)

The FTIR analyses methods for the experiments were developed and improved as per manufacturer’s guidelines [104]. However, some uncertainties may remain in the analyses of multicomponent product spectrum, such as over-lapping analyses areas of OH from H$_2$O and 1-butanol and narrow analyses areas for C=O in aldehydes and ketones. In addition, the uncertainty in the repeated experiments in the calculations for conversion, selectivity and yield was found to be ±2 percentage points.
3. Dehydration of 1-butanol with γ-Al₂O₃

The kinetic experiments were carried out for 1-butanol dehydration over the γ-Al₂O₃ coated catalyst in a microreactor. Before describing the kinetic modeling, the calculated chemical equilibria of the reactions are presented.

3.1 Chemical equilibrium

The chemical equilibrium of the individual reactions (Section 1.2.1) was evaluated with ReaEqu module in Flowbat software [105]. The three reactions are: (A) direct dehydration of 1-butanol to 1-butene, (B) formation of dibutyl ether and (C) subsequent dissociation/dehydration of dibutyl ether to 1-butene. The thermodynamic data for these reactions (equilibrium constants and reaction enthalpies) as functions of temperature are shown in Table 6.

\[
\begin{align*}
\text{C}_4\text{H}_9\text{OH} & \rightarrow \text{C}_4\text{H}_8 + \text{H}_2\text{O} & \text{(A)} \\
2\text{C}_4\text{H}_9\text{OH} & \rightleftharpoons \text{C}_4\text{H}_9\text{OC}_4\text{H}_9 + \text{H}_2\text{O} & \text{(B)} \\
\text{C}_4\text{H}_9\text{OC}_4\text{H}_9 & \rightarrow 2\text{C}_4\text{H}_8 + \text{H}_2\text{O} & \text{(C)}
\end{align*}
\]
Table 6. Equilibrium constants and heat of reactions A, B and C as function of temperature. Summing reactions B and C yields reaction A, and thus $K_A=K_B \cdot K_C$, which is consistent with laws of thermodynamics. Reproduced from Publication I with permission from Elsevier.

<table>
<thead>
<tr>
<th>$T$ ($^\circ$C)</th>
<th>$K_A$</th>
<th>$K_B$</th>
<th>$K_C$</th>
<th>$\Delta H_A$ (kJ/mol)</th>
<th>$\Delta H_B$ (kJ/mol)</th>
<th>$\Delta H_C$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>14800</td>
<td>3.47</td>
<td>4269</td>
<td>34.26</td>
<td>-22.02</td>
<td>56.28</td>
</tr>
<tr>
<td>346</td>
<td>15800</td>
<td>3.32</td>
<td>4756</td>
<td>34.25</td>
<td>-21.96</td>
<td>56.22</td>
</tr>
<tr>
<td>352</td>
<td>16860</td>
<td>3.19</td>
<td>5287</td>
<td>34.24</td>
<td>-21.91</td>
<td>56.15</td>
</tr>
<tr>
<td>358</td>
<td>17960</td>
<td>3.06</td>
<td>5865</td>
<td>34.23</td>
<td>-21.85</td>
<td>56.08</td>
</tr>
<tr>
<td>364</td>
<td>19110</td>
<td>2.94</td>
<td>6492</td>
<td>34.22</td>
<td>-21.80</td>
<td>56.02</td>
</tr>
<tr>
<td>370</td>
<td>20300</td>
<td>2.83</td>
<td>7171</td>
<td>34.21</td>
<td>-21.74</td>
<td>55.95</td>
</tr>
<tr>
<td>376</td>
<td>21550</td>
<td>2.73</td>
<td>7906</td>
<td>34.20</td>
<td>-21.69</td>
<td>55.88</td>
</tr>
<tr>
<td>382</td>
<td>22850</td>
<td>2.63</td>
<td>8700</td>
<td>34.18</td>
<td>-21.63</td>
<td>55.82</td>
</tr>
<tr>
<td>388</td>
<td>24200</td>
<td>2.53</td>
<td>9555</td>
<td>34.17</td>
<td>-21.58</td>
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</tr>
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<td>25610</td>
<td>2.45</td>
<td>10480</td>
<td>34.15</td>
<td>-21.53</td>
<td>55.68</td>
</tr>
</tbody>
</table>

The thermodynamic data in Table 6 reveals that reactions A (direct dehydration of 1-butanol to 1-butene) and C (dehydration of dibutyl ether to 1-butene) can be treated as irreversible, whereas reaction B (formation of dibutyl ether) has to be treated as reversible. The thermodynamic data showed that high equilibrium conversion of 1-butanol (up to 99%) for the desired reaction A can be achieved with high selectivity to 1-butene within the range of studied temperatures.

3.2 Kinetic experiments and modeling results

The experiments were performed (Publication I) at 346-397 °C and at 1-butanol partial pressure of 7.5 -20.4 kPa. 1-Butanol conversion of ca. 70% and high selectivity (>90%) to 1-butene was observed at partial pressure < 13 kPa. Other products detected in the product gas were water, dibutyl ether and butene isomers, such as cis-2-butene, trans-2-butene and isobutene. The butene isomers were formed in lower quantities, less than 4% of the formed products in total. The formation of dibutyl ether was low, selectivity up to 5% at 397 °C, but as high as 14% was observed at temperature of 346 °C. However, the equilibrium conversions (up to 99%) could not be achieved because of lower residence times.
in the experiments although relatively high conversions (88%) were observed. Thus, from experimental results it was concluded that the desired dehydration of 1-butanol to 1-butene was achieved at higher temperatures >380 °C and at lower partial pressures <13 kPa. These observations were consistent with the previous literature [27,48].

The experimental data of 1-butanol dehydration reaction over γ-Al₂O₃ was explained by both simple power-law kinetic expressions and more complicated surface reaction mechanism based kinetic expressions. The power-law models are typically a first attempt to describe the kinetic data [I], which means that intricate catalytic behavior is reduced to simple rate equation applying certain constant reaction orders. The power-law model necessitates for fixing the order of the reaction to a constant value. For 1-butanol dehydration over γ-Al₂O₃ with partial pressure range of 2.6-26.6 kPa, Berteau et al. [27] have demonstrated the existence of different regimes for the apparent reaction orders between zero (p_{1-Butanol} > 13.3 kPa) and one (p_{1-Butanol} < 13.3 kPa). Even though the mechanistic feature for 1-butanol dehydration has been proposed by Berteau et al. [27] it has not been used for determining kinetics of 1-butanol dehydration, before this work [I].

### 3.2.1 Power-law kinetics

Based upon the experimental observations and the literature [27], a reaction scheme for 1-butanol dehydration on γ-Al₂O₃ was suggested (Publication I), as presented in Fig. 14. For determining kinetics, the power-law model considers reactions between the bulk species neglecting the surface reaction steps.

![Fig. 14. Overall reaction scheme for 1-butanol dehydration modified from [27]. Reproduced from Publication I with permission from Elsevier.](image)

The reactions A and C were assumed irreversible and the reaction B as reversible based on the thermodynamic studies of the reaction system (Section 3.1). Butene isomers were lumped together with 1-butene. The rate equations for the different reactions are presented in Eq. 13-15, when assuming reaction orders to follow the law of mass action [I]:

```
(0.008-0.031 s) in the experiments although relatively high conversions (88%) were observed. Thus, from experimental results it was concluded that the desired dehydration of 1-butanol to 1-butene was achieved at higher temperatures >380 °C and at lower partial pressures <13 kPa. These observations were consistent with the previous literature [27,48].

The experimental data of 1-butanol dehydration reaction over γ-Al₂O₃ was explained by both simple power-law kinetic expressions and more complicated surface reaction mechanism based kinetic expressions. The power-law models are typically a first attempt to describe the kinetic data [I], which means that intricate catalytic behavior is reduced to simple rate equation applying certain constant reaction orders. The power-law model necessitates for fixing the order of the reaction to a constant value. For 1-butanol dehydration over γ-Al₂O₃ with partial pressure range of 2.6-26.6 kPa, Berteau et al. [27] have demonstrated the existence of different regimes for the apparent reaction orders between zero (p_{1-Butanol} > 13.3 kPa) and one (p_{1-Butanol} < 13.3 kPa). Even though the mechanistic feature for 1-butanol dehydration has been proposed by Berteau et al. [27] it has not been used for determining kinetics of 1-butanol dehydration, before this work [I].

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```
```
\[ r_1 = k_1 \cdot c_{BuOH} \]  
\[ r_2 = k_2 \cdot (c_{BuOH}^2 - \frac{1}{K_{eq}} \cdot c_{H_2O} \cdot c_{DBE}) \]  
\[ r_3 = k_3 \cdot c_{DBE} \]

where ‘BuOH’ is 1-butanol and ‘DBE’ is dibutyl ether. The temperature dependency of equilibrium constant in the rate equation for the reaction B was determined by using the van’t Hoff equation \[ [106] \].

\[ \ln \frac{K_{eq}}{K_{eq0}} = \frac{\Delta H^o}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \]  

where \( K_{eq} \) and \( K_{eq0} \) are the equilibrium constants at \( T_0(K) \) and \( T(K) \) respectively, \( \Delta H^o \) is the heat of reaction (J/mol) and R is the ideal gas constant (J/mol.K).

