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Applications of Zeolitic Coatings in Microstructured Reactors

PROEFSCHRIFT

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Summary

A microreactor is a structured device with channel dimensions of 10 – 500 μm, in which chemical reactions are performed on the micro– to milliliter scale. The high specific surface area-to-volume ratio within microstructured reactors (typically $10^3$ – $10^5$ m$^2$ m$^{-3}$) in combination with the thin catalytic coatings at the walls of the reactor channels (typically 0.1 – 10 μm) are beneficial for heat and/or mass transfer limited processes. Therefore, microreactors are in particular suited for highly exothermic and fast reactions allowing precise temperature control and isothermal operation in contrast to conventional reactor systems. Consequently, microreactors can be used as a tool for intrinsic kinetic measurements and complex mechanistic studies. Moreover, the small reactor volume provides fast response and analysis times, and inherently small amounts of waste, which make microreactors a natural platform for high-throughput screening studies of catalysts. In such rapid catalyst development and optimization trajectories, the time-to-market of novel chemical products or improved chemical processes can be reduced considerably.

In this thesis, a high-throughput microreactor (HTMR) is developed for the screening of catalytic coatings for potential (micro)reactor applications. The molybdenum based HTMR consists of eight microstructured compartments, in which different catalytic coatings can be screened in parallel at realistic process conditions. All essential reactor design issues as fluid flow distribution, isothermal conditions, and sampling of product gases as well as the geometries of the separate reaction sections are optimized using three-dimensional computational fluid dynamics (CFD) simulations. The results of the CFD simulations of fluid flow, temperature, and concentration distributions used in the design, show a good agreement with experimental data in all cases. A novel concept of a low pressure-drop fluid flow distribution header is applied for flow equalization in the reactor compartments. The flow non-uniformity is below 2% in the range of Reynolds numbers of 6 – 113, as confirmed by Laser Doppler Anemometry. No differences in the temperature distribution in the HTMR are observed at a total heat input up to 100 W. Furthermore, a maximum difference in the average rate of reaction of only 2.3% between different reactor compartments is obtained at realistic screening conditions in ethylene ammoxidation over identical Co-ZSM-5 coatings. Finally,
the cross talking noise of product gases in the adjacent reactor compartments is below 0.1% according to the CFD model, when the sampling capillaries are positioned at least 4 mm inside the reactor compartments, and the gas flow profile in the reactor outlets is not disturbed (iso-kinetic suction intake). The experimental results show that even though idealized assumptions are made in the CFD models, a good correspondence is obtained in practice. Thus, this study shows the importance of the design of microstructured reactors through simulation prior to fabrication and experimentation.

The HTMR concept is demonstrated in the screening of zeolitic coatings in ethylene ammoxidation to acetonitrile. The hydrothermal synthesis of zeolites on a substrate is an elegant method to obtain thin zeolitic coatings, which are chemically bonded to the surface of the substrate. A general method is developed for the in-situ crystallization of zeolite crystals on a metal substrate, which is demonstrated for zeolite Beta and ZSM-5 coatings on a molybdenum substrate. Prior to the hydrothermal synthesis, the surface of the substrate is modified by an etching procedure which increases the roughness at the nanoscale level. The larger number of irregularities on the surface increases the positions where zeolite crystals can nucleate or anchor. Subsequently, thin films of Al₂O₃ (170 nm) and TiO₂ (50 nm) were successively deposited by atomic layer deposition (ALD) on the substrate. The internal Al₂O₃ film protects the Mo substrate from oxidation up to 550°C in an oxidative environment. A high wettability of the external TiO₂ film after UV irradiation increases zeolite nucleation on its surface. A superhydrophilic behavior (> 15 OH nm⁻²) for at least 3 h is obtained after UV irradiation of the TiO₂ surface.

Highly crystalline zeolite Beta coatings in a range of Si/Al ratios of 10 – 25 are synthesized on the TiO₂/Al₂O₃/Mo (TAMo) substrate by hydrothermal synthesis. The coatings are obtained from a viscous Na, K, and TEAOH containing aluminosilicate precursor mixture with silica sol as reactive silicon source. A mechanism for the in-situ growth of zeolite Beta coatings is proposed. According to this mechanism, the deposition of an amorphous gel layer on the substrate surface in the initial stage of the synthesis is an important step for the crystallization of continuous zeolite Beta coatings. The heating rate of the precursor mixture and the synthesis temperature are optimized to control the level of supersaturation and to stimulate the initial formation of a gel layer. The synthesis conditions are optimized to obtain coatings varying from a single layer of zeolite Beta crystals up to a thickness of 5 μm in the whole range of Si/Al ratios studied. ZSM-5 coatings in a range of Si/Al ratios of 16 – 50 are also synthesized on TAMo substrates from a Na, TPA containing synthesis solution with TEOS as silicon source. The thickness of the ZSM-5 coatings is adjusted from a single crystal layer to 45 μm by applying different H₂O/Si ratios.
The application of zeolitic coatings in the HTMR requires a scale-up of the hydrothermal synthesis procedure to obtain a large number of identical zeolitic coatings. The scale-up procedure is applied for the \textit{in-situ} synthesis of ZSM-5 coatings on a set of 72 substrates with dimensions of $40 \times 9.8 \times 0.1$ mm$^3$ in a total synthesis volume of 3 L. A coverage of $14.8 \pm 0.4$ g m$^{-2}$ was obtained on all plates in the scale-up procedure. The low deviation per individual plate (< 3%) indicates the uniformity of the synthesis conditions in the scale-up procedure.

Finally, the activity and selectivity of various series of Co-ZSM-5 and Co-BEA coatings (Si/Al = 15 – 23) with a thickness of 1 μm were determined in ethylene ammoxidation. A high-throughput screening of the zeolitic coatings was performed in the HTMR in a wide range of reactant partial pressures and temperatures to optimize the coating composition as well as the reaction conditions. Zeolite Beta coatings are about two times more selective towards the acetonitrile formation than ZSM-5 coatings. The rate of acetonitrile formation increases by a factor 6 by decreasing the Si/Al ratio from 23 to 15. The effect of the Co/Al ratio is less pronounced. The addition of small amounts of boron decreases the selectivity to acetonitrile in the whole range of Si/Al ratios studied. A maximum TOF of 0.8 s$^{-1}$ is obtained at 500°C, with a selectivity to acetonitrile of 58%. The optimized zeolitic coatings show higher reaction rates than pelletised Co-ZSM-5 catalysts.
Samenvatting

Een microreactor is een gestructureerd apparaat met kanaaldimensies van 10 – 500 μm, waarin chemische reacties worden uitgevoerd op de micro tot milliliter schaal. De hoge specifieke oppervlak tot volume verhouding in microgestructureerde reactoren (typisch $10^3 – 10^5$ m$^2$m$^{-3}$) is aantrekkelijk voor warmte- en/of massatransport gelimiteerde processen. Daarom zijn microreactoren bij uitstek geschikt voor sterk exotherme en snelle reacties, aangezien nauwkeurige temperatuurcontrole en isotherme operatie mogelijk zijn in tegenstelling tot conventionele reactorsystemen. Vandaar dat microreactoren gebruikt kunnen worden als een hulpmiddel voor intrinsiek kinetische metingen en complexe mechanistische studies. Bovendien zorgt het kleine reactorvolume voor snelle respons- en analysetijden, en inherent voor kleine hoeveelheden afval, wat microreactoren tot een natuurlijk platform maakt voor het snel screenen van katalysatoren. In dergelijke snelle katalysatorontwikkeling en optimalisatietrajecten kan de vereiste tijd tot commercialisering van nieuwe producten of verbeterde chemische processen aanzienlijk worden gereduceerd.

In dit proefschrift is een high-throughput microreactor (HTMR) ontwikkeld voor het screenen van katalytische lagen voor potentiële (micro)reactortoepassingen. De van molybdeen vervaardigde HTMR bestaat uit acht microgestructureerde compartimenten, waarin verschillende katalytische coatings parallel kunnen worden getest bij realistische procescondities. Alle belangrijke reactorontwerp-aspecten, zoals de gasstroomverdeling, de isotherme condities, en het afzuigen en monsteren van gasproducten, evenals de geometriën van de afzonderlijke reactorsecties, zijn geoptimaliseerd met gebruikmaking van driehdimensionale stromingssimulaties. Het resultaat van de stromingssimulaties van gassen, de temperatuur- en concentratieverdeling, welke gebruikt zijn in het reactorontwerp, tonen in alle gevallen een goede overeenkomst aan met de experimentele data. Een nieuw concept voor een gasstroomverdeler met een lage drukval aan de inlaat van de reactor is toegepast voor het gelijkmatig verdelen van de gasstroom in de reactorcompartimenten. De stromings-niet-uniformiteit was minder dan 2% in de range van Reynolds getallen van 6 – 113, zoals bevestigd door Laser Doppler Anemometrie. Er zijn geen verschillen in de temperatuurverdeling waargenomen bij een warmte-input tot 100 W. Verder is een maximaal verschil verkregen in de gemiddelde reactiesnelheid van slecht 2.3% tussen de
verschillende compartimenten bij realistische testcondities in de ammonoxidatiereactie van etheen over identieke Co-ZSM-5 lagen. Tenslotte, de interferentie van gasproducten in de aangrenzende reactorcompartimenten is kleiner dan 0.1% wanneer de monsternamencapillairen ten minste 4 mm in de reactorcompartimenten zijn gepositioneerd en het gasstromingsprofiel in de reactoruitlaat niet verstoord is (iso-kinetische afzuiging). De experimentele resultaten tonen aan dat ondanks de geïdealiseerde aannames in de simulatiemodellen, een goede overeenkomst is verkregen met de praktijk. Derhalve toont deze studie het belang aan voor het ontwerp van microgestructureerde reactoren middels simulatie alvorens fabricatie en in bedrijfname.

Het concept van de HTMR is toegepast in het screenen van zeoliete lagen in de ammonoxidatiereactie van etheen naar acetonitril. De hydrothermale synthese van zeolieten op een substraat is een elegante methode voor het verkrijgen van dunne zeoliete lagen, die chemisch gebonden zijn aan het oppervlak van het substraat. Een algemene methode is ontwikkeld voor de in-situ kristallisatie van zeolietkristallen op een metallic substraat, welke is toegepast voor zeoliet Beta en ZSM-5 lagen op een molybdeen-substraat. Voor de uitvoering van de hydrothermale synthese, wordt het oppervlak van het substraat gemondficierd door middel van een etsprocedure, welke de ruwheid vergroot op nanoschaalniveau. Het onregelmatig gestructureerde oppervlak vergroot de posities waar nucleatie of verankering van kristallen kan plaatsvinden. Vervolgens zijn dunne films van Al₂O₃ (170 nm) en TiO₂ (50 nm) achterevenvolgens afgezet door middel van Atomic Layer Deposition (ALD). De binnenste Al₂O₃-film beschermt het Mo-substraat tegen oxidatie tot 550°C in een oxiderende omgeving. De hoge hydrofiliciteit van de buitenste TiO₂-film na UV-radiatie verhoogt de zeolietnucleatie op het oppervlak. Een superhydrofiel gedrag (> 15 OH nm⁻²) voor tenminste drie uur werd verkregen na UV-behandeling van het TiO₂-oppervlak.

Hoog-kristallijne zeoliet Beta lagen in een range van Si/Al verhoudingen van 10 – 25 zijn gesynthetiseerd op het TiO₂/Al₂O₃/Mo (TAMo) substraat door middel van hydrothermale synthese. De lagen zijn verkregen uit een visceuze Na, K en TEAOH bevattende precursormix met silicasol als reactieve silicium bron. Een mechanisme wordt voorgesteld voor de in-situ groei van zeoliet Beta-coatings. Volgens dit mechanisme is de afzetting van een amorf gellaag op het substraatoppervlak in het beginstadium van de synthese een belangrijke stap voor de kristallisatie van continue zeoliet Beta lagen. De opwarmsmoelheen van de precursormix en de synthetesemperatuur zijn geoptimaliseerd om het niveau van oververzadiging te controleren en om de initiële vorming van een gellaag te stimuleren. De synthesecondities zijn geoptimaliseerd om lagen te verkrijgen, variërend van een enkele laag van zeoliet Beta-kristallen tot een laagdikte van 5 μm.
in de gehele range van bestudeerde Si/Al-verhoudingen. ZSM-5 lagen in de range van Si/Al-verhoudingen van 16 – 50 zijn ook gesynthetiseerd op TAMo-substraten van een Na en TPA bevattende synthese oplossing met TEOS als siliciumbron. De dikte van de ZSM-5 lagen is gevarieerd van een enkele laag van kristallen tot een dikte van 45 μm door verschillende H2O/Si-verhoudingen toe te passen.

De toepassing van zeolietlagen in de HTMR vereist een opschaling van de hydrothermale syntheseprocedure om een groot aantal identieke zeolietlagen te verkrijgen. De opschaalprocedure is toegepast voor de in-situ synthese van ZSM-5 lagen op een set van 72 substraten met dimensies van 40 × 9.8 × 0.1 mm3 in een synthesevolume van 3 L. Een bedekking van 14.8 ± 0.4 g m⁻² werd verkregen op alle plaatjes na de opschaalprocedure. De lage afwijking per individueel plaatje (< 3%) toont de uniformiteit aan van de synthesesecondities in de opschaalprocedure.

Tenslotte zijn de activiteit en selectiviteit bepaald van verschillende series Co-ZSM-5 en Co-BEA lagen (Si/Al = 15 – 23) met een dikte van 1 μm in etheen-ammostidatie. Het snel (high-throughput) screenen van de zeolietlagen werd uitgevoerd in de HTMR in een range van reactant partiaaldrukken en temperaturen om zowel de laagcompositie als ook de reactiecondities te optimaliseren. Zeoliet Beta lagen zijn een factor twee selectiever in acetonitril vorming in vergelijking tot ZSM-5 lagen. De acetonitrilvormingssnelheid stijgt met een factor zes, wanneer de Si/Al-verhouding wordt verlaagd van 23 tot 15. De invloed van de Co/Al-verhouding is minder uitgesproken. De toevoeging van kleine hoeveelheden boor vermindert de selectiviteit naar acetonitril in de gehele range van Si/Al-verhoudingen bestudeerd in dit onderzoek. Een maximale Turn Over Frequency (TOF) van 0.8 s⁻¹ is verkregen bij 500°C met een selectiviteit naar acetonitril van 58%. De geoptimaliseerde zeolietlagen hebben een hogere reactiesnelheid in vergelijking tot Co-ZSM-5 katalysatorkorrels.
1

Introduction

Abstract

Microreactors form now-a-days a new class of chemical reactors. A microreactor is a device that enables chemical reactions to be performed on the micro- to milliliter scale. The extremely large surface area-to-volume ratio within microreactors is the main contributor to the benefits of microreactors compared to conventional reactor types. The catalytic material for the chemical reaction is usually deposited as a thin coating at the walls of the reactor channels. Zeolite interfaces are excellent candidates for microreactor applications because of their remarkable and versatile possibilities in adsorption and catalysis. Zeolites form an important class of microporous crystalline oxide materials, which offer a unique opportunity for catalytic reactions. In this chapter the reader is introduced briefly in the main subjects of this thesis, viz. microreactors and zeolitic coatings. Furthermore, the scope of the research and the lay-out of the thesis are briefly explained.
1.1 Microstructured reactors

A micro(structured) reactor is a chemical reactor that is characterized by its very small dimensions, viz. reactors with a typical channel diameter of 10 – 500 μm and a channel length of 5 – 50 mm. The small dimensions result in an inherent large surface area-to-volume ratio in the order of \(10^3 - 10^5 \text{ m}^2 \text{ m}^{-3}\), which leads to remarkable differences in reaction conditions as compared to large scale reactors. This large surface area-to-volume ratio contributes to the main intrinsic advantages of microstructured reactors, viz. (a) high heat and mass transfer rates (reaction kinetics), (b) a well defined laminar fluid flow profile inside the reactor channels (hydrodynamics), and (c) a close contacting of the chemical reactants with the catalytic coating at the walls of the reactor channels (process intensification). Therefore, microreactors are in particular suitable for chemical reactions that are fast, highly endo- or exothermic and that require short contact times. The advantages are closely related in most of the microreactor applications, but will be discussed separately in the next sections. Furthermore, a short overview is presented, in which the state-of-the-art techniques are summarized for the deposition of catalytic coatings (d).

(a) Reaction kinetics

The small characteristic dimensions in microreactors compared to conventional macro-scale reactors, cause increased temperature and concentration gradients, which are the driving forces for heat and mass transfer, respectively. The additional large surface area–to–volume ratio, i.e. a large transfer area, results in high heat and mass transfer rates, allowing in most cases isothermal reactor operation and negligible mass transport restrictions. Microreactors can typically have heat transfer coefficients of 20 kW m\(^{-2}\) K\(^{-1}\) when fabricated from a highly conductive metal [1]. This allows the application of strongly exothermic reactions inside the microchannels without hot-spot formation. In case of mass transfer limited processes, microreactors have a considerable benefit, since the chemical reaction proceeds at the interface between the fluid and a catalytic layer within the microchannels. Thus, thin catalytic coatings are preferred to relatively large catalyst pellets or extrudates with a low effectiveness factor in fast catalytic processes, in order to minimize the bulk catalyst phases with a reduced chemical processing.

Consequently, microreactors can be used as a tool for intrinsic kinetic measurements and for the determination of complex mechanisms of catalytic reactions. Moreover, the small reactor volume provides fast response and analysis times, and inherently small amounts of waste, which make microstructured reactors a natural platform for high-throughput screening studies of catalysts [2, 3].
Introduction

In such rapid catalyst development and optimization trajectories, the time-to-market of novel chemical products or improved chemical processes can be considerably reduced.

(b) Hydrodynamics

Laminar fluid flow is generally obtained inside microstructured reactors, because of the small length scales and the corresponding low Reynolds numbers. Consequently, the transport processes are strongly dominated by molecular diffusion perpendicular to the flow direction. Well-known mathematical models describe the heat and mass transfer processes in the microchannels accurately, which can be used in computational fluid dynamics studies to obtain reliable reactor models and to predict fluid flow profiles [4-6]. Modeling of macro-scale reactors is often more difficult and thus less reliable, because the fluid flow is usually turbulent.

The absence of turbulence in the fluid flow profiles implies that non-forced mixing of separate flows in microchannels is solely dependent on intermolecular diffusion. This slow mixing can have additional value for phase transfer reactions and separation devices [7]. However, fast mixing is a critical issue for many applications in multi-flow (liquid-phase) microreactors. The mixing between separate reactant flows can be induced at the microscale in the millisecond range both by applying an exterior energy input, e.g. ultrasound and bubble-induced vibrations, or by splitting and combining of the fluid flow, e.g. by positioning of multi-lamellae in the inlet reactor section [8].

(c) Process intensification

Process intensification in micro process technology aims at the reduction of equipment size by several orders of magnitude leading to substantial savings in capital cost, improvement of intrinsic safety, reduction of environmental impact, and increase of the yield and selectivity of chemical processes [9]. An intensified contacting between the fluid flow and the thin catalytic coatings is ensured inside the channels of a microreactor, and as a result all of the catalytic material is available for reaction. Therefore, higher yields can be obtained in microreactors compared to conventional packed bed reactors. The small channel diameters also create a narrow residence time distribution, because of the short radial diffusion path lengths. Moreover, a fast quenching of the chemical reaction is possible in the millisecond range, which gives a full control of the contact time. Both the short residence time distribution and the fast quenching are especially beneficial for consecutive reactions, in which a high selectivity to an intermediate is desired, leading to higher quality products, and thus to more profitability and environmentally benign processes. Higher selectivities are also obtained by
minimizing the homogeneous reactions in the fluid phase in the small reactor channels.