The rate equations for the respective reactions (Eq. 17-20) contain two Arrhenius parameters, the activation energy (\( E \)) and the frequency factor (\( A \)), to be determined for each equation (Eq. 7). The rate equations for the dehydration reactions (Fig. 14) were employed directly for the parameter estimation with mass balances for the species taken into account as:

\[ \frac{dc_{BuOH}}{dt} = (-2r_1 - 2r_2) \cdot \rho_b \]  
\[ \frac{dc_{C_4H_8}}{dt} = (2r_1 + 2r_3) \cdot \rho_b \]  
\[ \frac{dc_{H_2O}}{dt} = (2r_1 + r_2 + r_3) \cdot \rho_b \]  
\[ \frac{dc_{DBE}}{dt} = (-r_2 - r_3) \cdot \rho_b \]

where \( \rho_b \) is the catalyst bulk density (kg/m\(^3\)).

### 3.2.2 Kinetics based on surface reaction mechanism

The surface reaction mechanism, based on recent understanding from the spectroscopic studies [45,48], was formulated for 1-butanol dehydration over \( \gamma \)-\( \text{Al}_2\text{O}_3 \). Two sites were considered: Site 1, Lewis acid-base site that is an unsaturated cationic site and Site 2, a surface hydroxyl bound to unsaturated cationic site. The main suppositions and equations for surface reaction mechanism are presented in this section and the respective derivations can be found in the supplementary material of the Publication I.

Site 1: Lewis acid-base site
Site 2: surface hydroxyl bound to unsaturated cationic site

![Lewis acid-base site and hydroxyl group](image)

The formation of 1-butene is presented in Fig. 15. The attack on Lewis acid-base site (Site 1) forms dissociatively adsorbed alcohol with new OH and leads to formation of butoxy species. The adsorption of 1-butanol on surface OH groups (Site 2), releasing water, forms butoxy species as well (Fig. 15).

**Adsorption on Lewis acid-base sites (site 1)**

**Adsorption on OH sites (site 2)**

![Chemical reaction scheme](image)

*Fig. 15. Adsorption reaction scheme for alkene formation, adapted from Phung et al. [48]. Reproduced from Publication I with permission from Elsevier. Modified to add the symbol for the reaction rate ($r_1$).*

The formation rate of butene obtained in terms of butoxy species can be written as [I]

$$r_1 = k_1 \theta_{\text{butoxy}}. \quad (21)$$

Here, the surface coverage of the butoxy species at equilibrium is written as [I]
\[
\Theta_{\text{butoxy}} = \frac{K_{1cBuOH}}{1 + K_{1cBuOH} + K_{2cH2O}}. \tag{22}
\]

For formation of dibutyl ether, two different pathways were considered. In the first pathway (Fig. 16), single site mechanism (from here on referred to as mechanistic model I) forms ether by nucleophilic substitution reaction where the undissociatively (molecularly) adsorbed alcohol reacts with the butoxy group, as proposed by Phung et al. [48] and Bertau et al. [27]. Phung et al. [48] proposed that the alcohol molecule adsorbs undissociatively on the OH of alkoxide. The undissociated 1-butanol was assumed to be loosely and rather unspecifically H-bonded to the surface and to prevail in rapid equilibrium with the gas-phase 1-butanol, therefore; its driving force is related to gas-phase 1-butanol concentration. The term single site is related to one chemically bound surface species (butoxy formation).

![Fig. 16. Surface reaction scheme for mechanistic model I for ether formation, adapted from Phung et al. [48]. Reproduced from Publication I with permission from Elsevier. Modified to add the symbol for the reaction rate (r2).](image)

The rate equation for the mechanistic model I (Fig. 16) for formation of dibutyl ether is written as

\[
r_2 = k_2 (\Theta_{\text{butoxy}} \cdot c_{\text{BuOH}})^{\Theta_{\text{butoxy}}} c_{\text{H2O}} \cdot c_{\text{DBE}} / K_{eq} c_{\text{BuOH}}. \tag{23}
\]

The second mechanism (Fig. 17, only molecular forms of 1-butanol are depicted) for the formation of ether was considered to be a dual site mechanism, adapted from Bertau et al. [27] and Decanio et al. [28]. The dual site mechanism (referred to as mechanistic model II from here onwards) requires the participation of alkoxides on adjacent sites. In this dual site mechanism, two neighboring butoxy species (formed through Site 1 and Site 2, Fig. 17) undergo a nucleophilic attack of the Lewis acid-base alkoxide species on the positively polarized carbon in basic alkoxide species. Assuming two different types of surface species, even though theoretically interesting, would have led to over parametrization of the kinetic model and consequent inability to determine the parameter values by fitting. Therefore, for simplicity one type of alkoxide species were assumed.
Considering the dual site mechanism (mechanistic model II), the rate equation for the formation of dibutyl ether can be written as

\[ r_2 = k_2 \left( \theta_{\text{butoxy}} - \frac{\theta_{\text{butoxy}}^2 c_{\text{H}_2\text{O}} c_{\text{DBE}}}{K_{eq} c_{\text{BuOH}}} \right). \]  (24)

The proposed surface reaction mechanisms (formation of 1-butene and dibutyl ether) contain two Arrhenius dependent rate constants \(k_1\) and \(k_2\) and two adsorption equilibrium constants \(K_1\) and \(K_2\). Thus, compared to the power-law model (Eq. 13-15) there are no more degrees of freedom in the surface reaction models. The mass balances for each component for the mechanistic models were written based on the developed rate equations.

\[
\frac{dc_{\text{BuOH}}}{d\tau} = (-r_1 - 2 r_2) \cdot \rho_b \]  (25)

\[
\frac{dc_{\text{C}_4\text{H}_8}}{d\tau} = (r_1) \cdot \rho_b \]  (26)

\[
\frac{dc_{\text{H}_2\text{O}}}{d\tau} = (r_1 + r_2) \cdot \rho_b \]  (27)

\[
\frac{dc_{\text{DBE}}}{d\tau} = (r_2) \cdot \rho_b \]  (28)
3.2.3 Kinetic parameters

The estimated kinetic parameters using both the power-law and surface reaction mechanism based kinetic expressions in the 1D-pseudohomogeneous plug flow model, are presented in Table 7. The estimated parameters were physically meaningful and comparable to the literature, as compared in Table 7. In Fig. 18 the experimental data (·) and the model prediction (line) are presented for weight hourly space velocity (WHSV) of 521 h⁻¹ and for different temperatures, which shows that the model simulation reproduced the experimental data.