The small reactor volume and inventory lead to inherent safety during handling of dangerous chemicals as well as to an excellent process control [10]. Therefore, microreactors facilitate the use of distributed or mobile production units, e.g., for on-the-spot and on-demand production of toxic or hazardous chemicals [11]. Because of its compact size, microreactors are under development to be applied as a small and lightweight fuel cell processor unit as an alternative for battery packs to power portable electronic equipment [12]. Furthermore, they can be operated safely in the explosive reaction regime, and thus avoid the use of large diluent reactant streams [6, 13]. This may also lead to higher conversion of chemicals, since higher reaction temperatures, pressures and reactant concentrations can be used compared to conventional reactors.

The easy scale-up by scale-out principle is applicable for microreactors, which allows the scaling-up of a process by using a large number of identical small units without change of the microreactor geometry [14]. In recent times, the purist numbering-up approach is supplemented by allowing a smart increase in scale and using correlations to describe the dimensional effects, which is an intermediate approach between scale-out and scale-up. This refers to the ease and repeatability in realising the respective experimental conditions and in the ease to have smart scaled-out microreactors.

(d) Catalyst incorporation techniques

The efficient use of microstructured catalytic reactors requires a shaping of the catalyst usually by deposition of thin catalytic coatings at the walls of the reactor channels. Over the last decade, many methods have been developed or considerably improved to deposit catalytic coatings on a substrate. When a high catalytic surface area is required, various techniques can be applied to create porous surfaces, viz. zeolite hydrothermal synthesis [15, 16], anodic oxidation [17-19], electrophoretic deposition [20], sol-gel synthesis [21-24], washcoating [25], and several vapor deposition techniques [26, 27]. If a high catalytic surface area is not required then the following techniques for catalyst deposition are commonly applied: sputtering [28], atomic layer deposition [29-31], and the electrochemical depositions in ionic melts [32, 33].

Another possibility for catalyst incorporation is the use of very small catalyst particles in either a fixed bed microreactor or in small catalyst particle containers along which the fluid flow is directed [34]. However, such devices require a large pressure drop and are extremely sensitive to channel blocking. A very costly alternative for catalyst incorporation is the micromachining in the catalyst material itself [35].
1.2 Zeolitic coatings for catalytic applications in microreactors

Zeolite interfaces are excellent candidates for microreactor applications because of their remarkable and versatile possibilities in adsorption and catalysis. The present overview discusses briefly general aspects of (a) zeolite catalysts and (b) zeolitic coatings.

(a) Zeolite catalysts

Zeolites are microporous crystalline solids with a three dimensional macromolecular structure. The framework consists of a pore system with channels in one, two or three dimensions and it may contain linked cages and cavities. About 40 different zeolites have been discovered in nature, while more than 130 zeolites have been synthesized thus far [36]. The apertures of the pores are in the range of 3 – 10 Å, which coincides with the dimensions of many (in)organic molecules, e.g. hydrocarbons. The size of the pore apertures and the variety in channel structures define the accessibility and the intracrystalline diffusion of...
molecules in the zeolite framework. In Figures 1.1 and 1.2 the porous networks of ZSM-5 (MFI) and zeolite Beta (BEA) are shown, which are synthesized in this study.

Generally, zeolites are built up from net neutral SiO$_2$ and negatively charged AlO$_2^-$ tetrahedra, connected via the oxygen atoms. The difference in the valency of the Si$^{4+}$ and Al$^{3+}$ cations results in a negative charge, located at one of the O anions connected to the aluminum cation. The negative charge is balanced by low valent cations, e.g. Na$^+$, K$^+$, and template ions that are present in the pores. Generally, these non-framework cations are easily exchangeable by functional metal cations e.g. Co, Cu, Fe, Pd and so on, which are of interest for heterogeneous catalysis. When the cationic sites are replaced by protons (H$^+$), they can have a high number of strong acid sites, the so-called Brønsted acid sites. Brønsted acidity is exploited in many organic reactions, including crude oil cracking, isomerization, and fuel synthesis [37, 38].

Transitional metal cations exchanged in zeolites are usually atomically dispersed on the coordinately unsaturated sites to balance the negative charges of the zeolite framework. They show an exceptional redox activity in Si-rich (Si/Al > 10) zeolites [39, 40]. These cations provide unique catalytic centers, as Lewis-acid sites, with a high site density that is usually not achievable by bulk or supported metal oxides. At sufficiently large pore dimensions of the zeolite, hydrocarbons or other basic molecules may adsorb and transform at the catalytic sites in the inner pore volume of the zeolite.

(b) Zeolitic coatings

Zeolitic coatings are defined as composite materials, comprising a substrate onto which zeolites are physically or chemically bonded [41]. They are especially of interest for use as catalysts, adsorbents, membranes, and sensors [42]. Zeolitic coatings can be deposited on a substrate by means of slurry coating, wash-coating, or hydrothermal synthesis. In the slurry coating method, zeolitic coatings are obtained after contacting of the substrate with a dispersion of zeolite crystals, followed by evaporation of the liquid. The main disadvantage of this technique is the relatively weak Van der Waals bonding that is obtained of the zeolite crystals with the substrate. In wash-coating, the zeolite crystals are “glued” to the substrate with a binding agent, which causes a low accessibility of the crystallites. Moreover, both these methods result in rather non-homogeneous coatings, in which the crystals are randomly oriented. In case of hydrothermal synthesis, also called in-situ synthesis, the zeolite crystals can be directly grown on a substrate from a synthesis precursor gel.

In-situ synthesis is an elegant method to obtain thin, homogeneous coatings, consisting of oriented zeolite crystals, which are firmly attached to the substrate by
chemical bonding between the crystallites and the hydroxyl groups on its surface. Prior to the in-situ synthesis, the substrate surface can be modified to improve hydrophilicity, to increase the number of surface irregularities and stability. An improved hydrophilicity and number of defect sites increases the number of positions where the crystals can nucleate and anchor. Furthermore, the surface hydrophilicity or wettability is of importance with respect to the compatibility of the substrate surface with the precursor solution. A high surface stability of the substrate in highly alkaline media is required to prevent its dissolution in the zeolite synthesis solution. Zeolitic coatings can be prepared by in-situ crystallization from both a diluted and concentrated synthesis solution. In a diluted precursor solution, the zeolite crystals are directly grown on the substrate surface. After an induction period, the zeolite coverage on the substrate linearly increases with the synthesis time, which is controlled by the transport of the nutrients from the liquid phase to substrate surface, until the precursor solution is depleted in nutrients. In case a concentrated precursor solution is used for the in-situ synthesis, an intermediate condensed gel layer is deposited on the substrate surface, from which the zeolitic coating evolves. Here, the growth of the zeolitic coating is commonly kinetically controlled, because of the abundance of nutrients at the gel-liquid interface.

Commonly, the envisioned application of zeolitic coatings determines the deposition method, and the combination of the zeolite type with the shape and material of the substrate. Remarkable advances have been made in the last decade with respect to the development of the deposition methods, the use of substrates of a different nature and characteristics, and the improvement of the orientation and thickness of the zeolitic coatings. For example, NaA zeolite was synthesized in-situ on ceramic hollow fibres for membrane applications [43]. Zeolite Beta washcoatings were prepared in alumina monoliths for acylation of aromatics [25]. Oriented ZSM-5 crystals were in-situ grown on a cantilever device and used as a humidity sensor [44]. Application of zeolitic coatings can also improve the catalyst performance, as demonstrated in the case of membrane reactors [45], distillation units [46], catalytic packings [47, 48], monoliths [25], and DeNOx reactors [49].

Fast catalytic reactions involving large heat effects can be further intensified when they are carried out over zeolitic coatings with a thickness up to 10 μm, which are directly grown in the channels of a microstructured reactor, fabricated in a metal substrate. The mechanical stability at elevated temperatures and the relatively high heat conductivity of the metal substrate are beneficial for the isothermal microreactor operation in highly exothermic reactions. The large geometrical surface area of the channel walls provides a large interface area between the reactants and the coating. The absence of both binder and macropores improves mass transfer in the coating [15, 50]. Heat transfer is enhanced by the
chemical bonds between the coating and the substrate, and the higher apparent density of the coating [51]. Recently, a few applications of zeolitic coatings in microreactors were reported. ZSM-5 coatings were synthesized in stainless steel microchannels and tested in the selective catalytic reduction of NO with ammonia, which resulted in a higher catalyst activity compared to a conventional catalyst due to the absence of mass transfer limitations [15]. TS-1 zeolitic coatings with a thickness of 3 μm were synthesized on 500 μm wide microchannels and used in epoxidation of 1-pentene [52]. A higher productivity for the Knoevenagel condensation reaction over zeolitic coatings in a microreactor was reported in [53]. A recent review of zeolitic coatings in micro-scale applications is given in [54].

1.3 Scope and lay-out of the thesis

Despite the recent development of sophisticated micro reactor design and its fabrication, the reactor performance is often limited by the activity of the state-of-the-art catalysts. To fully exploit the benefits of catalytic microreactors, and to increase the drive towards its applications in chemical processes as a superior alternative to conventional reactor systems, a strong focus is required within the microtechnology community towards the development and optimization of catalytic coatings. However, the development of novel and superior catalytic coatings for microstructured reactors is often an empirical process, which is based on conventional catalyst know-how and common sense. Therefore, high-throughput testing of libraries of coatings for desired catalytic properties is required at realistic process conditions to speed up this development and optimization trajectory. Microstructured reactors can be used as a tool for high-throughput screening of catalytic coatings and for kinetic studies.

In the ZeMiR (Zeolitic MicroReactors; STW project EPC.5543) project, carried out at the Eindhoven University of Technology (TU/e), a microreactor was developed for the screening of catalytic coatings for potential microreactor applications. The high-throughput microreactor is applied in the screening of zeolitic coatings in the highly exothermic ethylene ammoxidation. Therefore, synthesis protocols are also developed for the in-situ growth of zeolitic coatings on a substrate, as well as a scale-up procedure to obtain a large number of identical zeolitic coatings. The main results of the ZeMiR project are described in this thesis, in which each of the chapters can be read as a separate research paper.

In Chapter 2 the general design considerations are discussed for the development of a high-throughput microreactor for the screening of catalytic coatings, such as material choice, reactor operation, fluid flow distribution, and product sampling and quenching. The design criteria are set in a way that fluid
flow, temperature, and concentration distributions within the separate reactor compartments of the microreactor are negligible. The geometries of the separate microreactor sections are optimized by computational fluid dynamics (CFD) simulations with the Fluent software to fulfill the design criteria.

The high-throughput microreactor is fabricated and assembled according to the design. Its experimental performance is discussed in Chapter 3. The fluid flow, temperature, and concentration gradients within the microreactor are established within the margins set in the design study. A novel concept of a low pressure-drop flow distribution header is experimentally validated by Laser Doppler Anemometry. The temperature and concentration gradients are validated at typical process conditions during the screening of catalytic coatings.

A general method is developed for the in-situ growth of zeolitic coatings on a metal substrate. The method is exemplified in Chapter 4 for the synthesis of a single layer of zeolite Beta crystals on a molybdenum substrate. Surface parameters of the substrate as roughness, hydrophilicity, and stability are optimized. Subsequently, hydrothermal synthesis conditions as temperature and time are optimized for a zeolite Beta precursor mixture with a Si/Al ratio of 23 to obtain a single layer of zeolite Beta crystals. Finally, the cobalt exchanged zeolite Beta coatings are tested in a microreactor in ethylene ammoxidation.

The experimental results presented in Chapter 4 showed that lower Si/Al ratios are required to obtain a higher catalyst activity. In Chapter 5 the synthesis conditions as temperature and heating rate are optimized for the in-situ growth of crystalline zeolite Beta coatings on a molybdenum substrate in a range of Si/Al ratios of 10 – 25. Furthermore, a synthesis mechanism is proposed for zeolite Beta coatings from a viscous Na, K, and TEA containing precursor gel.

The hydrothermal synthesis conditions as temperature, time and heating rate as well as the composition of the synthesis solution are optimized for ZSM-5 coatings on a molybdenum substrate with Si/Al ratios of 16 – 50 in Chapter 6. Furthermore, a scaling-up procedure is described to obtain a large number of identical zeolitic coatings from a one-pot synthesis. A 3L autoclave is designed, in which 72 substrates can be simultaneously treated.

In Chapter 7 various series of Co-ZSM-5 and Co-Beta coatings are screened in the high-throughput microreactor in ethylene ammoxidation for the production of acetonitrile. In this approach the effect of the zeolite type, the elemental composition, the addition of a boron promoter, and the reaction conditions on the catalyst activity and selectivity are investigated in a parallel fashion. The optimized coatings do indeed show a higher activity compared to pelletized zeolite catalysts.

Finally, the main conclusions of this thesis and the outlook are presented in Chapter 8.
Bibliography

36. http://www.iza-online.org
Design of a Molybdenum High-Throughput Microreactor for High Temperature Screening of Catalytic Coatings

This Chapter is adapted from:

Abstract
This paper focuses on a computational fluid dynamics (CFD) approach to optimize the design parameters for a high-throughput microreactor prior to reactor micromachining and assembling. A molybdenum based microreactor has been designed for the screening of catalytic coatings in the 100 – 800°C temperature range for gas phase reactions involving large heat effects ($\Delta H_{298} = \pm 1500 \text{ kJ mol}^{-1}$). The microreactor consists of eight microstructured compartments, each with a cross section of $2.28 \times 10.18 \text{ mm}^2$ and 40 mm in length. Up to a number of eight 100 μm thick molybdenum plates, with a deposited catalytic layer with a thickness up to 10 μm, can be inserted in each compartment at distances of 130 μm from each other. Using the CFD code Fluent® 6.0, it is demonstrated that a low pressure drop flow distribution header distributes the reactants equally in all reactor compartments in a flow range of 50 – 1000 cm$^3$ min$^{-1}$ (STP). The sampling section allows to analyze the reaction products from a selected compartment without interference of product gases from adjacent compartments by insertion of the sampling capillaries 4 mm inside the reactor compartment outlets. The quench section provides a fast quench of the effluent gases in the millisecond range to avoid consecutive reactions. The corrosion resistance of the reactor can be improved by atomic layer deposition of a 200 nm Al$_2$O$_3$ film.
2.1 Introduction

In the overall optimal design of a catalytic process, the choice of the catalyst with its operating conditions is the critical step, which defines the costs of the reaction against the costs of product recovery and by-product treatment. For secondary screening of heterogeneous catalysts, there exist two types of reactor concepts, viz. (1) multi-tubular fixed bed reactor modules, which closely resemble conventional catalyst testing apparatus, and (2) microreactor arrays, in which usually catalytic coatings can be screened [1]. Table 2.1 presents the state-of-the-art in reactors for high-throughput experimentation studies with respect to the secondary screening of heterogeneous catalysts in gas phase reactions. Many catalytic processes have a potential for improving the overall performance by

Table 2.1 Secondary gas phase screening reactors reported in literature; reactor, reaction and catalyst characteristics.

<table>
<thead>
<tr>
<th>Reactor characteristics</th>
<th>Process characteristics</th>
<th>Catalyst system / library</th>
<th>ΔHf\textsuperscript{298} (kJ mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi tubular reactors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz (n.d.)</td>
<td>D/I</td>
<td>Cu-Cr/act. Carbon</td>
<td>-283</td>
</tr>
<tr>
<td></td>
<td>n.d. 250 CO + ½O₂ → CO₂</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>600 N₂O → N₂ + ½O₂</td>
<td>Fe-ZSM-5</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>150 NO + NH₃ + ¼O₂  →</td>
<td>Mn₂O₃-WO₃/γ-Al₂O₃</td>
<td>407</td>
</tr>
<tr>
<td></td>
<td>N₂ + ½H₂O</td>
<td></td>
<td>2,4</td>
</tr>
<tr>
<td>Brass (1)</td>
<td>I</td>
<td>Au/Co₃O₄, Au/TiO₂</td>
<td>-283</td>
</tr>
<tr>
<td></td>
<td>16 n.d. 180 CO + ½O₂ → CO₂</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>St. steel (5)</td>
<td>I</td>
<td>Pt/TiO₂, Cu/Al₂O₃</td>
<td>-802</td>
</tr>
<tr>
<td></td>
<td>49 10 550 CH₄ + 2O₂ → CO₂ + 2H₂O</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Quartz (5)</td>
<td>I</td>
<td>Pt/Coₓ₋ₓCeₓ, Gd₂O₃ₓ₋ₓsₓ</td>
<td>+247</td>
</tr>
<tr>
<td></td>
<td>10 30 700 CH₄ + CO₂ → 2CO + 2H₂</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/Coₓ₋ₓSm₂O₃ₓ₋ₓsₓ</td>
<td></td>
</tr>
<tr>
<td>Alumina (5)</td>
<td>I</td>
<td>Mn-Na₂WO₄/SiO₂</td>
<td>-88</td>
</tr>
<tr>
<td></td>
<td>64 7,5 550 C₃H₈ + ½O₂ → C₃H₆ + H₂O</td>
<td></td>
<td>9,10</td>
</tr>
<tr>
<td></td>
<td>500 C₃H₈ + ½O₂ → C₃H₆ + H₂O</td>
<td>metal-oxides/γ-Al₂O₃</td>
<td>-106</td>
</tr>
<tr>
<td></td>
<td></td>
<td>metal-oxides/γ-Al₂O₃</td>
<td>117</td>
</tr>
<tr>
<td>Quartz (n.d.)</td>
<td>I</td>
<td>Au/carrier</td>
<td>-283</td>
</tr>
<tr>
<td></td>
<td>15 n.d. 800 CH₄ + ½O₂ →</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>½C₂H₆ + ½H₂O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 C₃H₈ + 5O₂ → 3CO₂ + 4H₂O multi-metal/TiO₂</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>250 CO + ½O₂ → CO₂</td>
<td>Au/carrier</td>
<td>-283</td>
</tr>
<tr>
<td>Microreactors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ceramic (1)</td>
<td>D</td>
<td>Pt-Pd-In/γ-Al₂O₃</td>
<td>+206</td>
</tr>
<tr>
<td></td>
<td>80 5 350 C₆H₁₂ → C₆H₆ + 3H₂</td>
<td></td>
<td>12-14</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>Pt-Pd-In-Na/γ-Al₂O₃</td>
<td>-1838</td>
</tr>
<tr>
<td></td>
<td>550 NO + C₆H₆ + 4O₂ →</td>
<td></td>
<td>12,15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>½N₂ + 3CO₂ + 3H₂O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>Pt-Zr-V/γ-Al₂O₃</td>
<td>-802</td>
</tr>
<tr>
<td>Aluminum (n.d.)</td>
<td>I</td>
<td>Au/carrier</td>
<td>-2043</td>
</tr>
<tr>
<td></td>
<td>35 10 450 CH₄ + 2O₂ → CO₂ + 2H₂O</td>
<td></td>
<td>11,12</td>
</tr>
<tr>
<td>Ceramic (5)</td>
<td>I</td>
<td>Pt-Zr-V/γ-Al₂O₃</td>
<td>-802</td>
</tr>
<tr>
<td></td>
<td>256 10 450 CH₄ + 2O₂ → CO₂ + 2H₂O</td>
<td></td>
<td>18,19</td>
</tr>
<tr>
<td></td>
<td>250 CO + ½O₂ → CO₂</td>
<td>Au/carrier</td>
<td>18</td>
</tr>
<tr>
<td>Titanium (n.d.)</td>
<td>-</td>
<td>γ-Al₂O₃ wash coating</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>10 14 450 no reaction reported</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n.d. denotes not determined.