![1-Butanol conversion at 521 h⁻¹](image)

**Fig. 18.** Model fit plot of power-law model for 1-butanol conversion against temperature and WHSV 521 h⁻¹. Experimental points are denoted by ‘·’. Reproduced from Publication I with permission from Elsevier.
Table 7. Parameter estimation results (Publication I) with power-law and mechanistic models I and II. $K_1$ and $K_2$ are fixed adsorption parameters for the formation of butoxy species on site 1 and site 2. Reproduced from Publication I with permission from Elsevier.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Model results</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Power-law</td>
<td>Mechanistic I</td>
</tr>
<tr>
<td>$E_1$ (kJ/mol)</td>
<td>132</td>
<td>134</td>
</tr>
<tr>
<td>$A_1$ (s$^{-1}$)</td>
<td>2.71·10$^9$</td>
<td>2.10·10$^{10}$</td>
</tr>
<tr>
<td>$E_2$ (kJ/mol)</td>
<td>100</td>
<td>106</td>
</tr>
<tr>
<td>$A_2$ (s$^{-1}$)</td>
<td>3.43·10$^6$</td>
<td>3.12·10$^6$</td>
</tr>
<tr>
<td>$E_3$ (kJ/mol)</td>
<td>140</td>
<td>$K_1$=0.5</td>
</tr>
<tr>
<td>$A_3$ (s$^{-1}$)</td>
<td>1.37·10$^8$</td>
<td>$K_2$=0.4</td>
</tr>
</tbody>
</table>

Explanation factor $R^2$ for the estimated parameters was about 99% for all three models, which is quite reasonable [I]. The parity plot for the power-law and mechanistic model I (Fig. 19) shows a good fit of the model against the experimental data.
3.3 Reactor simulations

To simulate the reactor concentration profiles inside the free channel and in the heterogeneous catalyst layer (Fig. 20), a dynamic 2D heterogeneous model was developed for microchannel reactor (MCR) to study mass transfer limited and kinetically controlled regimes. Plug flow and uniform conditions within all the channels were assumed so that a single channel model could be applied to explain the whole reactor domain.
More details about the dynamic model assumptions and mathematical equations are provided in the supplementary data of Publication I. The main mathematical equations were the mass balances for each component in the MCR free channel and in the catalyst layer.

Mass balance in the cylindrical coating for each component in dimensionless radial coordinate \( z=r/R_1 \) was described as follows:

\[
\varepsilon_p \frac{\partial c_i}{\partial t} = \frac{D_{ei}}{R_1^2} \left( \frac{\partial^2 c_i}{\partial z^2} + \frac{1}{\varepsilon} \frac{\partial c_i}{\partial z} \right) + r_i \rho_p, \ c_i = c_i^S (29)
\]

where \( \varepsilon_p \) is the porosity of the catalyst layer taken as 0.5, \( c_i = c_i^S \) is the concentration of component \( i \) in the catalyst layer (mol/m\(^3\)), \( D_{ei} \) is the effective diffusivity of component \( i \) (m\(^2\)/s), \( R_1 \) is the radius of the inner empty channel space taken as 225 \( \mu \)m (Fig. 20), \( r_i \) is the reaction rate for component \( i \) and \( \rho_p \) is the catalyst layer density (kg/m\(^3\)) that is calculated as catalyst mass divided by the layer volume.

Dynamic mass balance in the free gas channel for each component in the dimensionless axial coordinate \( x=l/L \) was described as:

\[
\frac{\partial c_i}{\partial t} = - \frac{u}{\varepsilon_b L} \frac{\partial c_i}{\partial x} - \frac{2(1-\varepsilon_b)}{\varepsilon_b R_1^2} D_{ei} \frac{\partial c_i}{\partial z} \bigg|_{z=1}, \ c_i = c_i^b (30)
\]

where \( c_i = c_i^b \) is the concentration of component \( i \) in the free channel (mol/m\(^3\)), \( \varepsilon_b \) is the reactor channel void fraction, \( u \) is the fluid flow velocity (m/s) and \( L \) is the length of the reactor (m).

Analogous continuum models were developed for a Packed Bed Reactor (PBR) as well for comparison purposes. In PBR, catalyst particles were assumed of
standard size (diameter) between 250-420 µm. More details about the PBR dynamic model assumptions and mathematical equations are provided in the supplementary data of Publication I. The main mathematical equations in the PBR were mass balance of the catalyst particle and the reactor bulk flow for each component.

Mass balance of the catalyst particle for each component in the dimensionless radial coordinate \(z=r/R_p\) was described as follows:

\[
\varepsilon_p \frac{\partial c_i}{\partial t} = \frac{D_{ei}}{R_p^2} \left( \frac{\partial^2 c_i}{\partial z^2} + \frac{2}{z} \frac{\partial c_i}{\partial z} \right) + r_i' \rho_p
\]  \hspace{1cm} (31)

where \(\varepsilon_p\) is the porosity of the catalyst particle used as 0.4, \(R_p (r=0 \rightarrow R_p)\) is the radius of the particle, \(r_i\) is the reaction rate for component \(i\) and \(\rho_p\) is the catalyst particle density (kg/m\(^3\)) [99].

Mass balance in the reactor for each component in the dimensionless axial coordinate \((x=l/L)\) was described as:

\[
\frac{\partial c_i}{\partial t} = -\frac{u}{L \varepsilon_b} \frac{\partial c_i}{\partial x} - \frac{3D_e(1-\varepsilon_b)}{\varepsilon_b R_p^2} \frac{\partial c_i}{\partial z} \bigg|_{z=1}.
\]  \hspace{1cm} (32)

The effective diffusion coefficients \(D_{ei}\) of components were obtained by using the mean pore transport model (excludes Knudsen diffusion) [79] from the molecular diffusion coefficients \(D_i\), the particle porosity \((\varepsilon_p)\) used as 0.5 or 0.4 and tortuosity \((\tau)\) used as 2 [77,107]

\[
D_{ei} = \left( \frac{\varepsilon_i}{\tau} \right) D_i.
\]  \hspace{1cm} (33)

Wilke approximation [108] was used to obtain the molecular diffusion coefficient from the binary diffusion coefficients \(D_{ik}\) with mole fractions \((x_i)\) of each component

\[
D_i = \frac{1-x_i}{\sum_{k=1, k \neq i}^{N} \frac{x_k}{D_{ik}}}. \hspace{1cm} (34)
\]

Binary molecular diffusion coefficients used in Wilke equation were estimated using Fuller-Schettler-Giddings [109] equation.

\[
D_{ik} = \frac{(T)^{1.75} \left( \frac{1}{D_i} \right) \left( \frac{1}{D_k} \right) \left( \frac{1}{P} \right) \left( \frac{1}{v_i^2 + v_k^2} \right)}{(P) \left( \frac{1}{v_i^2 + v_k^2} \right)} \cdot 10^{-7} \text{m}^2/\text{s}
\]  \hspace{1cm} (35)

Here, \(T\) is the temperature (K), \(P\) is the total pressure (atm) and \(M\) is the molar mass (g/mol) of component \(i\) and \(k\). The volume contributions \((v_i)\) of the molecules were obtained from the literature [108] and are presented in Table 8 together with other parameters used for the simulations.
Table 8. Parameters used in simulations and volume contributions of the molecules ($\nu_i$) in determination of binary molecular diffusion coefficients using Eq. 35.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Volume contribution ($\nu_i$)</th>
<th>MCR</th>
<th>PBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_4$H$_9$OH</td>
<td>91.3</td>
<td>$R_1$ 225 (um)</td>
<td>Radius of PBR 3.5 (mm)</td>
</tr>
<tr>
<td>Ar</td>
<td>16.1</td>
<td>$\delta_s$ 15-200 (um)</td>
<td>$R_p$ 100-210 (um)</td>
</tr>
<tr>
<td>C$_4$H$_8$</td>
<td>81.9</td>
<td>$L$ 25 (mm)</td>
<td>$L$ 5 (mm)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>12.7</td>
<td>$m_{\text{cat}}$ 18/13 (mg)</td>
<td>$m_{\text{cat}}$ 18 (mg)</td>
</tr>
<tr>
<td>C$_4$H$_9$OC$_4$H$_9$</td>
<td>173.2</td>
<td>$\rho_p$ 0.5</td>
<td>$\rho_p$ 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\tau$ 2</td>
<td>$\tau$ 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\rho_p/m_{\text{cat}}/\text{volume}$ (kg/m$^3$)</td>
<td>$\rho_p$ 1255 (kg/m$^3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D_{\text{ei}}$ Eq. 33-35</td>
<td>$D_{\text{ei}}$ Eq. 33-35</td>
</tr>
</tbody>
</table>

3.3.1 Concentration profiles in catalyst layer

The simulated concentration profiles [I] for the reactant (1-butanol) inside the catalyst layer along the dimensionless radial coordinate $z$ are presented in Fig. 21. The dimensionless distance into layer $z$ was normalized where $z=1$ represents the catalyst layer surface and $z=0$ represents the reactor wall. Different catalyst layer thicknesses were simulated to visualize MCR coating range (15 $\mu$m to 30 $\mu$m). The simulations were extended for the MCR up to catalyst layer thicknesses of 40, 50, 100 and 200 $\mu$m, in order to further visualize the effect of increasing layer thickness on the MCR performance.
Fig. 21. Simulated 1-butanol concentration profile inside the catalyst layer for different layer thicknesses (in µm) at 391 °C. The higher catalyst layer thicknesses correspond to ranges of radius for the standard particle size used in packed-bed reactor simulations. Simulation parameters as in Table 8. Reproduced from Publication I with permission from Elsevier.