- \(\Delta T\) denotes measured temperature difference (K) within the reactor system without reaction.
- Screening mode; Differential (D) or Integral (I) mode.
- Number of parallel reactors or parallel microreactor channels.
- Measured flow deviations (%) within one reactor system.
improving either the active component itself or the catalyst texture. For some catalytic processes it is especially of interest to develop catalytic coatings for microreactor applications, e.g. in case for processes involving large heat effects or for on-the-spot and on-demand handling and production of hazardous chemicals. Some examples are listed in Table 2.2.

Table 2.2 Examples of catalytic processes for potential microreactor applications.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH²⁹⁸</th>
<th>T°C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + ½O₂ → CO₂</td>
<td>-283</td>
<td>150-160</td>
<td>21</td>
</tr>
<tr>
<td>H₂ + ½O₂ → H₂O (parallel reaction)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO + 3H₂ → CH₄ + H₂O</td>
<td>-210</td>
<td>180-200</td>
<td>22</td>
</tr>
<tr>
<td>NH₃ + C₆H₆ + 3/2O₂ → CH₃CN +3H₂O</td>
<td>-506</td>
<td>475-500</td>
<td>23</td>
</tr>
<tr>
<td>(CH₃)₂NNH₂ + 4O₂ → 2CO₂ + N₂ + 4H₂O</td>
<td>-1799</td>
<td>500-600</td>
<td>24</td>
</tr>
<tr>
<td>C₆H₁₀ ↔ C₆H₁₂ + H₂</td>
<td>+126</td>
<td>700-750</td>
<td>25</td>
</tr>
<tr>
<td>CH₄ + 2H₂O ↔ 4H₂ + CO₂</td>
<td>+165</td>
<td>800-850</td>
<td>26</td>
</tr>
<tr>
<td>NH₃ + CH₄ ↔ HCN + 3H₂</td>
<td>+ 252</td>
<td>1100-1150</td>
<td>27</td>
</tr>
</tbody>
</table>

A major issue in the development of secondary gas phase screening reactors is to operate the whole device at the same conditions. However, in extreme cases, flow non-uniformities up to 30% (Table 2.1) within one reactor system are obtained, which is often the result of an inadequate design of the flow distribution unit. Furthermore, when the reactor is constructed of materials with a low thermal conductivity, temperature gradients above 5 K within one device are reported, already in absence of the catalytic reaction (Table 2.1). Even higher gradients are expected during the reaction, especially when large heat effects are involved. Most of the reactors, except for those constructed from ceramics, quartz, titanium, and high-temperature steel alloys, have a maximum operating temperature of about 550°C, while numerous catalytic applications require temperatures higher than this. Furthermore, these devices are often made from materials with a relatively low thermal conductivity. Therefore, they cannot be used for kinetic or catalyst screening studies of reactions with high thermal effects, since isothermal reactor operation is not feasible. In order to realize such applications, microfabrication techniques have to be developed or optimized for producing microchannels in refractory metals or aluminide intermetallics, which have a high thermal conductivity, mechanical stability and melting point.

In the development of a high-throughput microreactor (HTMR) for high temperature applications (Table 2.2) several issues have to be considered such as material choice, reactor geometry, catalyst incorporation techniques, and microreactor fabrication methods. In this way, CFD simulations can provide detailed information on design parameters and reactor performance. This latter aspect is evident in order to avoid relatively large performance deviations, as
summarized in Table 2.1 for other screening devices. This non-ideality can be attributed to a point of controversy between an experimental based and a simulation based reactor development approach.

Lack of data for the application of a HTMR in high temperature reactions with large heat effects prompted us to study the behavior of this system using the CFD code Fluent®6.0. Therefore, this paper focuses on a CFD approach in order to show the importance of reactor design through simulation prior to experimentation. The design methodology covers all essential issues for the application of a HTMR. A flow distribution header is designed to provide equal contact times in the separate reactor compartments. The intrinsic characteristics of both the microreactor geometry and material provide near-isothermal conditions. Furthermore, to achieve results with a high accuracy, the reaction products from one compartment have to be analyzed without interference from products from adjacent compartments. Finally, the effluent fluid flow has to be quenched in the millisecond range to avoid consecutive non-catalytic reactions.

2.2 Development of a high-throughput microreactor

2.2.1 Geometry and material choice

Microstructured plate-type reactors can be effectively used for testing of catalytic coatings. A large number of plates, on which the catalytic coating is deposited, can be efficiently utilized within the micrometer range. In this way a large surface area is available for contacting of the reactants and the catalytic coating. Furthermore, microstructured reactors with adequate characteristics and dimensions guarantee a negligible pressure drop and the absence of external transport resistances in the whole range of reaction conditions [28, 29]. Near-isothermal reactor operation can be realized in a plate-type microreactor by the effective dissipation of reaction heat by a proper choice of the thermal conductivity of both the plate and reactor material [28-31]. Table 2.3 presents the physical data of various materials from which (micro) reactors are or can be manufactured.

It is clear that only a limited number of materials can be used at elevated temperatures, because of either a relatively low melting point, e.g. in case of aluminum and copper, or a low mechanical stability, e.g. quartz and nickel. A further selection of reactor materials is based on the thermal conductivity, which narrows the material choice to silicon, high-temperature steel alloys and some of the refractory metals. Several refractory metals satisfy all design criteria, which enables its application in high temperature processes involving large heat effects. Molybdenum was selected for both the reactor material and the material for the
Table 2.3 Physical properties of reactor materials [32].

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{melt}}$ °C</th>
<th>$\lambda$ W m$^{-1}$ K$^{-1}$</th>
<th>E GPa</th>
<th>$\alpha$ $10^{-6}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Design criteria</strong></td>
<td>&gt; 1200</td>
<td>&gt; 125</td>
<td>&gt; 150</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Mo$^a$</td>
<td>2620</td>
<td>138</td>
<td>315</td>
<td>5</td>
</tr>
<tr>
<td>Quartz</td>
<td>1607</td>
<td>0.22</td>
<td>70</td>
<td>0.4</td>
</tr>
<tr>
<td>AISI 316$^b$</td>
<td>1507</td>
<td>50</td>
<td>196</td>
<td>10</td>
</tr>
<tr>
<td>Ni</td>
<td>1452</td>
<td>91</td>
<td>196</td>
<td>12.7</td>
</tr>
<tr>
<td>Si</td>
<td>1420</td>
<td>80-150</td>
<td>100-110</td>
<td>4.2</td>
</tr>
<tr>
<td>Cu</td>
<td>1083</td>
<td>390</td>
<td>128</td>
<td>16.8</td>
</tr>
<tr>
<td>Al</td>
<td>660</td>
<td>220</td>
<td>71</td>
<td>23.2</td>
</tr>
</tbody>
</table>

$^a$ $T_{\text{melt}} > 1200$°C, $\lambda > 125$ W m$^{-1}$ K$^{-1}$, E > 150 GPa, and $\alpha < 10^{-5}$ K$^{-1}$ are the design criteria.

$^b$ Prizes of Mo (99.9%) and AISI 316 for a rod with diameter and length of 50 mm are 800$ and 150$, respectively (Goodfellow, 2006).

The HTMR is designed to screen eight sets of catalytic coatings with a maximum thickness of 10 μm, which are deposited on molybdenum plates with dimensions of $40 \times 10$ mm$^2$ and a thickness of 0.1 mm, and which have a minimal rate of reaction of about 0.01 s$^{-1}$ in terms of turnover frequency (TOF). Therefore, the reactor consists of eight identical microstructured compartments (Figure 2.1). This arbitrary chosen number of compartments can be increased when this specific reactor concept is proven to operate adequately. Up to a total number of eight molybdenum plates with the deposited catalytic coatings can be inserted in each of the compartments. If necessary, the number of catalytic coatings as well as the coating thickness can be varied to operate the HTMR in the differential reactor mode, which considerably simplifies the kinetic analysis and allows the direct interpretation of intrinsic kinetic data for process development [33]. The catalytic layer can be deposited on the substrate by means of various techniques, such as anoxic oxidation, sol-gel synthesis, hydrothermal synthesis or sputtering [34].

Based on the selected thickness of the molybdenum plates, eight rectangular shaped cavities with curved edges of 130 μm height, 400 μm width were produced along the compartment length of 40 mm by electric discharge machining (EDM) [34, 35]. The electrode for machining molybdenum was a 0.1 mm wire of brass material, coated with zinc. In this EDM study two grades of molybdenum were tested, a molybdenum alloy containing 0.5% Ti and 0.08% Zr, and pure molybdenum (Mo 99.99+%). The former molybdenum grade offers a considerable higher strength at temperatures above 1300°C. However, because of the additives, the EDM processing in the molybdenum alloy resulted in irregularly shaped microstructures, which contained microcracks that could affect the performance of
molybdenum parts adversely if the surface is stressed in tension. On the contrary, the EDM process worked well in case molybdenum with a high purity was used. All microstructures were produced along the length of the reactor with a tolerance below 4 μm.

Molybdenum readily starts to oxidize in air at 300°C at atmospheric pressure [36], which urges the need for a protective coating. Molybdenum disilicide (MoSi₂) is a promising material for high temperature structural applications because of its relatively high thermal conductivity and excellent oxidation resistance [37-39]. However, MoSi₂ disintegrates to a powder when subjected to oxidizing environments in the 400-600°C range, which is known as the “pest” effect [40-42]. MoSi₂ composites might offer a possible solution for protection of molybdenum in the full temperature range [43, 44].
Another possibility to protect molybdenum below 550°C is atomic layer deposition (ALD) of a thin Al₂O₃ layer [45]. ALD is a process capable of depositing ultra-thin, conformal films of a variety of materials with atomic-level thickness control [45-48]. Recently, Groner et al. reported that the ALD process of Al₂O₃ films is applicable on a wide variety of substrates, including molybdenum, and is an excellent choice for both insulating and protective purposes [48]. In the present study a series of molybdenum substrates, on which Al₂O₃ layers were deposited by ALD up to 500 nm, were tested in air and water vapour (2.3 vol.%) up to 600°C. The layer thickness and temperature are crucial parameters for the alumina film stability. Above 550°C the Al₂O₃ films detached from the molybdenum surface. Also film destruction was observed below 550°C for films with a thickness larger than 300 nm. The film destruction was likely caused by the difference in the linear expansion coefficient for alumina film and the underlying molybdenum. On the contrary, no mass increase was observed due to the formation of molybdenum oxides for a 200 nm Al₂O₃ film up to 550°C for at least 150 h.

2.2.2 HTMR layout

The HTMR consists of three separate zones, viz. the flow distribution header, the reactor section, and the quench section (Figure 2.1). The flow distribution header is designed in a way that the inlet fluid flow is both preheated to the reaction temperature and equally distributed in the eight reactor compartments in the full flow range of 50 to 1000 ml min⁻¹ STP (Section 2.3.1). Thermocouples are positioned in the reactor section to monitor axial and radial temperature distributions (Figure 2.1). In the quench section, the temperature of the outlet gases should be decreased from the reaction temperature to ca. 120°C within milliseconds to minimize the formation of by-products downstream of the reactor (Section 2.3.2). The quench section is made of AISI-316 stainless steel and is separated from the hot reactor section by a 3 mm thick ceramic ring. The sampling system consists of 24 capillaries, which are positioned slightly inside the compartments to avoid cross talking between different catalyst compositions (Section 2.3.3). Three capillaries per compartment are used to validate the data and to measure possible radial concentration gradients. The outlet gas composition from the separate compartments is sent to a mass spectrometer, by selecting one of the sampling capillaries via a multi-positional valve system.

Actually, the main drawback of the present reactor concept is a considerable heat transfer resistance at the contact area between the individual plates and the main body of the reactor. With the present reactor design the temperature non-uniformity can be estimated, considering the case when no physical contact is realised between the molybdenum plates, containing the catalyst coating, and the reactor body. The difference between the temperature of a Mo plate and the reactor
housing is estimated at a typical case when a flow of 1000 cm$^3$ min$^{-1}$ (STP) passes the reactor. The reactant concentration was assumed to be 50 mol%, $\Delta H_{298} = -500$ kJ mol$^{-1}$, with a conversion of 15%. In this case, the total heat ($Q$) to be transferred from the reaction zone is 28 W (64 plates) or 0.44 W per single molybdenum plate. The effective heat transfer area is the area between a single molybdenum plate and the main body of the reactor. The cross section area ($S$) is equal to $3.2 \cdot 10^{-5}$ m$^2$, which is four times the distance in which the plates are inserted inside the cavities ($4 \times 0.2$ mm) times the reactor length (40 mm) (Figure 1). Furthermore, the gas thermal conductivity ($\lambda$), and the distance between a Mo plate and the wall of the microstructure ($l$) is assumed to be 0.2 W m$^{-1}$ K$^{-1}$ at 500°C and 0.015 mm respectively. This distance, $l$, is estimated as half the difference between cavity in the reactor wall (0.13 mm) and the thickness of a plate (0.10 mm). Substituting these values in Eq. 2.1, the temperature non-uniformity, $\Delta T$, between a single plate and the main reactor body can be calculated:

$$\Delta T = \frac{Q \cdot l}{S \cdot \lambda} \quad (2.1)$$

The temperature non-uniformity is less than 1 K, which approaches isothermal reaction conditions.

### 2.3 CFD simulation of a high-throughput microreactor

#### 2.3.1 Flow distribution header

In the inlet section of the HTMR, the fluid flow has to be preheated from room to reaction temperature and has to be distributed equally in the eight reactor compartments. The flow enters the flow distribution unit at a typical flow in the range of 50-1000 cm$^3$ min$^{-1}$ (STP) and it is divided in half by the symmetrical design of the inlet tube. Therefore, only half of the complete geometry of the flow distributor and the corresponding four reactor compartments were simulated in the CFD model. A new concept of a flow distributor for flow equalization is introduced by positioning of a thick walled screen in front of the reactor compartments. The geometry of the module is shown in Figure 2.2. Such geometry of the thick walled screen has all the benefits of a structured design, such as an improved pressure recovery due to a negligible pressure drop via the unit, and virtually clog-free behaviour. Moreover, the most critical drawback of flow distributors is eliminated, viz. a limited range for fluid flow velocities.

However, the flow has to be distributed equally in four reactor compartments. To reach this goal, the direction of the reactor compartments is shifted by a 90° turn relative to the direction of the elongated channels of the thick walled screen. In this
The elongated vertically positioned channels of the thick walled screen and the horizontal positioned compartments of the reactor are shown in the cross sectional view (A + B). For symmetry reasons only half of the device is shown. The design parameters and dimensions (in mm) are indicated. The area of the numerical CFD simulation is shown in rectangular area.

The fluid flows in a half circular motion, which causes the flow to travel in all directions (180°) at the screen/reactor interface. This eliminates the possibility of local concentration non-uniformities or streaking, and allows the flow to be distributed equally in the reactor compartments. To get the uniform flow in the reactor compartments, special care has to be taken with respect to two design parameters only (a and b, Figure 2.2). In the present design study, distance a (separation) was defined as the minimum length between two adjacent reactor compartment walls. Distance b was defined as a minimum length between the top wall of the reactor compartment and a side wall of a channel of the screen.

The cross section of the reactor compartments was fixed at 10 × 2 mm² based on the typical range of contact times required for catalytic coating testing (viz., 0.1 - 10 s). This value is slightly different from the actual value, but it was taken to facilitate grid generation for the CFD simulations. In the design of the fluid flow distribution unit, the total open area of all the channels of the thick walled screen was fixed at the value of 80 mm², which corresponds to the cross section of four reactor compartments. The equal open area in the reactor and channels of the screen guarantees the lowest pressure drop via this unit. The effect of the number of the channels and the distance between the channels (pitch) on the flow distribution was investigated. It was found that there is only a small effect of these...
parameters on the flow distribution when the total number of channels was more than six. However, a smaller number of screen channels leads to a relatively large width of individual channels, and as a result a longer screen length is required to preheat the inlet fluid flow. On the other hand, a large number of channels would hamper the manufacturing of the device considerably. Therefore, we have chosen a design of the thick walled screen with eight channels, in which all the channels have a width of 1.03 mm with a distance of 0.25 mm in between. At a fixed height of the channels of 10 mm, a minimum screen length of ca. 4 and 7 mm is required to preheat the inlet fluid flow to 500 and 800°C, respectively. To satisfy the most severe case, the screen length was fixed at the latter value (7 mm).

After the establishment of the basic design parameters, a study was performed to find the optimal $b/a$ value. Again, for reasons of symmetry in the geometry, only half the geometry including four screen channels was used in the CFD simulations (Figure 2.2). The temperature was fixed at 25°C at the four channel inlets of the thick wall screen. Uniform static pressure of 101100 Pa was specified at the four reactor compartment outlets. The thick walled screen and reactor temperature were fixed at 500°C. Physical parameters of air were used for definition of gas phase properties. Distance $a$ was fixed at 0.25 mm and the flow distribution was investigated at several different $b/a$ ratios. At first, a uniform flow distribution was applied at the inlet of the channels of the screen. At $b = 0$ the flow distribution was non-uniform with a maximum flow in the second and third reactor compartments (Figure 2.3(a)). At larger $b/a$ ratios, a larger percentage of the total fluid flow goes via the first and fourth reactor compartments. Figure 2.3(a) shows that there exist an optimal value for the $b/a$ ratio between 0.5 and 1.0 at which a uniform flow distribution can be obtained.

To characterize the degree of flow non-uniformity, parameter $s$ was introduced, which is defined as the mean square deviation from the average flow value:

\[
s = \sqrt{\frac{\sum_{i=1}^{n} (u_i - \bar{u})^2}{n-1}}
\]

(2.2)

where $u_i$ is the area averaged velocity in the compartment $i$. To compare the results obtained at different flow velocities, the degree of flow non-uniformity, $\delta$ (%), in percent from the total flow was defined as:

\[
\delta = \frac{s \cdot 100}{u}
\]

(2.3)

Figure 2.3(b) shows that parameter $\delta$ has a minimum in the range of $b/a$ ratios in between 0.80 and 0.83, depending on the flow velocity. At the $b/a$ value of 0.81, the mean square deviation does not exceed 0.5% for all fluid flow velocities studied.
Figure 2.3  (a) Flow distribution in the reactor compartments as a function of the $b/a$ ratio. (b) Mean square deviation from the average value as a function of the $b/a$ ratio at fluid flow velocities of 100 and 1000 cm$^3$ min$^{-1}$ (STP).