The model simulations (Fig. 21) showed that beyond 40 µm, the reactant concentration profile starts to change significantly. This means that along the dimensionless distance inside the catalyst, as we move away from the surface of the catalyst towards the plate wall, a lower concentration of the reactant molecules is available.

To further understand the concentration distribution inside the catalyst layer, effectiveness factor was calculated for the catalyst using the main reaction A (direct dehydration to 1-butene). The effectiveness factor compares the observed reaction rate to the reaction rate observed in the absence of internal diffusional limitations [107]. Considering characteristic length for the channel geometry [107], the effectiveness factor ($\eta$) for any geometry can be written as,

$$\eta_i = \frac{\tan (\varphi_i)}{\varphi_i}.$$  (36)

Here, Thiele modulus ($\varphi_i$) for reaction $i$ is calculated from following equation for the $n^{th}$ order equation [107]

$$\varphi_i = R_p \sqrt{\frac{k_c n^{-1}}{D_{ei}}},$$  (37)

where $D_{ei}$ is effective diffusion coefficient (m²/s), $k$ is the reaction rate (1/s) and $R_p$ is the characteristic length (m) [107,110].
Table 9. Effectiveness factor for the dehydration reaction (A) to butene. Reproduced from Publication I with permission from Elsevier.

<table>
<thead>
<tr>
<th>Catalyst layer thickness (µm)</th>
<th>Effectiveness factor ( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.97</td>
</tr>
<tr>
<td>25</td>
<td>0.93</td>
</tr>
<tr>
<td>30</td>
<td>0.91</td>
</tr>
<tr>
<td>40</td>
<td>0.85</td>
</tr>
<tr>
<td>50</td>
<td>0.79</td>
</tr>
<tr>
<td>100</td>
<td>0.52</td>
</tr>
<tr>
<td>200</td>
<td>0.27</td>
</tr>
</tbody>
</table>

The effectiveness factor (Table 9) for the catalyst layer thickness utilized in the MCR experiments (15 µm to 30 µm) was between 0.97-0.91. Hence, for the MCR experiments the mass transfer resistance was minimal as compared to catalyst particle size used in a typical PBR.

3.3.2 Comparison of MCR and PBR

A comparison of the concentration profile of 1-butanol inside the catalyst layer (average thickness, 25 µm) and in PBR using spherical particles (radius, 100-210 µm) is shown in Fig. 22. The catalyst mass in both the reactors was considered approximately 18 mg [I].

Fig. 22. Concentration profile of 1-butanol inside MCR with layer thickness 25 µm and PBR with spherical particle radius of 100 µm, 155 µm and 210 µm. Simulation parameters as in Table 8. Reproduced from Publication I with permission from Elsevier.
The 1-butanol concentration inside the spherical catalyst particle (Fig. 22) with diameter of 200-420 µm decreases appreciably as compared to the MCR catalyst layer (25 µm). This clearly shows that the internal mass transfer resistances are insignificant for the MCR but prominent for the particles in PBR. Theoretically, in PBR, the particle size could be reduced in order to avoid internal mass transfer resistances; however, this will lead to increased pressure drops along the catalyst bed.

### 3.4 CFD simulations of MCR

Microchannel reactor described by a heterogeneous model with flow properties was simulated to include flow field non-idealities using CFD studies [II]. Different authors in the literature have coupled flow behavior with reaction in 2D [111–113]. The 2D-axisymmetric and 3D models were studied in this work using COMSOL Multiphysics®. The solved model equations [114] and boundary conditions are discussed in detail in the Publication II. Similar to the 2D-PFR-type dynamic model strategy (Section 3.3), a single channel was assumed. The channel was assumed to consist of free channel (bulk fluid flow) domain and catalyst layer domain.

The flow field in the free channel was considered as laminar and is given by Navier-Stokes equations: the conservation of momentum (Eq. 38) and the continuity equation (Eq. 39),

\[
\rho \frac{\partial u}{\partial t} + \rho (u \cdot \nabla)u = \nabla \cdot (-P I + \tau) + F \tag{38}
\]

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0 \tag{39}
\]

where \( \rho \) is the fluid density (kg/m\(^3\)), \( u \) is the fluid velocity (m/s), \( \tau \) is the viscous stress tensor (Pa), \( F \) is the volume force vector (N/m\(^3\)), \( P \) is the pressure (Pa), \( I \) is the identity tensor and \( \nabla \) is the differential operator.

The transfer of the components in the free channel (bulk fluid phase) was described by the convection-diffusion equation (Eq. 40)

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) + u \cdot \nabla c_i = 0, \quad c_i = c_i^b \tag{40}
\]

where \( c_i = c_i^b \) is the concentration of component \( i \) in the free channel (mol/m\(^3\)) and \( D_i \) is the molecular diffusion coefficient of component \( i \) (m\(^2\)/s).

The transfer of the components in the catalyst layer was described by the diffusion and reaction equation (Eq. 41). The reaction source term \( (R_i) \) was described by the rate equations using power-law kinetics described in Section 3.2.1.
\[
\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_{ei} \nabla c_i) + R_i = 0, \quad c_i = c_i^s
\]

(41)

where \(c_i = c_i^s\) is the concentration of component \(i\) in the catalyst layer (mol/m\(^3\)) and \(D_{ei}\) is the effective diffusivity coefficient of component \(i\) (m\(^2\)/s). The molecular and effective diffusion coefficients were calculated using Eq. 33-35.

The equations for the transfer of species were coupled at the interface with boundary conditions to describe the diffusion-reaction of the species across the interface from bulk fluid phase to the catalyst layer [2].

3D slice for the velocity field of the bulk flow in the free channel (Fig. 23) shows that the flow in the center of the channel is dominated by convection, and close to the catalyst surface \((r=R)\), the velocity reaches zero due to parabolic velocity profile development.

![Velocity profile (m/s) contours for bulk phase in 2D-revolution for simulation parameters in Table 8. Reproduced from Publication II with permission from Elsevier.](image)

Concentration contours for the free channel for the reactant 1-butanol and product 1-butene are presented in Fig. 24a and b in steady state with residence time of 0.03 s at 391 °C [2]. The concentration gradients were present in both the axial and radial direction of the flow. The axial gradients along the length of the reactor are formed due to the transfer and reaction of 1-butanol. The radial concentration gradients arise from the residence time differences in the radial volume elements and diffusion-reaction of the components in the catalyst layer [79].
The concentration contours in the catalyst layer at steady state for the reactant (1-butanol) and product (1-butene) are presented in Fig. 24c and d. When observing Fig. 24a and b in combination with the Fig. 24c and d, variation in both axial and radial direction can be seen for the concentration of reactant (1-butanol) and product (1-butene). The visible concentration gradients in the axial direction are because of the applied Dirichlet boundary conditions, which means that the catalyst surface concentration is corresponding to the next radial spatial point in the bulk fluid flow ($r=R$). Since bulk fluid flow is convection dominating (as discussed above) and due to the diffusion-reaction (within the catalyst layer), the concentration of the components changes in the axial direction as well.
3.5 Remarks on PFR and CFD model simulations

The results obtained from the 2D–PFR–type model (Matlab®) and 3D–model (COMSOL Multiphysics®) are compared in Fig. 25 [II]. The deviation between the two models' results in the 1-butanol concentration was between 2–25 % as the layer thickness was increased from 15 µm to 200 µm. For the catalyst layer thickness of 15–25 µm the results for the concentration profile obtained from 2D and 3D models were relatively close to each other.

![Simulated 1-butanol concentration profiles](image)

**Fig. 25.** Simulated 1-butanol concentration profiles inside the catalyst layer for 15–200 µm layer thicknesses close to the entrance for residence time of 0.03 s. 2D-PFR-type model (dashed lines) and 3D-CFD model (solid lines). Reproduced from Publication II with permission from Elsevier.