Now consider the flow distribution in the reactor compartments at a non-uniform flow distribution specified at the channel inlets of the screen. Actually, the typical geometry of the inlet chamber before the channel inlets has a conical shape providing more flow along the centreline and less near the walls. Therefore, the central channels of the screen would receive more flow than the outermost ones. Figure 2.4 shows three flow distributions taken in the channels of the thick walled screen by using a “standard” conical geometry of the inlet chamber, viz. an inlet tube with an outer and inner diameter of 3 and 2 mm, respectively, a chamber length of 11 mm, and an angle between the centreline and the wall of $22^\circ$. Below a flow rate of 20 cm$^3$ min$^{-1}$ (STP), the flow non-uniformity in the channels of the screen did not exceed 1% from the average value. The flow non-uniformity increases considerably at higher fluid flows (Figure 2.4). Deviations of 12 and 30% from the average value were obtained at a flow velocity of 100 and 1000 cm$^3$ min$^{-1}$ (STP), respectively. However, at the fixed parameters $a = 0.3$ mm and $b = 0.24$ mm, the non-uniformity in the reactor compartments calculated by Eq. 2.3 was 0.35 and 0.80%, respectively. Thus, the design criterion to obtain flow non-uniformity below 1% in the distribution unit is satisfied. Based on the values obtained, the height of the channels of the screen ($h$) was fixed at

$$ h = 4.6a + 4c, $$

where $c$ is the width of the reactor compartment. This gives a height of the channels of 10.42 mm at $a = 0.3$ mm and $c = 2.26$ mm. The estimated mechanical precision of module assembling is $5 \cdot 10^{-3}$ mm, which would guarantee a flow non-uniformity in the reactor compartments below 1%.
2.3.2 Quench section

The geometry of the quench section is shown in Figure 2.5. Assuming that the coolant temperature does not significantly change in the coolant chamber, only a quarter of the complete unit was required to be simulated in the CFD model. The inner diameter of a sampling capillary was fixed at 1.0 mm. The fluid flow through the capillary was estimated at 1 cm$^3$ min$^{-1}$ (STP) for analysis. Three criteria were used in the design of this quench section. First of all, the temperature of the effluent gases inside the capillary has to decrease from reactor temperature to approximately 120°C within a millisecond time range. Secondly, the temperature of the hot ends of the stainless steel capillaries may not exceed 350°C to prevent them from corrosion. The outer diameter of the sampling capillary defines the metal cross section and, therefore, the heat transfer rate. Finally, the temperature of the product main stream has to be decreased to ca. 150°C to avoid damaging of the electronic multi-positional valves positioned downstream of the module.

Figure 2.6 demonstrates the calculated temperature profiles in the hottest part of the device – in the close vicinity of the central sample capillary (half of the actual geometry is shown). In the most severe case, having a flow velocity of 1000 cm$^3$ min$^{-1}$ (STP) and a temperature of the outlet gases of 500°C, the temperature of the products drops to ca. 300°C already after 3 mm in a sampling capillary with an outer diameter of 1.2 mm. This corresponds to a quenching time of only 0.5 ms. The temperature at the hot end of the capillary is about 320°C, while the temperature of the main stream drops to 120°C at the distance of 7 mm from the capillary inlet, which satisfies the design criteria. If the fluid flow velocity is fixed at its lower design value of 100 cm$^3$ min$^{-1}$ (STP), the quenching of the reaction products occurs within 1 mm distance (Figure 2.6).
2.3.3 Sampling section

The outlets of the reactor compartment were designed at a distance of 250 μm from each other. To minimize the cross-talking noise between the adjacent compartments, it is necessary that product sampling occurs inside the compartments [16]. In order to find a minimal distance for capillary inlets inside a compartment, a typical case was studied. A 10 vol.% oxygen in helium mixture was fed in every other compartment, while a 10 vol.% nitrogen in helium mixture was fed in the adjacent compartments. The computational domain is shown in Figure 2.7 together with the specifications of the geometry of the sampling section. Due to the symmetry, only two adjacent compartments were used in the CFD simulations. Furthermore, only one capillary was considered, which was positioned in the center of the compartment. The linear velocity at the capillary inlet was equal to that in the main stream, that is an iso-kinetic suction intake of product gases. In this way the capillary only slightly disturbs the fluid flow profile, and the modeling of one capillary appears to be sufficient. All outlets were specified as outflow regions with flow weighting factors proportional to the cross sectional area of the outlets. The latter condition was required to account for iso-kinetic suction intake. Both inlets were defined as pressure inlets with a pressure drop providing the desired linear velocity of 0.02 m s\(^{-1}\) at the inlet position.
Figure 2.8 shows the molar concentration of oxygen in the nitrogen flow versus the position of the capillary inlet inside the compartments (distance $d$). The oxygen concentration depends strongly on the flow rate and on the distance $d$. The minimum distance of the capillary inlet inside the compartment is 4 mm at a minimum flow velocity of 12 cm$^3$ min$^{-1}$ (1/8 of the total value), which is required for an accurate product analysis in catalyst screening studies.

Figure 2.8 shows the molar concentration of oxygen in the nitrogen flow versus the position of the capillary inlet inside the compartments (distance $d$). The oxygen concentration depends strongly on the flow rate and on the distance $d$. The minimum distance of the capillary inlet inside the compartment is 4 mm at a minimum flow velocity of 12 cm$^3$ min$^{-1}$ (1/8 of the total value), which is required for an accurate product analysis in catalyst screening studies.

Figure 2.8 (a) Oxygen concentration profile at the inlet and outlet of two reactor compartments. The inlets of the sampling capillaries are inserted in the compartments. See Fig. 7 for definitions. (b) Area averaged oxygen concentration in the capillary (# 3). Total flow 1: 50 cm$^3$ min$^{-1}$, 2: 75 cm$^3$ min$^{-1}$, 3: 100 cm$^3$ min$^{-1}$ (STP).
2.4 Conclusions

A novel molybdenum based high-throughput microreactor (HTMR) has been designed for the screening of catalytic coatings in high temperature gas phase reactions (up to 800°C) involving high heat effects ($\Delta H_{298} = \pm 1500$ kJ mol$^{-1}$). The HTMR consists of eight microstructured compartments, which can be loaded with catalytic coatings. Both the plate type geometry of the HTMR and the high heat conductivity of the molybdenum reactor material allow for near isothermal reactor operation required for kinetic or catalyst screening studies.

All critical design issues in the development of a microreactor for the screening of catalytic coatings were investigated by means of a three dimensional CFD study, prior to microreactor fabrication, assembling and operation. A low-pressure drop fluid flow distribution header has been designed, which is capable of equalizing the inlet fluid flow equally in the reactor compartments in a range of 50 – 1000 cm$^3$ min$^{-1}$ (STP). The flow distributor has a structured geometry, viz. a thick walled screen, of which the elongated rectangular channels are positioned with a 90° turn relative to the reactor compartments. The fluid flow is also preheated to the reaction temperature in this inlet section. A quench section has been designed to effectively quench the effluent fluid flow within a millisecond time range to avoid consecutive reactions downstream of the reactor. In the sampling section, the cross talking noise of product gases between adjacent compartments can be minimized by (1) the positioning of the sampling capillary inlets at a distance of 4 mm inside the compartments, and (2) an iso-kinetic suction intake of product gases.

Electrical discharge machining (EDM) of molybdenum material containing impurities as Ti and Zr is not suitable for producing microstructures. However, EDM of a high purity molybdenum (99.99+ %) material was reproducible with tolerances below 4 μm. The corrosion resistance of molybdenum was considerably improved by deposition of a 200 nm Al$_2$O$_3$ film by means of atomic layer deposition. No significant oxide formation of molybdenum was observed after an exposure of 150 h at 550°C in an oxidative environment.

Appendix A

The area-averaged values of the gas velocity, $u_i$, are calculated in every compartment from the results of the simulations as follows:

$$u_i = \frac{\int \int u \, dx \, dy}{\int \int dx \, dy},$$

(A1)

where $b2$ and $b1$ are the height of a reactor compartment ($2 \cdot 10^{-3}$ m) and the height of a screen channel ($1 \cdot 10^{-2}$ m), respectively, and $a2$ and $a1$ are the width of a reactor compartment.
compartment \( (1 \cdot 10^{-2} \text{ m}) \), and the width of a screen channel \( (1.03 \cdot 10^{-3} \text{ m}) \), respectively. The average flow value in the four compartments considered for simulation, \( \bar{u} \), is calculated as follows:

\[
\bar{u} = \frac{1}{4} \sum_{i=1}^{4} u_i .
\]  

(A2)

Nomenclature

Roman symbols

- \( a \) minimum length between two adjacent reactor compartment walls [m]
- \( b \) minimum length between the top wall of the reactor compartment and a sidewall of a screen channel [m]
- \( c \) width of the reactor compartment [m]
- \( d \) position of the capillary inlet inside a reactor compartment [m]
- \( h \) height of the screen channel [m]
- \( i \) reactor compartment number, \( 1 \leq i \leq 4 \), [-]
- \( E \) tension modulus [GPa]
- \( l \) distance between a plate and the main body of the reactor [m]
- \( Q \) heat flux [W]
- \( s \) mean square deviation from the average flow value [-]
- \( S \) area of cross section (= four times the distance in which the plates are inserted inside the microstructure \( (4 \times 0.2 \text{ mm}) \) times the reactor length \( (40 \text{ mm}) \)) [m\(^2\)]
- \( T \) temperature [°C]
- \( T_{\text{melt}} \) melting temperature of material [°C]
- \( u_i \) area averaged velocity in the compartment \( i \) [m s\(^{-1}\)]
- \( \bar{u} \) average velocity in all compartments considered in simulations [m s\(^{-1}\)]

Greek symbols

- \( \alpha \) linear extension coefficient [K\(^{-1}\)]
- \( \delta \) flow non-uniformity [%]
- \( \lambda \) heat conductivity coefficient [W m\(^{-1}\) K\(^{-1}\)]
- \( \Delta H_{298}^0 \) heat of formation [kJ mol\(^{-1}\)]
- \( \Delta T \) temperature difference [K]

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Bibliography

Experimental Validation of the Performance of a Microreactor for the High-Throughput Screening of Catalytic Coatings

This Chapter has been submitted as:

Abstract
In this paper the results of CFD simulations of flow, temperature, and concentration distributions used in the design of a microreactor for the high-throughput screening of catalytic coatings [Mies et al., *Chem. Eng. J.* 101 (2004) 225] are compared with experimental data, and good agreement is obtained in all cases. The experimental results on flow distribution were obtained from Laser Doppler Anemometry measurements in the range of Reynolds numbers from 6 to 113. The measured flow non-uniformity in the separate reactor compartments was below 2%. The temperature distribution was obtained from thermocouple measurements. The temperature non-uniformity between the reactor compartments was below 3 K at a maximum heat production rate of 1.3 W in ethylene oxidation at 425°C over CuO/Al2O3/Al coatings. With respect to concentration gradients, a deviation from the average rate of reaction of only 2.3% was obtained at realistic process conditions in the ethylene ammoxidation process over identical Co-ZSM-5 coatings in all reactor compartments. The cross talking noise between separate compartments does not exceed 0.1% when the reactor parts have a smooth surface finish. This illustrates the importance of ultra-precision machining of surfaces in micro technology, when interfaces cannot be avoided.
Chapter 3

3.1 Introduction

Structured [1] and microstructured reactors [2,3] are more and more recognized for their unique properties and potential applications in chemistry and chemical process industry. They are particularly suited for highly exothermic and fast reactions allowing temperature control and isothermal operation. The efficient use of (micro)structured catalytic reactors requires a shaping of the catalyst usually by deposition of thin catalytic coatings at the walls of the reactor channels. Over the last decade, many methods have been developed or considerably improved to deposit catalytic coatings on a substrate: zeolite hydrothermal synthesis [4-8], anodic oxidation [9-11], electrophoretic deposition [12], sol-gel synthesis [13-16], washcoating [17], atomic layer deposition [18-20], several vapor deposition techniques [21,22], and electrochemical depositions in ionic melts [23,24]. The choice of the deposition method depends on the size of the coated substrate, scale of substrate structurization, as well as on the properties of the substrate and the active component.

The development of novel and superior catalytic coatings for structured reactors is often an empirical process, which is based on conventional catalyst know-how and common sense. Therefore, high-throughput testing (HTT) of libraries of coatings for desired catalytic properties is required at realistic process conditions to speed up this development and optimization trajectory. Moreover, HTT can be used for primary screening of large coating libraries to discover new potential candidates for a specific chemical process. Microstructured reactors can be used as a tool for high-throughput screening of catalytic coatings and for kinetic studies [25]. However, it is not straightforward to obtain identical process conditions in a large number of microchannels, due to the non-uniformity of the fluid flow distribution in the microchannels at low pressure drop. Therefore, a three dimensional design of the full reactor is often required before its fabrication and assembling. Especially, flow equalization between different channels and temperature uniformity are of importance. In our previous study we proposed a high-throughput microreactor (HTMR) for the screening of eight different catalytic coatings with turn over frequency (TOF) values of 0.1 – 10 s\(^{-1}\) in a flow range of 50 - 1000 mL min\(^{-1}\) [25]. The flexibility in the flow rate allows the testing of catalytic coatings in the differential reactor mode, which considerably simplifies the interpretation of the kinetic data. In this reactor design, the geometries of the low pressure-drop flow distributor and the gas sampling section were optimized using the CFD code Fluent [25]. We proposed an original design of a flow distribution header, consisting of a cone diffuser and a thick-walled screen for equalizing the flow distribution in microstructured reactors [25-28]. The influence of the different design parameters of a thick-walled screen on the flow non-uniformity has been
analyzed. According to the CFD study, the degree of flow non-uniformity does not depend on the flow distribution entering the thick-walled screen and is defined by the geometry of the thick-walled screen itself. The proposed screen configuration can minimize the ratio of the maximum flow velocity to the minimum flow velocity from 2 (without the screen) to 1.005 (with the screen) for a wide range of Reynolds numbers, which in turn can improve the performance of a downstream microreactor [29].

In the present paper, an experimental validation study is performed to compare the performance of the HTMR versus the design criteria, viz. the flow distribution in the separate reactor compartments, the temperature distribution, and the accuracy of sampling of the product gases. The flow distribution was studied using Laser Doppler Anemometry (LDA), which is a direct method for the determination of the fluid velocity in the separate micro structured compartments, while it does not disturb the fluid flow. Especially the accuracy in the measurement itself, as well as in the positioning of the relatively small measurement volume with respect to the channel outlets, makes the LDA technique a powerful tool for the fluid flow analysis in microstructured devices. The temperature distribution was measured by means of thermocouples. In addition, the concentration distribution was investigated at real process conditions in the ethylene ammoxidation process over zeolitic catalytic coatings.

3.2 Experimental

3.2.1 High-Throughput Micro Reactor

The HTMR (Figures 3.1(a-f)) comprises a cone diffuser, upstream connected to the inlet capillary (ID = 2.16 mm) (I), a thick walled screen (II), eight reactor compartments (III), an insulating ring (IV), an outlet flow confusor (V), and a sampling section (VI). Eight cavities of \(130 \times 400 \mu m^2\) were microfabricated by electrical discharge machining (EDM) in the side walls of each reactor compartment along the length of the reactor (inset of Figures 3.1(a) and 3.2). In this way, each reactor compartment can be loaded up to eight substrate plates with catalytic coatings. The center of the coordinate system \((x = 0, y = 0, z = 0)\) is on the center axes at the interface between the screen (II) and the reactor (III) (Figures 3.1(a) and 3.2). To monitor axial and radial temperature gradients, thermocouple T1 is positioned close to the external surface \((x = 14 \text{ mm}, z = 3 \text{ mm})\) and two thermocouples (T2, T3) are positioned along the center axis at \(z = 3\) and 37 mm, respectively. A band heater with a maximum power output of 300 W was used for the temperature control of the reactor and was positioned at its surface from \(z = 5\) to 43 mm (not shown in Figure 3.1(a)). In the plane of the cross section of the screen
Figure 3.1 (a) A schematic illustration of the high-throughput microreactor, which comprises a cone diffuser (I), a thick walled screen (II), eight reactor compartments (III), an insulating ring (IV), an outlet flow confusor (V), and a sampling section (VI). The dimensions and coordinates are indicated above the figure along the z-axis. The axial positions of the thermocouples are indicated with T1, T2, and T3. The inset of the HTRM compartment shows the eight micrstructured cavities in the side wall along length of the reactor. (b) The cone diffuser (I), is connected upstream to the inlet capillary (OD = 3 mm, ID = 2.16 mm). (c) The thick walled screen (II, z = -8 mm), consisting of two series of eight elongated channels, which are positioned with a 90-degree turn relative to the reactor compartments (III). The walls of reactor compartments are also visible through the open areas of the screen. (d) The upper four reactor compartments (III, z = 0 mm), which are loaded with four catalytic coatings per compartment. (e) The upper four compartment outlet flow confusers (V, z = 40 mm), which are poisoned against the reactor compartments. Three sampling capillaries (VI) are poisoned at 4 mm inside every compartment outlet. (f) The sampling and outlet section (VI) and the ceramic ring (IV), which separates the hot and cold HTMR parts. The eight sets of three sampling capillaries as well as the four common reactor outlets are visible. The two ceramic pins are for HTMR assembling purposes. The dimensions of the various reactor sections in Figures b-f are indicated in Figures 3.1(a), 3.2 and 3.4.

(II), two sets of eight elongated channels are positioned with a 90-degree turn relative to the reactor compartments. The screen distributes the flow equally over
the reactor compartments, and simultaneously preheats the inlet gas flow to the reaction temperature. Sections V and VI were maintained at 120°C. The main part of the outlet gas flow (ca. 99.5 vol.%) is directed to the four common outlets (ID = 6 mm, VI). The sampling section (VI) comprises 8 sets of 3 capillaries (ID = 1.0 mm, OD = 1.2 mm, *i.e.* three capillaries per compartment, positioned at 4 mm inside the flow confusor (V). 0.5 vol.% of the total flow is selected for product analysis by a multi-positional valve. Iso-kinetic suction-intake was maintained by a diaphragm micro pump. Sequential analysis of the product gases was automated via Lab-Jack software.

### 3.2.2 Flow Distribution

The fluid flow distribution in the HTMR compartments was investigated using Laser Doppler Anemometry (LDA). At the low velocities and small measurement volumes of interest to the present study, LDA measurements in gas flows are complicated and not very accurate. For low velocity and (nearly) isothermal flows, however, the flow behavior is fully determined by the Reynolds number. This allows for the replacement of gas by a liquid as flowing medium, when the Reynolds number is kept fixed. Assembled sections I – III of the HTMR (see Figure 3.1(a)) were positioned in a water/PVP-K90 (polyvinylpyrolidone; $M_w = 1.0 - 1.5 \cdot 10^6$ g mol$^{-1}$) solution with the z-axis parallel to the gravity vector. The gravitationally driven flow of the solution through the HTMR was set at 0.11, 0.20, 0.99, and 1.65 cm$^3$ s$^{-1}$ (STP). The properties of the fluid flow at the various flow conditions are given in Table 3.1. With these, the corresponding Reynolds numbers in the inlet capillary ($Re_{cap}$) were 6.7, 12.7, 64, and 113, respectively. The LDA analysis was performed at the outlets of the reactor compartments ($y = 0$ mm, $z = 40$ mm) along the x-axis from $x = -11.7$ mm to $x = 11.7$ mm (Figure 3.2). Each traverse along the x-axis consisted of LDA analysis at 133 positions. At each position, 20,480 LDA measurements were performed, from which both the average velocity at that position and its standard deviation were determined.