The simulated axial concentration profiles across the reactor length were also compared for the two models for two different catalyst layer thicknesses 25 and 200 µm (Fig. 26). For the layer thickness of 25 µm, the 3D model predicted lower conversion as compared to the 2D-PFR-type model. This is likely because of the differences pertaining to the application of the flow balance equations in the free channel. The 2D-PFR-type model assumes same concentration in free channel in radial volume element, whereas the 3D model applies laminar flow that leads to radial concentration gradients in the bulk fluid flow (free channel). Due to the axial and the radial gradients in the free channel, the conversion decreases because of less availability of the reactant closer to the catalyst layer.
However, for a thicker catalyst layer of 200 µm the variation in the concentration is minimal for both the 2D-PFR-type model and the 3D model. The minimal variation could be attributed to the slower reaction within the catalyst layer due to the mass transfer resistances, which in turn levels out the concentration gradients in the bulk flow.

Fig. 26. 1-butanol concentration profile in axial direction (free channel) across the reactor length, Matlab 2D–PFR–type-model (dashed lines) and COMSOL 3D model (solid lines). Reproduced from Publication II with permission from Elsevier.
4. Partial oxidation of 1-butanol with Au-Pd on TiO$_2$

1-Butanol partial oxidation in the gas phase was studied over monometallic Au and Pd as well as bimetallic Au-Pd nanoparticles (NPs) supported on TiO$_2$. The prepared catalysts were coated on the structured stainless-steel microchannel plates. The aim was to achieve durable and stable catalyst coatings together with reasonable catalytic activity and selectivity towards $n$-butyraldehyde. In total, 5 catalysts (Section 2.2) were characterized and tested in the CTMR.

4.1 Preparation and characterization of Au-Pd coated catalysts

4.1.1 Au-Pd NPs addition on TiO$_2$ support

The effect of addition of nanoparticles of Au and Pd on TiO$_2$ surface area and porosity was analyzed with N$_2$ physisorption. The measured adsorption and desorption isotherms for the prepared catalysts are presented in Fig. 27. The isotherms for all catalysts have hysteresis loops of type IV(a) and show the presence of mesopores [115].
The adsorption isotherms were used to calculate the BET surface area, while the desorption isotherms were used for the total pore volume and the median pore diameter of the prepared catalyst coating powders, presented in Table 10. These results showed an insignificant difference of ±5% in all the mentioned parameters between the TiO₂ support and the mono and bimetallic Au-Pd catalysts supported on TiO₂.
Table 10. Physical and textural properties of the coating powders. Reproduced from Publication III with permission from Elsevier.

<table>
<thead>
<tr>
<th>Catalyst code</th>
<th>BET Surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Median pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>53</td>
<td>0.21</td>
<td>16</td>
</tr>
<tr>
<td>0.6Au</td>
<td>53</td>
<td>0.25</td>
<td>16</td>
</tr>
<tr>
<td>0.6Pd</td>
<td>54</td>
<td>0.25</td>
<td>17</td>
</tr>
<tr>
<td>0.3Au0.3Pd</td>
<td>51</td>
<td>0.23</td>
<td>18</td>
</tr>
<tr>
<td>0.6Au0.6Pd</td>
<td>50</td>
<td>0.23</td>
<td>18</td>
</tr>
</tbody>
</table>

The pore size distribution for the coated catalyst powders is presented in Fig. 28. The pore size distribution shows that mesopores below 10 nm are also present in the catalysts. If the Au-Pd NPs were to block the mesopores, then the measured BET surface area and the pore volume of the Au-Pd catalysts would be significantly different from the TiO₂ support. Therefore, the effect of the addition of Au-Pd NPs on the properties of TiO₂ was minimal for the prepared noble metal catalysts.

The metal amounts of the prepared coatings were analyzed with two different measurement methods, XRF and ICP-OES (Table 11). The success for Au deposition was ca. 100%, whereas for Pd it was ca. 90% (ICP-OES). Therefore, a higher nominal value for Pd was applied to target similar wt.% of analyzed Pd.
to that of analyzed Au. In colloidal preparation method, Pd dissolution is reported in acidic pH [116] where Pd can exist as Pd$^{2+}$, and hence some of the Pd ions may be lost at this step of the preparation. Thus, the catalyst preparation method requires further improvement and optimization to achieve 100% success for deposition of the metal nanoparticles [III].

Table 11. Metal content of the catalyst powders: targeted and analysed by XRF and ICP-OES. Reproduced from Publication III with permission from Elsevier.

<table>
<thead>
<tr>
<th>Catalyst code</th>
<th>Au (wt.%)</th>
<th>Pd (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>targeted</td>
<td>XRF</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-</td>
<td>0.0</td>
</tr>
<tr>
<td>0.6Au</td>
<td>0.60</td>
<td>0.6</td>
</tr>
<tr>
<td>0.6Pd</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>0.3Au0.3Pd</td>
<td>0.30</td>
<td>0.3</td>
</tr>
<tr>
<td>0.6Au0.6Pd</td>
<td>0.60</td>
<td>0.6</td>
</tr>
</tbody>
</table>

n.a. Not analyzed

4.1.2 Au-Pd NPs: Effect of coating and calcination

The effect of calcination on the size distribution of the Au and Pd nanoparticles was studied by STEM. For this purpose, the coatings were scratched off from the coated plates after calcination. In Fig. 29a, a comparison is presented for the 0.6Au uncoated and uncalcined catalyst with the 0.6Au coated catalysts that were calcined at 300 °C and 450 °C, all in powder form. The metal particle size distribution was determined by using the STEM bright field images (Fig. 29b).

![Fig. 29. (a) Effect of calcination and coating on the gold particle size distribution for the 0.6Au catalyst. (b) Representative STEM image of the 0.6Au catalyst coated and calcined at 450 °C, showing Au nanoparticles on the TiO$_2$ support particles. Reproduced from Publication III with permission from Elsevier.](image-url)
The increase in the calcination temperature increased the average particle size (Fig. 29a) from 1.8 nm (uncoated, uncalcined) to 2.5 nm (coated & calcined, 350 °C) and further to 3.6 nm (coated & calcined 450 °C), as expected [III]. The increase in the particle size was likely due to sintering caused by elevated temperature. The calcination is necessary to remove the capping agent, PVA, which is reported to be removed completely above 350 °C [51,67,117]. However, the downside is that with calcination at 400 °C, the average NPs size can increase up to 6 nm [117]. In this study even after calcination at 450 °C, the average particle size was ca. 3.6 nm and more than 90% of the particles remained in the targeted range of 2-5 nm. The resistance to sintering was due to the strong interaction between the metal(s) and the TiO₂ support leading to the formation of extended areas at the metal-support interface that impeded the significant growth of particles [117].

The particle size distributions of the bimetallic catalyst (Fig. 30) and monometallic 0.6Au catalysts were found to be similar. For the gold catalyst, the average metal particle size was 3.6 nm and for the bimetallic catalyst 3.5 nm (both samples coated and calcined at 450 °C). This further illustrates that the achieved particle size distribution for the Au nanoparticles was in a range, where the Au in general was expected to be catalytically the most active, and in particular on TiO₂ support [61]. The results from the qualitative EDS analysis showed the presence of individual Au, Pd and titania NPs as well as mixed Au-Pd NPs [III].

Fig. 30. Metal particle size distribution of the 0.6Au and 0.3Au0.3Pd catalysts coated and calcined at 450 °C. Reproduced from Publication III with permission from Elsevier.
The TGA analysis for the 0.6 wt.% Au/TiO₂ catalyst is given in Fig. 31. The TGA analysis revealed that the weight loss of sample between 195-450 °C was ca. 0.5%. This weight loss likely corresponded to adsorbed CO₂ from atmosphere [118], since the sample was calcined at 450 °C (moisture was assumed to be desorbed below 195 °C). Therefore, the weight loss percentage and the derivative of the weight loss in this temperature range (195-450 °C) showed that the weight loss was insignificant (Fig. 31). In the literature, the results of TGA analysis [117] showed that insignificant amounts of PVA might be present on the support after the heat treatment (calcination at 450 °C). The presence of PVA prevents agglomeration during the preparation of the catalysts. Whereas, the calcination of the catalyst effectively removed PVA in our study, which was confirmed by insignificant weight loss between 195-450 °C (Fig. 31).