LDA measurements were performed in forward scatter, reference beam mode [30] (Figure 3.3), using a diode pumped 532 nm green laser and a frequency shift of 20 kHz. No tracer particles were added to the water/PVP-K90 solution, as the fluid

<table>
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<td>$\bar{V}_{comp}$, (mm s$^{-1}$)</td>
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<td>5.85 ± 0.05</td>
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<td>$\eta_{cap}$, (mm s$^{-1}$)</td>
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<td>59 ± 2</td>
<td>293 ± 10</td>
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<td>12.7 ± 0.4</td>
<td>64 ± 0.4</td>
<td>113 ± 0.4</td>
</tr>
</tbody>
</table>

The properties of the fluid flow for the LDA experiment are given in Table 3.1.
already contained sufficient natural seeding. The size of the cigar-shaped measurement volume was $1.19 \times 0.22 \times 0.22 \text{ mm}^3$. The measurement volume was positioned at a distance less than 1.0 mm from the outlets of the reactor compartments, with its longitudinal axis parallel to the longitudinal axis of the compartments in the $y$-direction, and thus perpendicular to the axial velocity profile in the $z$-direction. In this way, the location uncertainty in the velocity measurement data was reduced as much as possible (Appendix I). The LDA signal was processed by means of an IFA550 signal processor. Velocity bias was corrected for by means of the Time Between Data (TBD) correction method [31].

**Figure 3.2** Cross section of the microstructured reactor (III, $z = 0 \text{ mm}$) with an enlarged view of the microstructures in the side wall of the compartment at the right-hand side. The radial positions of the thermocouples are indicated with T1, T2, and T3. The center of the coordinate system ($x = 0, y = 0, z = 0$) is on the center axes at the interface between the screen (II) and the reactor (III).

**Figure 3.3** Schematic overview of the LDA set-up and the positioning of the HTMR relative to the LDA measurement volume.
3.2.3 Temperature distribution

The temperature distribution in the HTMR was determined in ethylene oxidation,

\[
\text{C}_2\text{H}_4 + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O} \quad \Delta H_{698}^0 = -1284 \text{kJ mol}^{-1} \quad (3.1)
\]
on CuO/Al₂O₃/Al coatings at 425°C with an ethylene concentration of 2 vol.% and an oxygen concentration of 0.5 – 12 vol.% in helium at a total flow of 250 ml min⁻¹. The evolved reaction heat was calculated from the CO₂ concentration in the effluent gas flow with the following equation,

\[
Q = \frac{0.5y_{\text{CO}_2} \cdot F_v \cdot \Delta H_{698}^0}{V_{\text{m}}}, \quad (3.2)
\]
where \(Q\) is the produced reaction heat (W), \(y_{\text{CO}_2}\) is the mole fraction of carbon dioxide (-), \(F_v\) is the total flow rate at STP conditions (m³ s⁻¹), \(V_{\text{m}}\) is the molar volume (m³ mol⁻¹), and \(\Delta H_{698}^0\) is the reaction enthalpy (J mol⁻¹).

Al₂O₃ coatings were prepared by anodic oxidation of aluminum substrates of 40 × 9.8 mm² with a thickness of 0.09 mm (99.99 wt.%; Goodfellow Cambridge Limited). Twelve aluminum plates per batch were oxidized simultaneously in a cylindrical 20 L electrolysis vessel. The preparation conditions are explained in details elsewhere [11]. A 15 µm alumina layer was produced under current control conditions with an anodic current density of 15 mA cm⁻² in an aqueous 10 wt.% oxalic acid solution at 3°C for 2 h under continuous stirring at 180 rpm. CuO/Al₂O₃/Al coatings were prepared by wet impregnation of the alumina layer by a 2.5 M aqueous copper nitrate solution for 1 h at 20°C. The excess of the impregnation solution was wiped of the plates with a tissue paper. The plates were calcined at 400°C for 1 h in air at a flow of 100 ml min⁻¹. The CuO loading was 2.3 wt.% of the mass of Al₂O₃, where the apparent density of the alumina layer is 2.0 g cm⁻³.

3.2.4 Concentration distribution

The concentration distribution at process conditions was determined in ethylene ammoxidation,

\[
\text{C}_2\text{H}_4 + \text{NH}_3 + \text{O}_2 \rightarrow \text{C}_2\text{H}_3\text{N} + 2 \text{H}_2\text{O}, \quad \Delta H_{698} = -418 \text{kJ mol}^{-1} \quad (3.3)
\]
on Co-ZSM-5 coatings at 425°C at equimolar oxygen, ethylene, and ammonia concentrations of 4 vol.% in helium at a total flow of 250 and 500 ml min⁻¹, respectively. Blank experiments were carried out on inert titanium plates to exclude the contribution of the reactor material to reactant conversion. Prior to the experiments, the CuO/Al₂O₃/Al and Co-ZSM-5 coatings were pretreated in helium for 1 h at 450 and 500°C, respectively.
ZSM-5 coatings were prepared via hydrothermal synthesis on molybdenum substrates of 40 × 9.8 mm² with a thickness of 0.1 mm (99.9+ wt.% Aldrich) from a synthesis mixture with the following molar oxide composition: 1 Al₂O₃ : 50 SiO₂ : 2500 H₂O : 0.5 Na₂O : 2 (TPA)₂O. The synthesis protocols and the scale-up procedure to obtain identical zeolitic coatings on 72 substrates are reported elsewhere [5]. The as-synthesized coatings were calcined and subsequently subjected to an ion exchange procedure in a 1 · 10⁻⁴ M cobalt acetate solution to obtain Co-ZSM-5 coatings [6]. A total weight of 4.5 mg of Co-ZSM-5 was obtained per plate. XPS analysis on the coatings after the post treatment resulted in Si/Al and Co/Al ratios of approximately 26 and 0.5, respectively.

The concentrations of the components in the effluent gas were analyzed with an online Varian micro-GC (CP-4900), equipped with TCD detectors. Helium was used as a carrier gas. The analysis time was 80 s for each injection. N₂, O₂, CH₄, NO, and CO were analyzed on a molsieve 5A column (0.25 mm ID, 10 m) operated at 175°C and 350 kPa. C₂H₄, C₂H₆, CO₂, NH₃, and H₂O were analyzed on a poraPLOT-U column (0.25 mm ID, 10 m) operated at 65°C and 200 kPa. CH₃CN and CH₃OH were analyzed on a poraPLOT-U column (0.25 mm ID, 10 m) operated at 175°C and 150 kPa. The carbon and nitrogen mass balances were closed within 95%.

3.3 Results and discussion

3.3.1 Flow distribution

(a) Flow simulation

A thick walled screen was designed and fabricated to obtain an equal flow distribution in the HTMR compartments [25]. The elongated rectangular channels of the screen were shifted by a 90-degree turn relative to the rectangular reactor compartments (Figure 3.4). In such a geometry, the fluid is forced to flow in half a circular motion at the interface between the screen channels and the reactor compartments. In this way, local flow non-uniformities are eliminated, and the flow is smoothly distributed in all of the reactor compartments. In previous CFD studies [25-27] the effect of different design parameters (a, c, d, and xᵢ, see Notations) of the screen on the flow non-uniformity in a downstream microstructured reactor was studied. An equation to calculate the optimum value of the key parameter of the screen (b, see Notation) was derived [27]. The true dimensions of the various parameters after fabrication of the HTMR sections are shown in Figure 3.4.

In the present study, three-dimensional CFD simulations were performed with the Fluent® 6.0 software to investigate the effect of the flow rate on the flow distribution in the HTRM compartments with the optimized geometry of the flow
Figure 3.4  The header consists of a cone diffuser and a thick-walled screen positioned in front of the microreactor. The upstream section (II) comprises a set of 8 elongated parallel upstream channels, and the microreactor (III) comprises a set of 8 elongated parallel downstream channels positioned at an angle of 90° with respect to the upstream channels. Parameter $a$ is the minimum length between two neighboring downstream channels, parameter $b$ is the distance in cross sectional view between a top wall of the first downstream channel and a side wall of the upstream channels. Parameter $c$ is the width of the upstream channels. Parameter $d$ is the height of the downstream channels. Parameter $h$ is the distance between the neighboring upstream channels. Parameters $l_{up}$ and $l_{down}$ are the lengths of upstream and downstream channels of the screen respectively.

distributor (Figure 3.4). Only a quarter of the total system was simulated for reasons of symmetry in the two central planes perpendicular to each other. The flow simulation was performed for empty reactor compartments and with the fluid properties of air ($\rho = 1.225 \text{ kg m}^{-3}$, and $\eta = 1.79 \cdot 10^{-5} \text{ Pa s}$). The fluid was considered as a continuous medium without slip-flow boundary conditions [3], since the Knudsen number – based on the compartment height - is well below the critical value of 10^{-2}. Laminar flow was assumed, because the $Re_{cap}$ number was always below 113. The gas was assumed to be incompressible, since the Mach number [3] was well below 0.3. The temperature was fixed at 25°C at the four flow distributor inlets, while the fluid flow was varied up to a value of 5.31 m s^{-1} ($Re_{cap} = 726$). Uniform static pressure of 101100 Pa was specified at the four reactor compartment
outlets, and the wall temperature was fixed at 500°C. The parameter $\delta$ was introduced to quantify the degree of flow non-uniformities in the separate reactor compartments in comparison with the total average flow velocity. The parameter $\delta$ is defined as the normalized mean square deviation from the average flow value, according to the following equation,

$$
\delta(\%) = \frac{100}{\bar{u}} \sqrt{\frac{\sum_{i=1}^{4} (u_i - \bar{u})^2}{3}} ,
$$

where $\bar{u}$ is the total average velocity, and $u_i$ is the area-averaged velocity in reactor compartment $i$. Figure 4.5 shows the simulation results for air expressed in the percentage of the flow non-uniformity at various $Re_{cap}$ numbers. The flow non-uniformity remained below 2% for all cases.

As described above, the LDA measurements were performed using water/PVP liquid mixtures as flowing medium rather than air, assuming that both will behave identically for identical Reynolds numbers. This assumption was checked by repeating the CFD simulations for water/PVP mixtures. This confirmed that the fluid flow profiles in the HTMR depend only on the Reynolds number and not on the physical properties of the fluid.

(b) LDA results

The LDA analysis was performed in an identical reactor configuration, using a water/PVP mixture as flowing medium. The flow of the water/PVP mixture through the HTMR was set in such a way that the $Re_{cap}$ number in the LDA experiments corresponded with the $Re_{cap}$ numbers used in the CFD study (Table 3.1).
The LDA measurements were performed at the outlets of the reactor compartments along the x-axis (Figure 3.1: z = 40 mm, y = 0). The compartments were not loaded with coated platelets for a good comparison with the CFD results (Section 3.3.1(a)). Figure 3.6 shows the velocity profiles obtained from the LDA experiments at four different Reynolds numbers. The parabolic velocity profiles for a laminar flow in a rectangular duct can be observed for each of the compartments. The velocity of the fluid was zero at the solid walls in between the compartments. Figure 3.7 schematically shows the dimensions of a HTMR compartment, where \( x' \) is specified as the x-axis for an arbitrary compartment \( i \). The exact solution for a fully developed laminar axial velocity profile for a rectangular duct \( i \) is given in [32]. An accurate approximate solution is as follows:

\[
\frac{\bar{v}_{\text{comp},i}}{v_{\text{max},i}} = \left( 1 - \left( \frac{x'}{(0.5W)} \right)^n \right) \left( 1 - \left( \frac{y}{(0.5L)} \right)^m \right)
\]

(3.5)

where \( i \) is compartment number 1 – 8, \( n = 2 \) and \( m \) depends on the ratio of the width (\( W \)) and length (\( L \)) of the duct, \( W/L = 0.22 \). For this ratio, \( v_{\text{max},i}/\bar{v}_{\text{slit},i} = 1.763 \). The average velocity can be calculated from the maximum velocity in compartment \( i \), which is in the center at \( x' = 0 \), and \( y = 0 \). The theoretical profile along the \( x' \) axis (\( y = 0 \)) in compartment \( i \) is as follows:

\[
v_{\text{comp},i}(x', y = 0, z = 40 \text{ mm}) = 1.76 \cdot \bar{v}_{\text{comp},i} \cdot \left( 1 - \left( \frac{x'}{(0.5W)} \right)^2 \right)
\]

(3.6)
Table 3.2 Maximum and average velocities in the HTMR compartments at the various LDA experiments (see Table 3.1).

<table>
<thead>
<tr>
<th>Re-number</th>
<th>$Re_{cap}$ = 6.7</th>
<th>$Re_{cap}$ = 12.7</th>
<th>$Re_{cap}$ = 64</th>
<th>$Re_{cap}$ = 113</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Comp. no.</td>
<td>$v_{max,i}^{comp}$</td>
<td>$v_{comp,i}^{max}$</td>
<td>$v_{comp,i}^{max}$</td>
<td>$v_{max,i}^{comp}$</td>
</tr>
<tr>
<td>1</td>
<td>(± 0.01) mm s(^{-1})</td>
<td>(± 0.01) mm s(^{-1})</td>
<td>(± 0.01) mm s(^{-1})</td>
<td>(± 0.01) mm s(^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>1.16</td>
<td>0.66</td>
<td>2.05</td>
<td>1.16</td>
</tr>
<tr>
<td>3</td>
<td>1.17</td>
<td>0.67</td>
<td>2.03</td>
<td>1.15</td>
</tr>
<tr>
<td>4</td>
<td>1.18</td>
<td>0.67</td>
<td>2.04</td>
<td>1.16</td>
</tr>
<tr>
<td>5</td>
<td>1.18</td>
<td>0.66</td>
<td>2.05</td>
<td>1.16</td>
</tr>
<tr>
<td>6</td>
<td>1.17</td>
<td>0.65</td>
<td>2.10</td>
<td>1.16</td>
</tr>
<tr>
<td>7</td>
<td>1.16</td>
<td>0.66</td>
<td>2.10</td>
<td>1.19</td>
</tr>
<tr>
<td>8</td>
<td>1.18</td>
<td>0.67</td>
<td>2.07</td>
<td>1.16</td>
</tr>
</tbody>
</table>

The theoretical velocity profiles of Eq. 3.6 for compartments 1 – 8 are also shown in Figure 3.6, which were scaled with the maximum measured velocity in each compartment. From these maximum velocities, the corresponding average velocities in compartments 1 – 8 were calculated with Eq. 3.6 (Table 3.2). The flow non-uniformities from the LDA results were calculated with Eq. 3.4, which are shown for each $Re_{cap}$ number in Figure 3.5. In all cases the normalized mean square deviation in the flow non-uniformity was below 2%, which corresponds well with the results obtained from the CFD simulations. The LDA results indicate that the flow distributor can be used for flows with a $Re_{cap}$ number of about 6 up to at least 113, which corresponds to a He flow through the HTMR of approximately 60 to 1200 ml min\(^{-1}\) (STP).

In our previous study [25] an optimum $b/a$ ratio of 0.81 was found at fixed values of parameters $a$, $c$ and $d$ of 250, 1030 and 2260 μm, respectively (Figure 3.4). However, due to the peculiarities of the micromachining process, the actual values of parameters $a$ and $c$ were 304 and 850 μm, respectively. Recently, we have shown that the optimum $b/a$ ratio depends also on the width of the thick walled screen channels ($c$) and, to a minor extent, on the height of the compartments ($d$), and the dimensionless length of the screen ($x_{ap}^+$) (Equation 7) [27]:

\[
\begin{align*}
    b(a, c, d, x_{ap}^+) &= 0.5 \cdot a + 0.1678 \cdot c + 0.035 \cdot c \cdot e^{-0.840 \cdot x_{ap}^+ \cdot 0.1986} + \\
    &\quad + (8.47 \cdot 10^{-3} \cdot c + 8.00 \cdot 10^{-6} \cdot c^2 - 1.06) \cdot e^{-1.02 \cdot \frac{d}{c}}
\end{align*}
\]

The dimensionless length of the screen channel ($x_{ap}^+ = \frac{l}{D_h Re}$) is a function of the $Re$ number. However, if the length of the screen channel is much longer than its hydraulic diameter, the third term in Eq. 3.7 becomes rather small. For example, at
of 5.0, the sum of the second and the third terms becomes $0.1683 \cdot c$. With the actual values of the design parameters $c$, $d$, the fourth term in Eq. 3.7 is always much smaller comparing to the first and second ones and, therefore, can be omitted. As a result, the optimum $b/a$ value can be found by a simplified equation:

$$\frac{b}{a} = 0.5 + \frac{0.1683 \cdot c}{a} \quad (3.8)$$

With the actual values of the design parameters, the optimum $b/a$ value equals 0.97. A flow non-uniformity below 0.5% can be obtained in the range of $b/a$ between 0.91 and 1.05 as was estimated in a previous study [27]. The flow non-uniformity depends on the deviation from the optimum $b/a$ value. This dependence can be approximated by an $n$-order polynomial function. The order of this function depends on the values of the design parameters, however, it is always between 1 (linear) or 2 (parabolic) [25,26]. Therefore, the actual flow non-uniformity at $b/a$ of 0.81 is expected to be between 1.0 and 2.0%. One can see, that no systematic trend is observed in the deviations between maximum velocities (Figure 3.6 and Table 3.2) at the various $Re$ numbers. This suggests that the flow non-uniformities are caused by small variations in the experimental conditions rather than by the deviation from the optimum $b/a$ ratio. For example, small fluctuations in the liquid flow rate within one traverse (Table 3.1) resulted already in deviation of ca. 3% from the average flow rate at the various $Re_{cap}$ numbers. Furthermore, the small inaccuracy in the positioning of the LDA measurement volume at the centre of the separate compartments (Appendix I) also contributed to the small deviation from the ideal flow distribution.

### 3.3.2 Temperature distribution

The HTMR is designed for catalyst screening in the differential reactor mode, i.e. at reactant conversions below 10%. The strongly exothermic ethylene oxidation was carried out over the CuO/Al₂O₃/Al coatings loaded in all compartments of the HTMR. The radial ($T_2-T_1$) and axial ($T_3-T_2$) temperature gradients in the HTMR were recorded as a function of the produced reaction heat (Figure 3.8). The axial and radial temperature gradients remained below 3°C in all cases. A maximum ethylene conversion of 25% was reached, which resulted in an overall heat production of 1.3 W. This is just a fraction of the heat produced by the electrical heaters (ca. 100 W). Therefore, the axial and radial temperature gradients do not depend on the heat produced in the reaction and are mainly determined by the position of the heating band (from $z = 5$ to 43 mm) relative to the interface with section VI maintained at 120°C (see Figure 3.1(e)). Thermocouple $T_3$ ($x = 0$ mm, $z = 37$ mm) was positioned at the reactor centerline close to the interface with section VI, while thermocouple $T_1$ ($z = 3$ mm, $x = 14$ mm) was positioned near the
reactor outer surface close to the flow distribution header (section I, Figure 3.1(b)). An excellent transport of the heat from the electrical heaters via the molybdenum ($\lambda = 140 \text{ W m}^{-1} \text{ K}^{-1}$) reactor walls is achieved which allows to level off both the radial and axial temperature distribution. Therefore, temperature gradients smaller than 3°C are expected between the reactor compartments during catalyst screening experiments.

### 3.3.3 Concentration distribution

**(a) Concentration distribution at process conditions**

The concentration distribution was investigated at typical process conditions for the screening of zeolitic coatings in the ammoxidation process of ethylene to acetonitrile at 425°C and a $R_{\text{cap}}$ number of 23.5 (250 ml min\(^{-1}\) He (STP)). Alternately, one compartment was loaded with four Co-ZSM-5 coatings, while the other compartments were loaded with four inert titanium plates. The Co-ZSM-5 coatings were subsequently tested at the same conditions in all eight compartments separately at steady state operation. The acetonitrile rate of formation, $r$ (in mole C\(_2\)H\(_3\)N g\(^{-1}\) s\(^{-1}\)), over the Co-ZSM-5 coatings in each compartment was analyzed in three fold, viz. three capillaries per compartment, as shown in Figure 3.9.

The parameter $\theta$ was introduced to quantify the degree of non-uniformities in the rates of reaction in the separate reactor compartments in comparison with the total average rate of reaction. The parameter $\theta$ is defined as the normalized mean square deviation from the average rate of reaction, according to the following equation,

$$\theta(\%) = \frac{100}{\bar{r}} \sqrt{\frac{\sum_{i=1}^{23} (r_i - \bar{r})^2}{23}},$$  \hspace{1cm} (3.9)
The rate of reaction (CH₃CN rate of formation in mol g⁻¹ s⁻¹) in ethylene ammoxidation over Co-ZSM-5 coatings, which were separately tested in each of the eight reactor compartments. Conditions: T = 425°C, Fᵥ = 250 mL min⁻¹, [C₂H₄], [O₂], and [NH₃] = 4 vol.% in He.

The cross talking noise, ν (in %), in the compartments of the HTMR. Compartment 3 was loaded with the active Co-ZSM-5 coatings, while the other compartments were loaded with inert titanium plates. Conditions: T = 425°C, Fᵥ = 500 mL min⁻¹, [C₂H₄], [O₂], and [NH₃] = 4 vol.% in He.

where $\bar{r}$ is the total average rate of reaction (28.5 μmol g⁻¹ s⁻¹), and $r_i$ is the rate of reaction calculated from the C₃H₅N concentration in the sampling capillary $i$. The non-uniformity in the rate of reaction was 2.3% while five-fold differences in the reaction rate ($r_i$) between different compartments were usually observed in a high-throughput screening of zeolitic coatings [33]. One can conclude that the difference in the reaction rate does not influence the screening results significantly. Furthermore, no systematic deviation in the reaction rate was observed neither between different reactor compartments nor the position of the sampling capillary in the compartment, viz. inner, outer or central position. Therefore, the deviation can be attributed to small differences both in the flow conditions and in the catalytic activity of the Co-ZSM-5 coatings.

(b) Cross talking noise in the sampling section

The CFD study [25] showed that the sampling of a product gas from a compartment without interference of gases from adjacent compartments can be obtained at iso-kinetic suction-intake by insertion of the sampling capillaries at 4 mm inside the confusor section (Figure 3.1(e)). A cross talking analysis of product gases was performed in the ethylene ammoxidation by loading the third compartment with four plates with Co-ZSM-5 coatings, while other compartments
were loaded with four inert titanium plates. The percentage of the cross talking noise, \(\nu(\%)\), in compartment \(i\) was calculated according to

\[
\nu = \frac{C_{\text{CH}_3\text{CN},i}}{C_{\text{CH}_3\text{CN},i=3}} \times 100\%,
\]

where \(C_{\text{CH}_3\text{CN},i}\) and \(C_{\text{CH}_3\text{CN},i=3}\) are the CH\(_3\)CN concentrations in compartment \(i\), and the third compartment, respectively. Without the interference of product gases from adjacent compartments, acetonitrile would only have been produced in the third compartment. However, an average cross talking noise of 2.3% over the three capillaries was obtained in the adjacent compartments 2 and 4 (Figure 3.10). The cross talking noise in the more distant first and fifth compartments was 0.5% and 0.2%, respectively. Identical results were obtained when the sampling capillaries were moved further by 2 mm inside the confusor section confirming that back diffusion of product gases is not an issue. This observation is in full agreement with the CFD results [25], also indicating that the product flow to the common reactor outlets (Figure 3.1(f)) is not disturbed by the sampling capillaries.

Since the fluid flow profile in the sampling section did not affect the cross talking noise, a detailed study was performed on the physical, metallurgical, and interfacial aspects of the separate HTMR sections. The interior microstructures were produced by electrical discharge machining in which deviations in the dimensions were obtained with an accuracy of 5 \(\mu\)m. Subsequently, a protective alumina film of 200 nm was deposited on the molybdenum surfaces by atomic layer deposition [6,24]. Assembling of the HTMR sections II, III, V and VI (Figure 3.1) was performed within an accuracy of 5 \(\mu\)m relative to each other. However, after cutting of the various parts from a molybdenum cylindrical bar, the surfaces were treated by conventional lathe machining creating a surface roughness \((R_a)\) of ca. 1.6 \(\mu\)m. Therefore, the interface between sections III and V (at \(z = 40\) mm) can be considered as a macroporous layer through which the gas molecules can easily diffuse (Figure 3.1).

The interface between sections III and V were treated with carbon paste to reduce the surface roughness. Furthermore, a metal plate was inserted in the lowest cavity of the second compartment just below the sampling capillaries \((x = 5.2\) mm, Figure 3.2) from \(z = 0\) mm to \(z = 47\) mm. In this way, the cross talking noise in the compartment was reduced from 2.3% to 0.1%. This experimental observation illustrates the importance of smooth surface finishing in micro technology [34], when interfaces cannot be avoided.
3.4 Conclusions

The CFD design results of a microreactor consisting of eight compartments for the high-throughput screening of catalytic coatings have been experimentally validated. The performance of the reactor was checked on distributions in fluid flow, temperature, and concentration in the separate reactor compartments. The flow non-uniformities in the reactor compartments remained below 2% in the range of Reynolds numbers of 6 – 113, which was analyzed by Laser Doppler Anemometry. These results were in agreement with the CFD design of the low-pressure drop flow distribution header. The temperature non-uniformity between the reactor compartments was below 3 K at a maximum heat production rate of 1.3 W in ethylene oxidation at 425°C over CuO/Al₂O₃/Al coatings. With respect to concentration gradients, a deviation from the average rate of reaction of only 2.3% was obtained at realistic process conditions in the ethylene ammoxidation process over identical Co-ZSM-5 coatings in all reactor compartments. Finally, the cross talking noise of product gases in the adjacent reactor compartments could be minimized below 0.1% according to the CFD model when (1) the sampling capillaries were positioned at least 4 mm inside the reactor compartments, (2) the gas flow profile in reactor outlets was not disturbed (iso-kinetic suction), and (3) internal leakages between reactor compartments at interfaces of separate reactor sections were negligible.

This paper illustrates the importance and relevance of proper microreactor design prior to the actual microfabrication of the reactor’s parts and their assembling. It shows that full 3D CFD design of the reactor allows for a proper evaluation of all relevant design issues (choice of reactor material, geometries, length of sampling capillaries, etc.) as well as for a detailed study of all relevant physical phenomena (flow distribution, mass and heat transport, axial dispersion, etc.). The clear advantage of CFD-based microreactor design is that it allows taking full advantage of the microscale in optimizing the reaction conditions. This paper also illustrates that a proper indepth study of the mass and heat transport taking place in the reactor provides guidelines for the actual required micromachining precision.

The results and conclusions of this paper suggest that most often it will be needed to design tailor-made microreactors for each particular application. Using off-the-shelf available parts (flow distributors, mixers, reaction compartments, etc.) for assembling a complete microreactor for a particular reaction may not provide the optimum configuration, leading to lower selectivities and yields than anticipated.
Appendix A: Corrections and uncertainty in velocity measurements

The ellipsoidal LDA measurement volume has dimensions of $1.19 \times 0.22 \times 0.22$ mm$^3$ (Figure 3.3). In order to be able to position the measurement volume as close as possible to the reactor outlets, its longitudinal axis (y-axis) was aligned in an angle $\frac{1}{2} \gamma$ with respect to the plane of the reactor outlets, with $\gamma = 15.75^\circ$ the angle between the two laser beams. As a result, the measured velocity component was not perfectly perpendicular to the outlet plane and a velocity correction had to be applied according to Eq. A1:

$$v_{\text{comp},i} = \frac{v_{\text{measured}}}{\cos \left( \frac{\gamma}{2} \right)}$$

Due to the finite dimensions of the measurement volume and the velocity gradients in the flow, not all measured particles have the same velocity. The velocity is determined as the average value over many particles and is assumed to be equal to the volume averaged velocity in the measurement volume. The uncertainty, $s$, of the local measured velocity is calculated according to equation A2:

$$s(v_{\text{comp},i}) = \frac{3\sigma}{\sqrt{N}},$$

where $\sigma$ is the standard deviation, and $N = 20,480$ is the number of measurements at that position. An additional uncertainty in the local measured velocity was caused by the deviation in the positioning of the measurement volume at the outlet of the reactor compartments in the LDA traverses along the x-axis ($z = 40$ mm). This deviation was experimentally determined at 0.03 mm. From Eq. 3.6 the uncertainties can be calculated with respect to the accuracy in positioning of the LDA measurement volume. This resulted in large uncertainties close to the walls of the compartments ($x' \approx \pm 1$, Figure 3.8), and low uncertainties at the center of the compartments ($x' \approx 0$, Figure 3.8). An example of the uncertainties caused by both the standard deviation (Eq. A1) and the deviation in positioning expressed in percentages of the local measured velocity is given in Table A.1. The total uncertainty of the values in Table 3.2 and Figure 3.7 was calculated as the square root of the squared sum of the two uncertainties per measurement position.

Table A.1 Uncertainties in the local measured velocity (in %) at Re = 64.

<table>
<thead>
<tr>
<th>LDA position, $x'$ (Figure 8)</th>
<th>0.02 mm ('center')</th>
<th>0.95 mm (close to the wall)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncertainty, $\sigma$ (%)</td>
<td>0.084</td>
<td>0.25</td>
</tr>
<tr>
<td>Uncertainty in position (%)</td>
<td>0.2</td>
<td>15</td>
</tr>
<tr>
<td>Total uncertainty</td>
<td>0.22</td>
<td>15</td>
</tr>
</tbody>
</table>
### Notations

**Roman letters**

- \(a\): separation, minimum length between two neighboring downstream reactor compartments walls, [mm]
- \(b\): offset, distance between a top wall of the first downstream reactor compartment and a side wall of the upstream channels of the thick walled screen, [mm]
- \(c\): width of the upstream channels of the thick walled screen, [mm]
- \(C_{CH_3CN,i}\): \(CH_3CN\) concentration in compartment \(i\), [vol.%]
- \(d\): height of the downstream reactor compartments, [mm]
- \(F_v\): total flow rate at STP conditions, [m\(^3\) s\(^{-1}\)]
- \(h\): distance between the neighboring upstream channels of the thick walled screen, [mm]
- \(\Delta H_r^\circ\): reaction enthalpy at 298 K, [kJ mol\(^{-1}\)]
- \(Kn\): Knudsen number, which is calculated with the following equation:
  \[
  Kn = \frac{\lambda}{L} (-), \text{ in which } \lambda (m) \text{ is the mean free path of a molecule, and } L (m) \text{ is the representative physical length scale, [-]}
  \]
- \(l_{up}\): length of the upstream channels of the thick walled screen, [mm]
- \(l_{down}\): length of the downstream compartments, [mm]
- \(L\): length of a rectangular compartment, [mm]
- \(M\): Mach number, which is calculated with the following equation:
  \[
  M = \frac{v}{a} (-), \text{ in which } v (m s\(^{-1}\)) \text{ is the fluid flow velocity, and } a (m s\(^{-1}\)) \text{ the speed of sound, [-]}
  \]
- \(M_w\): molar weight, [g mol\(^{-1}\)]
- \(N\): number of measurements, [-]
- \(Q\): total produced reaction heat, [W]
- \(r\): rate of reaction expressed as the number of produced moles of \(CH_3CN\) per catalyst weight per second, [mole g\(^{-1}\) s\(^{-1}\)]
- \(\bar{r}\): average rate of reaction in the eight HTMR compartments, [mole g\(^{-1}\) s\(^{-1}\)]
- \(Re_{cap}\): Reynolds number in inlet capillary, [-]
- \(Re\): Reynolds number, [-]
- \(s\): uncertainty in the local fluid velocity measured by LDA, [%]
- \(u_i\): area averaged velocity in the compartment \(i\) in the CFD simulation, [m s\(^{-1}\)]
- \(\bar{u}\): average flow value in the four compartments considered in the CFD simulations is calculated as follows, \(\bar{u} = \frac{1}{4} \sum u_i\), [m s\(^{-1}\)]
- \(\bar{v}_{cap}\): experimentally determined fluid velocity in the inlet capillary, [mm s\(^{-1}\)]
$v_{\text{max},i}$ maximum fluid velocity in compartment $i$ at $(x' = 0, y = 0$ in Figure 8), [mm s$^{-1}$]

$v_{\text{measured}}$ fluid velocity at the position of the LDA measurement without correction, [mm s$^{-1}$]

$V_m$ molar volume, 0.0224 [m$^3$ mol$^{-1}$]

$v_{\text{comp},i}$ corrected fluid velocity at the position of the LDA measurement in compartment $i$, [mm s$^{-1}$]

$\overline{v}_{\text{comp},i}$ average fluid velocity in compartment $i$, [mm s$^{-1}$]

$\overline{V}_{\text{comp}}$ average fluid velocity taken over all compartments, [mm s$^{-1}$]

$W$ width of a rectangular compartment, [mm]

$x$ position at the x-axis in the reactor coordinate system (Figure 1), [mm]

$x'$ position at the x'-axis in an arbitrary compartment coordinate system (Figure 7), [mm]

$x_{\text{up}}^*$ dimensionless length of the channel of the screen, [-]

$y$ position at the y-axis in the reactor coordinate system (Figure 1), [mm]

$y_{\text{CO}_2}$ mole fraction of carbon dioxide in effluent gas flow, [-]

$z$ position at the z-axis in the reactor coordinate system (Figure 1), [mm]

Greek letters

$\delta$ normalized mean square deviation from the average flow value, [%]

$\phi_{\text{z}}$ total fluid flow rate in the HTMR, [cm$^3$ s$^{-1}$]

$\gamma$ angle between the reference and the scatter laser beam in the fluid, [-]

$\eta$ dynamic viscosity, [mPa s]

$\lambda$ heat conductivity, [W m$^{-1}$ K$^{-1}$]

$\nu_i$ percentage of cross talking noise in compartment $i$, [%]

$\rho$ density, [kg m$^{-3}$]

$\sigma$ standard deviation in the LDA measurements at a single position, [-]

$\theta$ normalized mean square deviation from the average rate of reaction, [%]

Subscripts

$\text{cap}$ capillary

$\text{dwn}$ downstream channels of the screen

$i$ reactor compartment number, $1 \leq i \leq 8$

$m$ molar

$\text{slit}$ reactor compartment

$\text{up}$ upstream channels of the screen

$v$ volumetric

$w$ weight

Abbreviations

HTT high-throughput testing
HTMR  high-throughput microreactor
LDA  Laser Doppler Anemometry
TCD  Thermal Conductivity Detector
PVP  polyvinylpyrolidone

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References
Method for the \textit{In-Situ} Preparation of a Single Layer of Zeolite Beta Crystals on a Molybdenum Substrate for Microreactor Applications

This Chapter has been submitted as:


Abstract

A method for the hydrothermal synthesis of a single layer of zeolite Beta crystals on a molybdenum substrate for microreactor applications has been developed. Prior to the hydrothermal synthesis, the surface of the substrate was modified by an etching procedure which increases the roughness at the nanoscale level without complete elimination of the surface lay structure. Then, thin films of Al$_2$O$_3$ (170 nm) and TiO$_2$ (50 nm) were successively deposited by atomic layer deposition (ALD) on the substrate. The internal Al$_2$O$_3$ film protects the Mo substrate from oxidation up to 550$^\circ$C in an oxidative environment. A high wettability of the external TiO$_2$ film after UV irradiation increases zeolite nucleation on its surface. The role of the metal precursor (TiCl$_4$ and TiI$_4$), deposition temperature (300 vs. 500$^\circ$C) and film thickness (50 vs. 100 nm) was investigated to obtain titania films with the slowest decay in the superhydrophilic behavior after UV irradiation. Zeolite Beta coatings with a Si/Al ratio of 23 were grown at 140$^\circ$C for 48 h. After ion-exchange with a 10$^{-4}$ M cobalt acetate solution, the activity of the coatings was determined in the ammoxidation of ethylene to acetonitrile in a microstructured reactor. A maximum rate of reaction of 220 $\mu$mol C$_2$H$_3$N $g^{-1}$ s$^{-1}$ was obtained at 500$^\circ$C, with a carbon selectivity to acetonitrile of 42%.
4.1 Introduction

The three-dimensional large pore zeolite Beta (BEA) is now-a-days applied in a variety of catalytic gas and liquid phase processes. Important examples are the fluid catalytic cracking and dewaxing of petroleum oils [1], the alkylation and acylation of aromatics [2, 3], the isomerization of alkanes [4], the Fischer-Tropsch synthesis of iso-paraffins [5], DeNOx [6, 7], selective hydrogenations [8, 9], and the ammoxidation of light paraffins and olefins [10]. Next to these large scale processes, zeolite Beta is applied in the synthesis of fine chemicals [3]. Extrudates of zeolite Beta, consisting of zeolite crystals and a binder material, are often applied resulting in a low catalyst efficiency [11]. Application of zeolitic coatings improves the catalyst performance, as demonstrated in the case of membrane reactors [12], distillation units [13], catalytic packings [14, 15], monoliths [16], and DeNOx reactors [17].

Fast catalytic reactions involving large heat effects can be further intensified when they are carried out over zeolitic coatings with a thickness up to 5 μm, which are directly grown in the channels of a microstructured reactor, fabricated in a metal substrate [18, 19]. The highly exothermic ammoxidation of ethylene to acetonitrile over zeolite Beta coatings exemplifies such type of reactions. The large geometrical surface area of the channel walls provides a large interface area between the reactants and the coating. The absence of both binder and macropores improves mass transfer in the coating [11, 18]. Heat transfer is enhanced by the chemical bonds between the coating and the substrate, and the higher apparent density of the coating [20]. Therefore, methods have to be developed and optimized for the deposition of thin zeolitic coatings on the metal substrate. The hydrothermal synthesis method is an elegant way to grow a single layer of zeolite crystals directly in microchannels [18, 19, 21].

Molybdenum is often chosen as a substrate material for microreactor applications due to its high thermal conductivity and mechanical stability [22-24]. Above 350°C in the presence of oxygen, molybdenum oxidizes to orthorhombic MoO3 [25]. Furthermore, molybdenum dissolves during the in-situ growth of zeolitic coatings in the highly alkaline synthesis mixture [23]. Therefore, an approach for the development of Mo based (micro-)structured devices is to utilize the intrinsic properties of molybdenum through application of thin protective films on the metal surface [25-28]. Both chemical [29, 30] and structural [31, 32] properties of the substrate surface as well as its wettability are of importance for the zeolite in-situ growth. The surface roughness affects zeolite growth as well as the bonding of the zeolite crystals with the substrate. A roll casting process used for metal foil production usually produces a surface that has lay, i.e. the
predominant direction of the surface texture. Striations or peaks and valleys are usually observed on a metal foil in the direction that the tool was drawn across the surface. The presence of lay is important for hydrophilic properties of a surface.