![TGA analysis of the 0.6Au/TiO₂ catalyst in N₂ between 30 and 700 °C.](image)

**Fig. 31.** TGA analysis of the 0.6Au/TiO₂ catalyst in N₂ between 30 and 700 °C.

The 0.6Au catalyst coated plates were imaged with SEM (Fig. 32). The top view (Fig. 32a) shows that a uniform porous catalyst layer was formed. The thickness of the catalyst layer on top of the metal plate for a sawed cross-section is shown in (Fig. 32b). The average coating thickness achieved was 17 ± 7 µm for 13 channels, which was within the targeted range of <40 µm. The variation in the coating thickness arises most probably from the plate structure and due to the surface tension effects during drying of the coating suspension [11]. A reasonably thin coated catalyst layer (<40 µm) is necessary to avoid internal mass transfer resistance, and the catalyst-coated microreactor can be operated in the kinetic regime [77,88].
4.2 CFD simulations of the mixer

The CFD simulations of the designed mixer (Section 2.4.1), for the fluid flow and the 1-butanol concentration profile distribution, are discussed in detail in the Publication IV. The CFD simulations of the flow distribution in the mixer and in the lines showed a nozzle like effect and generation of high shear zones in the lines with bends [22], which aided to the development of a nearly constant velocity profile. The concentration distribution from the CFD simulations showed that the concentration profile significantly evened out in the vicinity of the outlet due to diffusion of the gases and dispersion induced by the flow. The development of concentration profile could also be attributed to the higher residence time of the gaseous mixtures in the inlet line as compared to the characteristic time scales for diffusion of the gases, which for these dimensions is ca. 50-75 ms [11]. Thus, it could be concluded from the simulation results that an even distribution of 1-butanol vapors in the carrier gas was likely achieved.

4.3 Au-Pd coated catalysts: activity, yield and reaction pathways

The partial oxidation of 1-butanol in air was studied over TiO$_2$, 0.6Au, 0.6Pd, 0.3Au0.3Pd and 0.6Au0.6Pd catalyst coated plates and with blank plates (without catalyst coating). The carbon balance for these experiments was between 94% and 98%. Stoichiometric ratios of 1-butanol and oxygen were used to favor selectivities towards partial oxidation products. The conversion of 1-butanol as function of temperature is shown in Fig. 33. In general, for all the catalysts the
conversion increased with increasing temperature. The highest conversion at 350 °C of approximately 80% was achieved with 0.3Au0.3Pd catalyst. However, at temperatures below 350 °C, the conversion over both 0.6Au0.6Pd and 0.6Pd was equal to that of 0.3Au0.3Pd. For the 0.6Au, the conversion was lower than over the other noble metal catalysts below 350 °C. At 350 °C, the conversion of 1-butanol over 0.6Au was the same as for 0.6Pd (ca. 64%). For TiO₂ support, the conversion of 1-butanol was clearly less than on the noble metal catalysts at temperatures above 250 °C, reaching approximately 31% at 350 °C. Interestingly, the experiment without any catalyst coating (referred as Blank in Fig. 33) resulted in similar conversion of 1-butanol at different temperatures as pure TiO₂ support, suggesting thermal decomposition reactions of 1-butanol and the inactivity of the pure support.

The yield of n-butyraldehyde over all the studied catalyst and blank plates is presented in Fig. 33. It is evident that the higher yield was achieved over 0.6Au catalyst compared to the other tested catalysts. Increasing the temperature from 165 °C to 300 °C for the 0.6Au catalyst increased the yield of n-butyraldehyde to ca. 20%. The trend continued at 350 °C, with increase in conversion up to 65%, however, the yield of n-butyraldehyde did not increase significantly as the share of CO, C₃H₆ and CO₂ started to increase as well [III]. Over all the Pd-containing catalysts (0.6Pd, 0.3Au0.3Pd and 0.6Au0.6Pd), the highest yield of n-butyraldehyde was achieved at 350 °C, approximately 10%, which in turn means that the Pd-containing catalysts favor formation of C₃H₆, CO and CO₂ as the temperature is raised from 165 °C to 300 °C.
The yield of the main products is shown in Fig. 34 for the corresponding catalysts and the blank experiment at 250 °C. In addition to n-butyraldehyde, other main products were water (not shown), butenes, CO, CO₂ and C₃H₆. The highest yield of the desired product (n-butyraldehyde (BuO)) was measured over the 0.6Au, being around 15%. However, addition of Pd to the Au catalyst (bimetallic
catalyst) shifted the product distribution towards lower carbon chain products, $\text{C}_3\text{H}_6$, CO and CO$_2$. Other observed products included dibutylether, $n$-butylbutyrate, $n$-butanoic acid and butane in trace amounts.

The presence of propene, CO and H$_2$ in the product gas over all the noble metal catalysts [III] suggested that the further reaction of $n$-butyraldehyde occurred via retro-hydroformylation reaction rather than decarbonylation and subsequent dehydrogenation. The reaction pathway is also supported by the studied thermodynamics for both the reaction routes. The decarbonylation reaction of $n$-butyraldehyde leads to formation of propane and CO. However, the higher amounts of propene were present in the product gas, whereas only trace amounts of propane were observed. The aforementioned observation indicates that the reaction path is retro-hydroformylation rather than decarbonylation and subsequent dehydrogenation.

Based upon the experimental observations a reaction scheme (Fig. 35) was proposed [III]. The desired main reaction to $n$-butyraldehyde takes place via oxidative dehydrogenation (1). The oxidative dehydrogenation (ODH) of 1-butanol by Mars-van Krevelen mechanism takes place at the interfacial region of Au nanoparticles and TiO$_2$ [62]. The $n$-butyraldehyde can also be formed by dehydrogenation of 1-butanol (2). The other undesired reactions considered are the dehydration of 1-butanol to butenes (3), decarbonylation of $n$-butyraldehyde to CO and propane (4), reversible dehydrogenation of propane to propene (5), reversible retro-hydroformylation reaction of $n$-butyraldehyde to propene, CO and H$_2$ (6), as well as the total oxidation of 1-butanol (7) and of $n$-butyraldehyde
(8) and oxidation of CO to CO$_2$ (9). The products observed in the trace amounts, such as dibutylether, 4-heptanone, n-butylbutyrate, n-butyric acid and butane, were not included in the proposed scheme.

![Proposed reaction scheme](image)

**Fig. 35.** Proposed reaction scheme for 1-butanol partial oxidation over the studied catalysts. (1) 1-Butanol oxidative dehydrogenation (ODH) to n-butyraldehyde, (2) dehydrogenation of 1-butanol to n-butyraldehyde, (3) dehydration of 1-butanol to butenes, (4) decarbonylation of n-butyraldehyde to CO and propane, (5) reversible dehydrogenation of propane to propene, (6) reversible retro-hydroformylation of n-butyraldehyde to CO, propene and H$_2$, (7) total oxidation of 1-butanol, (8) total oxidation of n-butyraldehyde, and (9) oxidation of CO to CO$_2$. Reproduced from Publication III with permission from Elsevier.

### 4.4 Kinetics of butanol partial oxidation over Au/TiO$_2$ coated catalyst

#### 4.4.1 Kinetic experiments

Catalyst screening [III] for the Au and Pd mono- and bimetallic catalysts supported on TiO$_2$ revealed that the Au/TiO$_2$ was selective towards n-butyraldehyde, whereas Pd/TiO$_2$ and Au-Pd/ TiO$_2$ were more selective towards total oxidation products. Therefore, the 0.6 wt.% Au/ TiO$_2$ catalyst was selected to generate kinetics data of 1-butanol partial oxidation reaction to n-butyraldehyde at 130-350 °C.

The experimental results [IV] for the 1-butanol conversion and n-butyraldehyde yield are presented in Fig. 37, for both the 1-butanol partial pressures 13.5 kPa (exp. 1-4) and 18 kPa (exp. 5-8) over the range of residence times (0.066 – 0.137 s). For both the partial pressures, the increase in the residence
time increased the share of the undesired products, \( \text{C}_3\text{H}_6 \), \( \text{CO} \) and \( \text{CO}_2 \). At partial pressure of 13.5 kPa, 350 °C and residence time of 0.137 s the yield of \( n \)-butyraldehyde increased up to 21%, whereas yield of \( \text{C}_3\text{H}_6 \) and \( \text{CO} \) increased to around 16% and the yield of \( \text{CO}_2 \) increased up to ca. 18%. The shift in the product distribution is likely due to the total oxidation and the subsequent reactions of \( n \)-butyraldehyde [III, IV].

The same trend for \( n \)-butyraldehyde yield, as for 13.5 kPa, was observed at 18 kPa partial pressure of 1-butanol with increasing temperature. The yield of \( n \)-butyraldehyde was slightly lower ca. 10-12% in the residence times between 0.066 and 0.137 s at 250 °C, and trends for the other main products (\( \text{C}_3\text{H}_6 \), \( \text{CO} \), \( \text{CO}_2 \)) were comparable to 13.5 kPa. The lower \( n \)-butyraldehyde yield at higher partial pressure (18 kPa) is caused by a lower conversion, as the selectivity remained the same. Products detected in trace amounts were \( n \)-butylbutyrate and \( n \)-butanoic acid.

### 4.4.2 Kinetic expressions based upon power-law and mechanistic models

Based on the experimental data (Sections 4.3 and 4.4.1), four reactions were selected as the most probable and representative ones within the studied range of the operation conditions (Fig. 36 and Table 12). The considered reactions were (relabelled from Fig. 35 in Fig. 36): the partial oxidation to \( n \)-butyraldehyde (1), dehydration to 1-butene (2), total oxidation of 1-butanol (3) and retro-hydroformylation of \( n \)-butyraldehyde (4). At the temperatures favorable for \( n \)-butyraldehyde, 250-300 °C, the reactions 1 and 3 are exothermic, whereas reactions 2 and 4 are endothermic (Table 12).

\[ \text{ODH (1): } \text{1-Butanol oxidative dehydrogenation} \]
\[ \text{dehydration (2): } \text{dehydration of 1-butanol to butenes} \]
\[ \text{total oxidation (3): } \text{total oxidation of 1-butanol} \]
\[ \text{retro-hydroformylation (4): } \text{retro-hydroformylation of \( n \)-butyraldehyde} \]
The rate laws of the respective reactions are described using power-law model and a mechanistic model based on assumed surface reaction steps in Table 12. The derivations for the mechanistic model were based on our experimental observations, as well as information from the literature for Au catalysts used for the oxidation of ethanol by Holz et al. [62] and Gong et al. [119] and for benzyl alcohol by Galvanin et al. [120]. To reduce the number of parameters in the parameter estimation, the kinetic expressions for reactions 3 and 4 in the mechanistic model (Table 12) were also described by the power-law due to their low significance for the reaction system. The final forms of the derivation for the kinetic expressions, used for the mechanistic model, are presented in Table 12. The derivation details and the applied assumptions are discussed in Publication IV.
Table 12. Main reactions occurring over Au/TiO$_2$ catalyst, heat of reaction (at 300 °C) and respective rate equations using power-law and mechanistic models based on the reaction scheme presented in Fig. 36.

<table>
<thead>
<tr>
<th>Index J</th>
<th>Reactions</th>
<th>Heat of reaction at 300 °C (kJ/mol)</th>
<th>Rate expression ($r_j$) Power-law</th>
<th>Rate expression ($r_j$) Mechanistic model</th>
</tr>
</thead>
</table>
| 1       | 1-butanol partial oxidation to $n$-butyraldehyde                         | 2 C$_4$H$_9$OH + O$_2$ → 2 C$_4$H$_8$ + 2 H$_2$O | $r_1 = k_1 c_{BuOH}^2 \cdot c_{O2}$ | $r_1 = R_{ODH}$  
|         |                                                                           | -348                                |                                  | $k_{3a} \cdot \frac{c_{BuOH} \cdot c_{O2}}{c_{H2O}^{0.25}}$  
|         |                                                                           |                                     |                                  | $= (1 + K_{BuOH} \cdot c_{BuOH} + K_{O2} \cdot c_{O2} + K_{H2O} \cdot c_{H2O} + K^{'Bu} \cdot c_{BuOH})^{2}$ |
| 2       | 1-butanol dehydration to butenes                                         | C$_4$H$_9$OH → C$_4$H$_8$ + H$_2$O | $r_2 = k_2 c_{BuOH}$            | $r_2 = R_{DHD}$  
|         |                                                                           | 33                                  |                                  | $k_{4a} \cdot \frac{c_{BuOH} \cdot c_{O2}}{c_{H2O}^{0.25}}$  
|         |                                                                           |                                     |                                  | $= (1 + K_{BuOH} \cdot c_{BuOH} + K_{O2} \cdot c_{O2} + K_{H2O} \cdot c_{H2O} + K^{'Bu} \cdot c_{BuOH})^{2}$ |
| 3       | 1-butanol total oxidation                                                 | C$_4$H$_9$OH + 6 O$_2$ → 5 H$_2$O + 4 CO$_2$ | $r_3 = k_3 c_{BuOH} \cdot c_{O2}$ | $r_3 = k_3 c_{BuOH} \cdot c_{O2}$ |
|         |                                                                           | -2504                               |                                  |                                |
| 4       | retro-hydroformylation                                                    | C$_4$H$_8$O → C$_3$H$_6$ + CO + H$_2$ | $r_4 = k_4 c_{Buah}$            | $r_4 = k_4 c_{Buah}$          |
|         |                                                                           | 121                                 |                                  |                                |
4.4.3 Kinetic parameter estimation and reactor simulations

The values for the obtained kinetic parameters with 1D-pseudohomogenous PFR model solved in Matlab®, for the power-law and mechanistic models comprising reactions in Table 12, are presented in Table 13 [IV]. A comparison with the literature values was not possible and no data was found for 1-butanol partial oxidation over the Au/TiO₂ catalyst. However, Jiang et al. [70] summarized that the activation energies of aliphatic alcohols to respective aldehydes (including 1-butanol) are between the region of 10-30 kcal/mol (40-125 kJ/mol). The activation energy of the main reaction, 1-butanol partial oxidation to n-butyraldehyde, in this work was estimated to be ca. 77 kJ/mol being in the reported range [70].

Table 13. Parameter values with 1D-pseudohomogenous PFR model solved in Matlab® for the reactions in Table 12 in the temperature range of 130-350 °C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value with 1D-pseudohomogenous PFR model in Matlab®</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Power-law model</td>
</tr>
<tr>
<td>$E_a_1$ [J/mol]</td>
<td>$77.4 \cdot 10^3$</td>
</tr>
<tr>
<td>$E_a_2$ [J/mol]</td>
<td>$18.8 \cdot 10^3$</td>
</tr>
<tr>
<td>$E_a_3$ [J/mol]</td>
<td>$74.5 \cdot 10^3$</td>
</tr>
<tr>
<td>$E_a_4$ [J/mol]</td>
<td>$46.8 \cdot 10^3$</td>
</tr>
<tr>
<td>$k_{1,ref}$ [m³/(mol·s)]</td>
<td>$8.8 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$k_{2,ref}$ [1/s]</td>
<td>$1.7 \cdot 10^{-2}$</td>
</tr>
<tr>
<td>$k_{3,ref}$ [m³/(mol·s)]</td>
<td>$1.2 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$k_{4,ref}$ [1/s]</td>
<td>$3.7 \cdot 10^{-2}$</td>
</tr>
<tr>
<td>$K_{BuOH}$</td>
<td>-</td>
</tr>
<tr>
<td>$K_{O_2}$</td>
<td>-</td>
</tr>
<tr>
<td>$K_{H_2O}$</td>
<td>-</td>
</tr>
<tr>
<td>$K_{Buald}$</td>
<td>-</td>
</tr>
</tbody>
</table>

The simulations performed using the 1D-pseudohomogenous model, with the estimated kinetic parameters using power-law and mechanistic kinetic expressions, were successfully able to reproduce the experimental results (Fig. 37 and Fig. 38.). Even though the reaction scheme was simplified to consider only 4 probable reactions, they were yet reflective of the overall experimental observations. A sensitivity analysis was performed, which showed that the estimated kinetic parameters were in the reasonable order of magnitude and meaningful [IV]. The variation in the values for activation energy for the reaction 2 ($E_a2$) between the power-law and the mechanistic models could be attributed to the correlations between the parameters for the first and the second reaction consuming 1-butanol simultaneously. Sensitivity analysis [IV] for the second reaction also showed that the mechanistic model provided less correlation and error compared to the power-law model.
Fig. 37. Conversion of 1-butanol and yield of main products detected at the outlet of the reactor plotted against the reactor temperature for experiments 1-4 (a-d) conducted at 13.5 kPa and experiments 5-8 (e-h) conducted at 18 kPa, Table 5. Symbols represent the experimental data, continuous lines the calculated profiles from 1D-pseudohomogenous model in Matlab using power-law kinetics [IV]. Reproduced from Publication IV with permission from Elsevier.