The substrate wettability can be improved by surface treatments [33, 34] or by deposition of a hydrophilic film [23]. For example, a titania film can be made superhydrophilic (> 15 OH nm\(^{-2}\)) by UV-irradiation [35, 36]. Titania thin films, deposited by atomic layer deposition (ALD), have been the subject of extensive research [37-39] due to different applications such as fuel cells, chemical sensors, and photocatalysis. Films that were grown below 140°C had an amorphous structure, whereas a polycrystalline structure appeared at deposition temperatures above 165°C regardless of the crystallinity of the substrate [37]. Films grown above 210°C revealed a polycrystalline anatase structure for a film thickness of 15 to 55 nm. The influence of the substrate on the TiO\(_2\) film growth has been investigated on substrates including Si [40], KBr [41], soda-lime glass [42], and MgO [43]. In all cases, anatase was formed at 300°C with no preferred orientation. The deposition of ALD titania films has been primarily focused on using the metal sources titanium chloride, titanium isopropoxide, and titanium ethoxide. Water is the primary non-metal precursor used for titania growth. More recently titanium iodide has been investigated as a possible precursor [44-46]. Compared with the more common TiCl\(_4\) based ALD process, the TiI\(_4\) based process yields a growth rate about four times higher on \(\alpha\)-Al\(_2\)O\(_3\) substrates at 600°C. Furthermore, the TiI\(_4\) process was found to produce films with a higher degree of crystallinity at lower temperatures. Therefore, the advantage of TiI\(_4\) in comparison to TiCl\(_4\) seems to be its relatively easy ligand release at temperatures above 300°C. Films grown at 400 and 500°C had a mixed anatase and rutile crystal structure, with rutile being the dominant phase. Precursors and deposition techniques additionally contribute to the phase formation.

This paper is focused on the development of a method for the hydrothermal growth of zeolite Beta coatings with a thickness of a single layer of crystals on a Mo substrate. The first part of the paper describes the surface modification of the molybdenum substrate prior to the hydrothermal synthesis. Then, synthesis conditions were optimized to yield a perfectly ordered single layer of zeolite Beta crystals. Finally, the activity of the Co-zeolite Beta coatings in the ethylene ammoxidation to acetonitrile in a microstructured reactor is reported.
4.2 Experimental

4.2.1 Surface modification of the molybdenum substrate

Experiments were carried out on 10 × 10 mm² and 40 x 10 mm² molybdenum (Aldrich, 99.9+ wt.%) substrates with a thickness of 100 μm. The substrates were boiled in xylene for 1 h to remove organic contaminations, dried at 140°C for 1 h, and treated by an etching mixture containing 4.3 vol.% H₂O₂ (Fluka) and 3.6 vol.% NH₄OH (Riedel de Haën) in distilled water. Then aluminum and titanium oxide thin films were successively deposited by atomic layer deposition (ALD) on the Mo substrates. The deposition of the films was performed in a flow type reactor of 0.196 L at a pressure of about 5 mbar. Trimethylaluminium (TMA) was used as the metal precursor for the alumina film, and titanium chloride (TiCl₄) or titanium iodide (TiI₄) for the titania film. H₂O was used in all cases as the oxidant. The H₂O, TMA, TiCl₄, and TiI₄ precursors were stored in reservoirs outside the reactor at temperatures of 22, 20, 22, and 110°C, respectively. In the TMA-H₂O and TiCl₂-H₂O processes the precursor pulses of 600 ms were separated by nitrogen pulses of 1200 ms. In the TiI₄-H₂O process, the following pulse sequence was applied: TiI₄ (2500 ms) - N₂ (2500 ms) - H₂O (600 ms) - N₂ (1200 ms). 2431 cycles were required for the deposition of an alumina film of 170 nm. For the deposition of titania films of 50 and 100 nm, a number of 1111 and 2222 cycles were required, respectively. Prior to the zeolite synthesis, the substrates were UV irradiated for 3 h at room temperature in a metal box (UV lamp: Hanovia 679A-36, 450 W, λ range: 220 to 1400 nm). The TiO₂/Al₂O₃/Mo substrate will be referred to as TAMo substrate hereafter.

4.2.2 Zeolite Beta precursor gel

The silica and alumina solutions were prepared separately. The silica solution was prepared by dissolving appropriate amounts of NaCl (Merck), KCl (Merck), and tetraethylammonium hydroxide (TEAOH, 40 wt.%, Fluka) in demineralized water, after which colloidal silica (Ludox HS-40, 40 wt.% in water) was added. The silica solution was stirred for 0.5 h until the mixture was homogenized. The alumina solution was prepared by dissolving NaOH (Merck) and NaAlO₂ (0.53 wt.% Al₂O₃, 0.44 wt.% Na₂O, Riedel de Haën) in demineralized water under continuous stirring. Subsequently, the silica solution was slowly added to the alumina solution, after which the mixture was shaken vigorously to prevent the formation of a gel. The synthesis mixture was stirred at high speed (600 rpm) for 1 h at room temperature. Gels of the following oxide molar composition were prepared for the synthesis: 1.6 Na₂O : 0.93 K₂O : 11.4 (TEA)₃O : 1 Al₂O₃:46 SiO₂ : 710 H₂O : 1.8 HCl.
4.2.3 Hydrothermal treatment

Directly after the UV irradiation step, the TAMo substrate was positioned in the synthesis mixture at 20 mm below the gas-liquid interface with 10 × 10 mm² surfaces parallel to the gravity vector. The synthesis was carried out in the temperature range of 140-150°C at autogenic pressure for a time interval up to 48 h. A 50 mL PEEK insert filled with 35 mL solution was positioned in a stainless steel outer shell of the autoclave and closed. In some experiments, the bare stainless steel autoclave was preheated to 180°C to provide a rapid heating of the synthesis mixture. In the latter case, the initial heating rate was 10°C min⁻¹ [47]. The zero of synthesis time was taken as the time when the autoclave was placed in a convection oven maintained at the synthesis temperature. The syntheses were performed at static conditions. After the synthesis, the autoclave was quenched in water to room temperature. The zeolite particles from the bottom of the autoclave were filtered through a 0.22 μm filter (Millipore), washed with demineralized water, and dried for 24 h at room temperature.

4.2.4 Characterization of substrate and coatings

The substrate surface roughness (Ra) was determined by Laser Scanning Confocal Microscopy (LSCM). The digitized two dimensional (2D) surface profile (Figure 4.1(a)) was corrected for the intrinsic waviness of the substrate (Figure 1(b)). The average Ra values were determined by Eq. (4.1) from three 2D height profiles taken at three different locations on the substrate parallel to the direction of the lay of the surface,

\[ Ra = \frac{1}{L} \int_{0}^{L} |r(x)|dx , \]  

where \( r(x) \) is the difference between the absolute height and the least square mean line of the 2D surface profile at position \( x \), and \( L \) is the total length of the analyzed 2D height profile.

![Figure 4.1](image_url)  

(a) A 2D surface profile of a substrate showing the intrinsic waviness. (b) The average roughness value, \( Ra \), is calculated from the 2D profile after correction of the waviness. The \( Ra \) value is calculated from the integral of the absolute value of the roughness profile (shaded area) divided by the length \( L \) (Eq. 4.1). (c) The \( Ra \) value does not provide information about the surface roughness at the nanoscale level.
profile (Figure 4.1(b)). $R_a$ does not include information about the frequency that the height profile crosses the least squares mean line. Furthermore, $R_a$ does not include information about the roughness of the surface at the nanoscale level (Figure 4.1(c)). Therefore, a second parameter was introduced to characterize the surface roughness by taking the weight loss per area (g m$^{-2}$) after the etching procedure. For example, a substrate which lost 4 g m$^{-2}$ after etching will be referred to as $S_4$, while the initial substrate will be referred to as $S_0$.

The hydrophilicity of the films was evaluated by contact angle measurements of water on the titania films using an automatic contact angle meter (DataPhysics OCA 30 equipment) at a relative humidity of 40%. A droplet of demineralized water of 2.0 $\mu$l was dropped on the surface of the substrate. The contact angle of the water droplet with the substrate was determined with SCA 20 software before the UV irradiation and 10 and 200 min afterwards.

The weight difference of the TAMo-substrate before and the TAMo-substrate with the zeolitic coating after the hydrothermal synthesis was determined with an analytical mass balance (Mettler Toledo XS105) and was used to calculate the zeolite coverage. The Si conversion of the synthesis mixture is defined as follows:

$$Si_{\text{conversion}} = \frac{mol(Si_{\text{powder}} + Si_{\text{coating}})}{molSi_{\text{precursor}}} \times 100\%,$$  \hspace{1cm} (4.2)

where the molar amounts of $Si_{\text{powder}}$ and $Si_{\text{coating}}$, are calculated from both the as synthesized zeolite powder and coatings after correction for the amount of water, template, and cations present in the zeolite.

The synthesized coatings were examined by X-ray diffraction (XRD) for phase identification and crystal orientation. XRD data were collected on a Rigaku geigerflex diffractometer using Cu Kα radiation (1.5405 Å). XRD patterns were recorded in the range of 5 – 50° 2θ using step scanning at 0.02° 2θ per step and a counting time of 4 s for each step. The coating surface coverage and crystal morphology were examined by scanning electron microscopy (SEM) using a JEOL JSM-840A microscope and atomic force microscopy using a Spema-B scanning probe microscope with Nova RC1 software. The crystal size distribution and the average crystal size were determined from SEM images of various positions on the surface, where the total number of analyzed crystals was at least 300. The elemental composition of the coatings was analyzed by X-ray photoelectron spectroscopy (XPS) on a VG Escalab MKII spectrometer, equipped with a dual Al/Mg Kα X-ray source and a hemispherical analyzer with a five-channeltron detector. Spectra were obtained using the aluminium anode (Al Kα=1486.6 eV) operating at 250 W and a constant pass energy of 20 eV with a background pressure of 2 $10^{-9}$ mbar. Nitrogen adsorption isotherms were obtained...
Method for the *In-Situ* Preparation of a Single Layer of Zeolite Beta Crystals

on an ASAP-2020 Micromeritics instrument with a standard procedure after vacuum pretreatment at 300°C for 12 h up to a residual pressure less than 0.1 Pa. The surface area of the zeolitic coating was measured by the BET method at −196°C in the range of relative pressures of 0.001 and 0.4. The pore size distribution was obtained with the Horvath-Kawazoe method. The full pore volume was calculated from the maximum adsorption value obtained from the N₂ adsorption isotherm.

### 4.2.5 Ethylene ammoxidation reaction

The as-synthesized coatings were subjected to a post treatment procedure consisting of calcination and ion exchange steps to obtain Co(II)-zeolite Beta coatings. The sequence and conditions of the various treatments are listed in Table 4.1. XPS analysis on the coatings after the post treatment resulted in a Si/Al ratio and Co/Al ratio of approximately 23 and 0.5, respectively.

The reaction was carried out in a molybdenum plate-type microreactor. Four coated TAMo substrates with dimensions of 40 × 10 × 0.1 mm³ were positioned in parallel inside the reactor compartment with a distance of 350 μm from each other. The reactor was operated in the differential mode [22]. Blank experiments were carried out on inert titanium plates to exclude the contribution of the reactor material to reactant conversion. A total catalyst weight of 0.0018 g was applied for the reaction. The Co-Beta coatings were pretreated in a helium flow of 33 mL min⁻¹ for 1 h at 530°C. Subsequently, the reactor temperature was decreased to the desired value, and the reactant mixture was introduced at a flow rate of 33 mL min⁻¹ (STP) with a composition of ethylene (2 vol.%), ammonia (2 vol.%),

<table>
<thead>
<tr>
<th>Table 4.1</th>
<th>Overview of the post-treatment steps used for coating activation</th>
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<tbody>
<tr>
<td>Step no</td>
<td>Process</td>
</tr>
<tr>
<td>1</td>
<td>water rinse</td>
</tr>
<tr>
<td>2</td>
<td>ultrasonic treatment</td>
</tr>
<tr>
<td>3</td>
<td>drying</td>
</tr>
<tr>
<td>4</td>
<td>calcination</td>
</tr>
<tr>
<td>5</td>
<td>calcination</td>
</tr>
<tr>
<td>6</td>
<td>ion-exchange</td>
</tr>
<tr>
<td>7</td>
<td>water rinse</td>
</tr>
<tr>
<td>8</td>
<td>drying</td>
</tr>
<tr>
<td>9</td>
<td>calcination</td>
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<td>calcination</td>
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<td>14</td>
<td>calcination</td>
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and oxygen (2 vol.%), balanced by helium. The reaction rate and product selectivity were determined at steady state conditions in the temperature range of 350 – 500°C, with a 1 h dwell at each temperature. The concentration of the components in the effluent gas was analyzed with an online Varian micro-GC (CP-4900), equipped with TCD detectors. Helium was used as a carrier gas. The analysis time was 80 s for each injection. N₂, O₂, CH₄, NO and CO were analyzed on a molsieve 5A column (0.25 mm ID, 10 m) operated at 175°C and 350 kPa. C₂H₄, C₃H₆, CO₂, NH₃ and H₂O were analyzed on a poraPLOT-U column (0.25 mm ID, 10 m) operated at 65°C and 200 kPa. CH₃CN and CH₃OH were analyzed on a poraPLOT-U column (0.25 mm ID, 10 m) operated at 175°C and 150 kPa. The carbon and nitrogen mass balances were closed within 95%. However, the carbon balance was only closed if the assumption was made that methanol was formed in equimolar amounts with another C₁ containing component (product Y), which could not be analyzed separately with the micro-GC applied.

The reaction rate is expressed either in terms of the acetonitrile formation rate per gram of zeolite per second or in terms of the turn-over frequency per single Co atom (TOF, s⁻¹). Carbon selectivity (Sᵢₖ) to a carbon containing product Pᵢ, and nitrogen selectivity (Sⱼₙₙ) to a nitrogen containing product Pⱼ, are defined as:

\[
Sᵢₖ = \frac{yᵢₖ \cdot nᵢₖ}{\sum_i yᵢₖ \cdot nᵢₖ} \cdot 100\% \tag{4.3}
\]

\[
Sⱼₙₙ = \frac{yⱼₙₙ \cdot mⱼₙₙ}{\sum_j yⱼₙₙ \cdot mⱼₙₙ} \cdot 100\% \tag{4.4}
\]

where \(yᵢₖ\) and \(yⱼₙₙ\) are the molar fractions, and \(nᵢₖ\) and \(mⱼₙₙ\) are the number of carbon and nitrogen atoms in the product molecule, respectively.

### 4.3 Results and discussion

#### 4.3.1 Effect of surface roughness on coverage

The surface roughness of the substrate was increased by a chemical etching procedure (Table 4.2). The LSCM scans of the TAMo substrates (S₀, S₄, S₅₅, S₁₂₀) prior to the synthesis are shown in Figures 4.2(a, c, e, g), respectively. The corresponding SEM images of the as synthesized zeolite Beta coatings are shown in Figures 4.2(b, d, f, h). After the synthesis, there are still uncovered areas present on the non-treated substrate S₀, which has a constant waviness profile obtained in a roll casting process. A closed layer of zeolite Beta crystals was obtained on S₄,
Figure 4.2  LSCM scans (scan area is $320 \times 320 \mu m^2$) of the TAMo substrates (a) $S_0$, (c) $S_4$, (e) $S_{55}$, and (g) $S_{120}$ (Table 4.1) and the corresponding scanning electron micrographs of the as synthesized zeolite Beta coatings (b, d, f, and h, respectively). The black arrows in the LSCM scans indicate the direction of the lay of the Mo foil parallel to which the 2D height profiles were digitized for the determination of the $R_a$ value. Synthesis conditions; $T$: 150°C, $t$: 30 h, heating rate: 10°C min$^{-1}$.

which has a similar surface roughness but a different surface morphology. Substrate $S_4$ was modified by a mild etching treatment only at the nanoscale level, which does not influence $R_a$ (Figure 4.1(c)). The zeolite coverage was increased by 35%, which is attributed to the increased number of surface irregularities. It was
Figure 4.3 Illustrations of the cross sections of the two dimensional surface profiles of the zeolite Beta coatings on a Mo substrate. Panel (a) shows the surface profile of the substrates $S_0$ or $S_4$, on which a single layer of zeolite Beta crystals (average crystal size is 1.5 $\mu$m) are visible (compare Fig. 4.3(a) with Figs. 4.2(a-d)). Panel (b) shows the surface profile of substrate $S_{120}$ (Table 4.2) with a $R_s$ value of 90 nm, consisting of large pockets in which zeolite Beta crystals can be deposited on top of each other (compare Fig. 4.3(b) with Figs. 4.2(g and h)).

shown that formation of silicalite-1 and zeolite Y was improved on a plastically deformed or mechanically destroyed copper substrate because of the higher number of surface imperfections, which are supposed to be nucleation centers for zeolite crystals [31, 32]. It is expected that surface irregularities are far more homogeneously distributed over the surface after chemical etching as compared to a mechanical surface treatment. Compared to $S_0$, $S_4$ has also a higher surface energy which is favorable for anchoring of small crystals. The average diameter of zeolite crystals is 1.5 $\mu$m. It is characteristic of $S_0$ and $S_4$ morphology that the difference in altitude between the highest and lowest points amounts 1.3 $\mu$m in the direction perpendicular to lay. This is less than the mean diameter of a zeolite crystal of 1.5 $\mu$m (see Figure 4.3(a)).

Substrates $S_{55}$, and $S_{120}$ were subjected to more severe etching treatments (Table 4.2), which resulted in an increased surface roughness (Figures 4.2(e, g)). For $S_{55}$ and $S_{120}$, the maximum difference between the top and bottom part of the substrate surface of 2.0 and 2.9 $\mu$m, respectively, is larger than the average diameter of the zeolite crystals. Therefore, the second layer of zeolite crystals can be deposited on top of the crystals located in the substrate pockets as schematically
shown in Figure 4.3(b). Thus, in order to obtain a single layer of zeolite crystals, the surface morphology has to contain a large number of imperfections, while the available pockets should not exceed the size of the crystals.

### 4.3.2 Effect of surface hydrophilicity on coverage

The alumina and titania films were successively deposited by ALD [27, 48]. The inner alumina film consists of a non-porous amorphous phase, which protects the substrate from oxidation in an oxygen containing mixture [22]. No reflections from molybdenum oxides were observed in the XRD patterns of a Mo substrate coated with a 170 nm thin alumina film after 10 h in an air-water mixture at 550°C (Figure 4.4(b)). The density of the alumina film of 3.5 g cm⁻³ is slightly lower than for α-Al₂O₃ (3.97 g cm⁻³), whereas their surface properties are reported to be

![Figure 4.4 XRD patterns of substrates after various surface modifications and treatments; (a) molybdenum (Mo) substrate, (b) Al₂O₃ (170 nm)/Mo substrate after 10 h of oxidation in an air/water (2.3 vol.%) mixture at 550°C, (c) TiO₂ (50 nm)/Al₂O₃ (170 nm)/Mo substrate (TAMo substrate). The reflections of the crystalline phases Mo (■), and anatase TiO₂ (●) are indicated in the figure.](image)
similar [27]. Because the alumina film contains less than 1 OH group per nm² [33], an outer titania film was deposited to increase the surface wettability of the substrate [34].