The mechanistic model (Fig. 38.) provided a slightly better fit ($R^2\sim99.4\%$) compared to power-law model ($R^2\sim99.0\%$) for the experimental data, hence indicating that the incorporation of the surface reaction steps is important for development of the kinetic model.
Fig. 38. Conversion of 1-butanol and yield of main products detected at the outlet of the reactor plotted against the reactor temperature for experiments 1-4 (a-d) conducted at 13.5 kPa and experiments 5-8 (e-h) conducted at 18 kPa, Table 5. Symbols represent the experimental data, continuous lines the calculated profiles from 1D-pseudohomogenous model in Matlab using mechanistic model [IV]. Reproduced from Publication IV with permission from Elsevier.

Due to only minor differences and simpler form of the power-law model compared to the mechanistic model, the power-law model was selected to compare the kinetic parameter estimation between the 1D-pseudohomogenous PFR model solved in Matlab® with the dynamic model solved in gPROMS. The parameter estimation results with the 2D dynamic model comparing with the 1D-pseudohomogeneous model are presented in Table 14. The fit of the 2D model with the experimental results is presented in Fig. 39. The model predictions show a window of error of roughly 15% and $R^2 \sim 98.0\%$. 
Table 14. Comparison of parameter values of the power-law for the reactions in Table 12 with 2D dynamic model solved in gPROMS and 1D-pseudo-homogenous model solved in Matlab.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value using power-law kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2D dynamic model in gPROMS</td>
</tr>
<tr>
<td>$E_{a1}$ [J/mol]</td>
<td>$63.7 \cdot 10^3$</td>
</tr>
<tr>
<td>$E_{a2}$ [J/mol]</td>
<td>$19.4 \cdot 10^3$</td>
</tr>
<tr>
<td>$E_{a3}$ [J/mol]</td>
<td>$149 \cdot 10^3$</td>
</tr>
<tr>
<td>$E_{a4}$ [J/mol]</td>
<td>$150 \cdot 10^3$</td>
</tr>
<tr>
<td>$k_{1,ref}$ [m$^3$(mol$\cdot$s)]</td>
<td>2.73</td>
</tr>
<tr>
<td>$k_{2,ref}$ [1/s]</td>
<td>4.02</td>
</tr>
<tr>
<td>$k_{3,ref}$ [m$^3$(mol$\cdot$s)]</td>
<td>$7.75 \cdot 10^{-2}$</td>
</tr>
<tr>
<td>$k_{4,ref}$ [1/s]</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Fig. 39. Conversion of 1-butanol and yield of main products detected at the outlet of the reactor plotted against the reactor temperature for experiments 1-4 (a-d) conducted at 13.5 kPa and experiments 5-8 (e-h) conducted at 18 kPa, Table 5. Symbols represent the experimental data, continuous lines the calculated profiles from 2D dynamic model in gPROMS using power-law kinetics [IV]. Model simulations show a poorer fit beyond 300 °C for n-butyraldehyde. Reproduced from Publication IV with permission from Elsevier.

The differences in the kinetic parameters (Table 14) between the 1D-pseudo-homogenous and the 2D model, for the dominating 1-butanol partial oxidation reaction, may arise due the different model setups/numerical solutions. However, the 2D dynamic model solved in gPROMS tends to overpredict the extent of retro-hydroformylation reaction beyond 300 °C compared to the 1D-pseudo-homogenous model. The reasons for these deviations are related to variations
in the values of the obtained kinetic parameters (Table 14). The mass transfer limitations described by the 2D model, with the dispersion effects in the fluid domain and the radial diffusion in the catalyst domain, could have caused lower values for the activation energy of the 1-butanol partial oxidation reaction in the 2D model [IV]. This can be illustrated by simulating the concentrations of 1-butanol and n-butyraldehyde in radial direction within the catalyst layer (Fig. 40). The 1-butanol concentration profile across the radial direction was almost flat, whereas the n-butyraldehyde has significant concentration gradient with higher concentration at the surface compared to the wall of the microreactor. This indicates that 1-butanol did not encounter internal mass transfer resistance, however n-butyraldehyde had a concentration gradient within the catalyst layer on account of consecutive reactions. Hence, a dynamic 2D model is necessary to explain the dynamic behaviour of a multicomponent reaction system.

![Dimensinal concentration profiles plot](image)

**Fig. 40.** Dimensionless concentration profiles along the dimensionless washcoat layer (ξ) with 2D dynamic model [IV]. The conditions were simulated for experiment 2 at 130 °C, Table 5. Reproduced from Publication IV with permission from Elsevier.

### 4.5 Catalyst coating stability and in-situ regeneration

The prepared coatings were stable and showed good adhesion. Multistep stress test and repeatability experiments are presented in Publication III. The pair of 0.6Au catalyst plates showed comparable results at comparable residence time (0.137 s) for the 1st run, stored for 6 months at ambient conditions and the 57th run [III]. The conversion of 1-butanol and yield of main products remained 80
within the experimental error. Thus, the catalytic activity of the 0.6Au coated plate was maintained throughout these experiments with no deactivation indicating high stability of the coating and *in situ* regeneration compared to the literature [64,67].
5. Conclusions

In this thesis, structured microreactors were used to study the heterogeneously catalyzed gas-phase reactions of 1-butanol to 1-butene and n-butyraldehyde. Microreactor plates coated with γ-Al₂O₃ were used for 1-butanol dehydration, whereas Au and Pd nanoparticles supported on TiO₂ were used for 1-butanol partial oxidation in a wall coated catalyst testing microreactor. Physicochemical characterization of the catalysts coupled with product analyses as well as kinetic and reactor modeling were performed for both the reaction systems.

The experimental results for the 1-butanol dehydration over γ-Al₂O₃ were in the kinetic regime due to a thin catalyst layer (15-30 µm). The operation in the kinetic regime was verified by satisfying empirical correlations for internal and external mass transfer criteria modified for microreactors as well as with detailed reactor simulations using the developed 2D model. The kinetics were successfully described using the power-law type kinetic model and with a mechanistic model. The heterogeneous model extension in a CFD study with flow field non-idealities provided useful insights on design strategies for microreactors. Most importantly, the catalyst layer thickness and diameter/length of the microreactor channels can be optimized to achieve the characteristic time for diffusion of the reactant molecule.

Titania-supported mono- and bimetallic gold and palladium heterogeneous catalyst coatings were successfully prepared and tested for the 1-butanol partial oxidation in a wall-coated structured microreactor. All the tested noble metal catalyst coatings were catalytically active. Gold nanoparticle catalysts supported on titania (Au/TiO₂) showed a good conversion of 1-butanol (up to 65% at 350 °C) and were the most selective of the tested catalysts towards n-butyraldehyde. The Au/TiO₂ catalyst coatings were durable and the regenerability of the coated catalyst provided reusable structured microreactors where the catalytic activity could be fully recovered. A reaction scheme for gas-phase 1-butanol partial oxidation was proposed, where direct partial oxidation of 1-butanol produced n-butyraldehyde and retro-hydroformylation led to propene, CO and hydrogen. The Au/TiO₂, which performed best in the catalyst screening studies, was selected to generate kinetic data at the optimal operation conditions. The kinetics of the reactions were described with the power-law and the mechanistic models and the experimental data was successfully reproduced with the quantitative explanation of reaction kinetics and microreactor simulations.
The successful application of coated microreactors for the dehydration and the partial oxidation of 1-butanol shows that the coated microreactors are excellent tools for kinetic studies. The mechanically and catalytically stable coatings of well-dispersed nano-gold on titania (Au/TiO$_2$) demonstrate a step forward towards the development of non-hazardous, stable, durable and reusable TiO$_2$ supported noble metal catalysts and coatings based on these catalysts. There is a potential to apply such catalyst systems in the downstream of an ABE fermentation plant for the development of alternative industrial processes for synthesis of value-added green chemicals.
References