The deposition temperature, the film thickness, and the nature of the titanium precursor (TiCl₄ and TiI₄) were varied to obtain an optimal hydrophilicity of the TiO₂ film after UV irradiation (Table 4.3). The difference between the thermal expansion coefficient of film and substrate has to be as small as possible to avoid crack formation. For the same reason, thinner films are more preferred [49]. The highest temperature in the zeolite post treatments is 500°C. Therefore, the ALD films should preferably be deposited at this temperature. Prior to the UV treatment, the lowest water contact angle of 44° was observed for a film of 50 nm deposited at 500°C from the TiCl₄ precursor. This film has a low density of surface OH groups because of thermal dehydroxylation of the surface resulting in a rather hydrophobic surface at this temperature. After the UV irradiation, superhydrophilic behavior (contact angle < 5°) was observed for all samples. The films obtained from TiCl₄ at 300°C remained superhydrophilic for at least 200 min while those obtained at 500°C showed a slight increase of the contact angle. One may conclude that the deposition temperature and the film thickness do not influence the performance of the films obtained in the TiCl₄-H₂O ALD process. However, the films obtained from TiI₄ became much more hydrophobic, especially those deposited at 500°C. This may be due to the different structure of the films. Both hydroxyl groups and chlorine ions can be easily incorporated in the film structure when TiCl₄ is used as a metal precursor. The TiI₄ process is faster comparing with the TiCl₄ one due to relatively easy ligand release at temperatures above 300°C. Therefore, the TiI₄ process produces films with a higher degree of epitaxy and with a lower content of the bulk OH groups. However, the uniform films obtained in the TiI₄ process show a fast decay in hydrophilicity. This effect is

### Table 4.3: ALD parameters and water contact angle on the TAMo substrates

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Thickness nm</th>
<th>Pretreatment/Titania precursor/Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>No UV</td>
</tr>
<tr>
<td>300</td>
<td>50</td>
<td>59 ± 3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>68 ± 9</td>
</tr>
<tr>
<td>500</td>
<td>50</td>
<td>44 ± 8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>77 ± 7</td>
</tr>
</tbody>
</table>

a  $R_a = 13$ nm (S0 from Table 4.1)
b  Time between UV treatment and contact angle analysis. TAMo substrates were positioned perpendicular ($\perp$) to the UV source; parallel ($=)$ values are given in the brackets.
c  Contact angle values below 5° can not be analyzed accurately.
especially pronounced at 500°C. Therefore, TiCl₄ was chosen as an ALD precursor for deposition of 50 nm titania films at 500°C. At these conditions, the anatase structure with the (101) plane as the predominant plane of crystallization has been identified as the main phase (Figure 4.4(c)). The anatase structure was also obtained on a silicon substrate at a deposition temperature of 500°C [48]. However, minor phases of rutile may be present, which could not be identified due to the thin layer of only 50 nm.

The growth of zeolite Beta coatings at 150°C is remarkably enhanced by the superhydrophilicity of the TAMo substrate. A TAMo substrate without UV irradiation has a coverage of ca. 50% of a single crystal layer (Figure 4.5(a)), while the UV irradiated substrate was completely covered with a single layer of zeolite Beta crystals after a synthesis time of 16 h (Figure 4.5(b)). The increased hydrophilicity of the substrate resulted in a better compatibility with the precursor gel. The zeolite crystals in the coating evolved from an amorphous gel layer, which was initially attached to the surface of the substrate [47]. The gel phase is still partly visible in Figure 4.5(b). Zeolite Beta crystals were firmly attached to the substrate due to the increased number of defect sites and hydroxyl groups on the TiO₂ surface. This clearly demonstrates that the wettability of the surface of the TAMo substrates influenced the zeolite Beta coating properties. Similar findings were reported in a study on the improvement of zeolite NaA nucleation sites on (001) rutile by means of UV-radiation [34].

### 4.3.3 In-situ synthesis of a single layer of zeolite Beta crystals

The crystallization period of zeolite Beta takes from 20 h to several weeks depending on the synthesis conditions [47, 50-52]. Zeolite Beta was obtained after 20 h from a Na, K and TEAOH containing precursor gel with a SiO₂/Al₂O₃ ratio of 50 and a temperature of 135°C [51]. Therefore, this recipe was taken as a good starting point for further optimization. In this study, the synthesis temperature was

\[\text{Figure 4.5} \quad \text{Scanning electron micrographs of zeolite Beta coatings without (a) and after (b) a UV irradiation procedure of the TAMo substrate (Sts, Table 4.2). Conditions; } T: 150°C, t: 16 \text{ h, heating rate: } 1°C \text{ min}^{-1}.\]
increased to 140-150°C, and silica sol was used as a reactive silica source to obtain higher nucleation and crystallization rates.

A single layer of zeolite Beta crystals on a substrate with a surface roughness of 14 nm corresponds to a zeolite coverage of 1.0 – 1.3 g m\(^{-2}\) depending on the average crystal size. A single layer of zeolite Beta crystals was obtained after 48 and 26 h at 140 and 150°C, respectively (Figure 4.6). Correspondingly, the induction period decreased from 30 to 24 h. Increasing the reaction temperature from 140 to 150°C, the crystallization rate increased with a simultaneous increase in the average crystal size from 0.82 (Figure 4.7(a)) to 1.57 μm (Figure 4.7(b)) while a narrow unimodal crystal size distribution (CSD) was preserved. The narrow CSD indicates that the crystals were grown from a gel layer initially deposited at the surface of the substrate. Initially, all crystals grew fast due to the very high concentration of nutrients both in the gel layer and in the liquid phase. The crystal growth rate reduced fast as the concentration of the nutrients was depleted in the gel layer in the course of the crystallization. Therefore, zeolite crystals with the same size at the end of the crystallization could be formed at different nucleation times and pass different crystal growth periods [47]. The zeolite Beta crystal size can be further
Figure 4.8 Scanning electron micrographs (a and c) and the corresponding AFM scans (scan area is 10 \times 10 \, \mu m^2) (b and d) of zeolite Beta coatings (a.s.) obtained at 140°C after 48 h (a and b), and 150°C after 30 h (b and d). Close-up SEM images of the coatings are shown in the insets (scale bar indicates 10 \, \mu m). See the caption of Figure 4.6 for the conditions.

decreased by a reduction of both the crystallization temperature [50] and the concentration of alkali cations, especially potassium [53].

Figures 4.8(a, c) show SEM images of the zeolite Beta coatings obtained at 140 and 150°C after 48 h and 30 h, respectively. The SEM inset (Figure 4.8(a)) and the AFM scan (Figure 4.8(b)) illustrate the perfectly closed single layer of well–arranged zeolite Beta crystals on the TAMo substrate at 140°C. At 150°C the sharp increase in coverage after 24 h (Figure 4.6) reduced the duration of the period (between 25 and 27 h of synthesis) to quench the crystallization process where the coverage (1 – 1.3 g m⁻²) corresponds to a single layer of crystals. After 30 h there are already some crystals present on top of the coating (Figure 4.8(c)). Moreover, in a synthesis after rapid heating (10°C min⁻¹) of the synthesis mixture at 150°C, the zeolite Beta coating consists already of two layers [48]. The inner layer, consisting of relatively small crystals, was grown directly on the surface at the substrate/gel interface, while the visible outer layer of larger crystals was crystallized into the gel layer starting from the gel/liquid interface. The AFM scan (Figure 4.8(d)) shows a more roughened coating morphology compared to the coating obtained at 140°C (Figure 4.8(b)). The crystal morphology seems to be
independent on the reaction temperature. At both temperatures, the crystals do not have a well-defined crystal habit, but appear to be roundly shaped. Some sharp edges or terraces can be observed on the large zeolite Beta crystals obtained at 150°C. The zeolite Beta coating thickness could be increased up to approximately 4 μm by repetition of the synthesis procedure at 150°C (Figure 4.6). A continuous coating with a rough morphology was obtained (Figure 4.9(a)). The SEM image in Figure 4.9(b) shows the cross section of the coating.

Zeolite Beta was the only crystalline phase present in the coatings. Some selected XRD results of the coatings are presented in Figures 4.10(d–f). The XRD patterns correspond well with the reference patterns of as-synthesized and calcined zeolite Beta powder (Figures 4.10(a, b)), which were obtained from a similar precursor gel composition as used in this study [43].

![Figure 4.9](image)

**Figure 4.9**  Scanning electron micrographs of (a) the surface and (b, tilting angle = 75°) the cross section of the zeolite Beta coating obtained after a repeated synthesis at 150°C (see also Figure 4.6). The layer thickness of the coating is approximately 4 μm. See the caption of Figure 4.6 for the synthesis conditions.

![Figure 4.10](image)

**Figure 4.10**  Reference XRD patterns of (a) as synthesized zeolite Beta powder [54] and (b) calcined zeolite Beta powder [54], and (c) of the TAMo substrate. XRD patterns of zeolite Beta coatings; (d) as synthesized, 150°C, 48h, (e) calcined, 150°C, 48h, and (f) repeated synthesis, as synthesized, 140°C, 48h.
faulting is often observed in the zeolite Beta structure [2]. The broad peak from both the (100) and (101) reflections in the $6 - 8^\circ$ 20 range indicates that polymorph A and polymorph B are approximately equally distributed in the BEA structure [55, 56]. Besides the (100) and (101) reflections, the XRD pattern from the coatings contain strong reflections with (hkl) values equal to (205), (302), (304), and (306). The zeolite Beta crystals in the coating have a preferred orientation, since the reflections from the crystallographic planes parallel to the crystallographic c-axis are not present in the XRD pattern (cf. the XRD patterns of Figures 4.10(a, d) of as-synthesized zeolite Beta powder and coating, respectively), while the (201) reflection is clearly visible (cf. the XRD patterns of Figure 4.10(b and e) of calcined zeolite Beta powder and coating, respectively). A repeated synthesis at 140°C resulted in a multilayer of zeolite Beta crystals. Figure 4.10(f) shows the XRD pattern of this as synthesized coating, in which the (008) reflection is visible. Apparently, the preferred orientation of crystals disappears when they grow or are deposited on top of the first layer of crystals on the TAMo substrate.

4.3.4 Activity of Co-Beta coatings in ethylene ammoxidation

Co-zeolite Beta coatings were prepared from the as synthesized zeolite Beta coatings with a Si/Al ratio of 23 via a series of calcination and ion exchange treatments (Table 4.1). A Co/Al ratio of 0.5 was obtained in the coatings after an ion exchange with $10^{-4}$ M aqueous cobalt acetate solution. The Co-zeolite Beta coatings were tested in a plate type microreactor in the highly exothermic ethylene ammoxidation. A maximum rate of acetonitrile formation of 220 $\mu$mol g$^{-1}$ s$^{-1}$ was reached at 500°C (Figure 4.11). Bare Co$^{2+}$ cations, balanced by two adjacent aluminum atoms in the zeolite framework, are the most active sites in the ammoxidation process [57, 58]. Thus, higher rates of reaction can be obtained when

![Figure 4.11](image)

**Figure 4.11** Activity and product selectivity of the Co-zeolite Beta coating (Si/Al = 21, Co/Al = 0.5) as a function of the reaction temperature. Product Y denotes an unknown C$_1$ containing product, most likely HCN. The coatings were tested at a total flow rate of 33 mL min$^{-1}$ (STP) consisting of 2 vol.% of ethylene, 2 vol.% ammonia and 2 vol.% oxygen, He-balance.
the aluminium content in the zeolite Beta framework is increased. At a Si/Al ratio of 23, the number of aluminium pairs in the zeolite Beta topology is approximately 30% of the total number of aluminium atoms, while approximately 80% is reached at a Si/Al ratio of 13 [59, 60].

The highest C-selectivity ($S_C$) to acetonitrile was only 42% which is two times lower than that reported over Co-Beta zeolite pelleted catalysts with a Si/Al ratio of 12 [62]. Furthermore, methanol was formed on the coatings with a selectivity of 20% at 500°C, which was not observed as a product on pelleted Co-Beta catalysts. In the presence of water, methanol can be formed on two adjacent bivalent cations [63]:

$$\text{CH}_3\text{CN} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCN}$$

A constant N-selectivity ($S_N$) to nitrogen of 80% was obtained confirming selective oxidation of ammonia at the applied reaction conditions. Recently we showed that indeed higher rates of reaction are obtained over zeolitic Beta coatings with a Si/Al ratio of 15 compared to Co-Beta zeolite pelleted catalysts because of the absence of transport limitations in the coatings [61].

### 4.4 Conclusions

A method was developed for the in-situ synthesis of zeolitic coatings on a metal substrate for application in a microstructured reactor. The method is exemplified in Figure 4.12 for the in-situ growth of a single layer of zeolite Beta crystals on a molybdenum (Mo) substrate. First the number of surface irregularities on the substrate was increased by a chemical etching procedure (step 1) to enhance both the number of nucleation sites and positions for zeolite crystals for anchoring. For a single layer of zeolite Beta crystals with a crystal size in the range of 0.5 – 1.5 μm a low surface roughness of 14 nm was required. Then, two thin films of Al$_2$O$_3$ (170 nm, step 2) and TiO$_2$ (50 nm, step 3), respectively, were successively deposited by atomic layer deposition (ALD) on the substrate. The internal Al$_2$O$_3$ film protects the Mo substrate from oxidation up to 550°C in an oxidative environment. A high wettability of the external TiO$_2$ film after UV irradiation increases zeolite nucleation at its surface. A stable superhydrophilic TiO$_2$ surface (water contact angle below 5°) for at least 200 min was obtained after deposition of a 50 nm film at 500°C from a TiCl$_4$ precursor. A perfectly ordered single layer of zeolite Beta crystals was obtained from a viscous Na, K, and TEAOH precursor gel with a SiO$_2$/Al$_2$O$_3$ ratio of 46 at a synthesis temperature of 140°C after 48 h (step 4).
Method for the In-Situ Preparation of a Single Layer of Zeolite Beta Crystals

The Co-Beta coatings (Si/Al = 23, Co/Al = 0.5) were tested in the ammoxidation of ethylene to acetonitrile in a microstructured reactor. A maximum rate of reaction of 220 μmol C₂H₃N g⁻¹ s⁻¹ was obtained at 500°C, with a carbon selectivity to acetonitrile of 42%. Higher rates of reaction can be obtained when the aluminum content in the zeolite Beta coating is increased.

Acknowledgements

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References

Method for the In-Situ Preparation of a Single Layer of Zeolite Beta Crystals

Optimization of Synthesis Parameters Affecting the Growth of Continuous Zeolite Beta Coatings in a Range of Si/Al Ratios

This Chapter has been submitted as:

Abstract
Highly crystalline zeolite Beta coatings in a range of Si/Al ratios of 10 – 25 were synthesized on a molybdenum substrate by hydrothermal synthesis. The average thickness of the coatings was ca. 2 μm corresponding to a coverage of 2.5 g m⁻². The coatings were obtained from a viscous Na, K, and TEAOH containing aluminosilicate precursor mixture with silica sol as reactive silicon source. A mechanism for the in-situ growth of zeolite Beta coatings is proposed. According to this mechanism, the deposition of an amorphous gel layer on the substrate surface in the initial stage of the synthesis is an important step for the crystallization of continuous zeolite Beta coatings. The heating rate of the precursor mixture and the synthesis temperature were optimized to control the level of supersaturation and to stimulate the initial formation of a gel layer. Coatings with a low Si/Al ratio of 15 were obtained at 140°C, while coatings with a higher Si/Al ratio required synthesis at 150°C.
5.1 Introduction

Zeolite thin coatings are of interest for use as catalysts [1-4], adsorbents [5, 6], and membranes [7]. Advantages of zeolite coatings compared to zeolite pellets or extrudates are an improved accessibility of the crystallites as well as the catalyst sites, an effective heat removal from the reaction zone via a metal substrate, and the absence of macropores in a single layer of crystals. The past decade has seen significant advances in the ability to synthesize different types of coatings with ordered structures from a wide range of different precursors. This has resulted in materials with unusual properties and broadened their application range towards sensors [8], host materials to integrate molecular electronics and other molecular devices within their frameworks [9]. As better and more diverse preparation protocols of zeolite structures become available, an increasing number of porous materials are likely to find use in applications not traditionally associated with such materials. The recent demonstrations of heteroepitaxial zeolite growth [10] and the deposition of nanoscale layers of the BEA type with a low dielectric constant [11] are only a few promising examples of developments that could lead to new device applications. Furthermore, the application of thin zeolite coatings in structured reactor types can be of interest from a catalytic point of view. Zeolite Beta is applied, for example, as a solid acid catalyst in the alkylation of benzene with ethylene or propylene [12]. It also shows an exceptional redox activity of the exchanged transitional metal ions at a Si/Al ratio above 10 [13]. It is likely that ion-exchanged zeolite Beta and other microporous materials will increasingly find new applications in catalysis [14-16]. For such applications, crystalline structures containing pores in the size range of above 0.6 nm and exhibiting thermal and hydrothermal stability are highly desirable, especially if the pore system is more than one-dimensional. An even more intensified contacting of the reactants with zeolite coatings can be obtained in microstructured reactors, which showed promising results in a series of different applications [17].

The zeolite growth on a substrate involves a complex interaction between the precursor mixture and the support, which depends strongly on the gel composition, the synthesis conditions, and the roughness and hydrophilicity of the substrate surface [18, 19]. Crystal size is a function of the ratio between the rate of nucleation and the rate of growth. Both rates increase with supersaturation, but the exponential law of the nucleation rate rises more sharply than a low-order power law of the growth rate [20-22]. As a consequence, smaller crystals and rapid syntheses are observed at a high supersaturation. At lower supersaturation the growth is favored at the expense of nucleation. The choice of the silica or alumina starting material can influence the size and morphology of zeolite crystals. More reactive silicon sources, for example silica sol, will provide a supersaturated
solution very rapidly and thus the formation of many nucleation sites simultaneously increasing the crystallization rate [23-25].

To increase the coating thickness, the synthesis conditions have to be chosen such that nucleation and crystallization are favored at the substrate surface and the rate of exhaustion of the nutrients in the bulk phase is minimized. Several parameters (alkalinity, ionic strength, dilution, and temperature) influence the silicate and aluminate solubility, and thus the concentration levels in the synthesis system. Furthermore, the presence of an amorphous gel also affects diffusion processes, which is especially of importance for the transport of nutrients to the substrate surface. Stirring of the zeolite synthesis mixture effectively modifies the crystallization kinetics [19]. Nucleation can be affected by other procedures, like aging of the synthesis medium, seeding, and selective crystallization poisoning. Potassium is well known to act as a crystallization poison for zeolite Beta [26].

This paper is focused on the preparation of thin coatings of zeolite Beta with Si/Al ratios in the range of 10 to 25 by hydrothermal synthesis. Synthesis conditions such as temperature and heating rate are optimized for a specific Si/Al value. The effect of rapid heating of the synthesis mixture has been studied as it strongly affects the level of supersaturation. Furthermore, a growth mechanism for the evolution of silicon-rich zeolite Beta coatings (Si/Al ratio > 10) is proposed. According to this mechanism, an amorphous gel layer is deposited at the surface of the substrate, which plays a crucial role in growth and properties of the crystalline zeolite Beta coatings.

5.2 Experimental

5.2.1 Zeolite Beta precursor gel

The silica and alumina solutions were prepared separately. The silica solution was prepared by dissolving appropriate amounts of NaCl (Merck), KCl (Merck), and tetraethylammonium hydroxide (TEAOH, 40 wt.%, Fluka) in demineralized water, after which colloidal silica (Ludox HS-40, 40 wt.% in water) was added. The silica solution was stirred for 30 min until the mixture was homogenized. The alumina solution was prepared by dissolving NaOH (Merck) and NaAlO$_2$ (0.53 wt.% Al$_2$O$_3$, 0.44 wt.% Na$_2$O, Riedel de Haën) in demineralized water under continuous stirring. Subsequently, the silica solution was slowly added to the alumina solution, after which the mixture was shaken vigorously to prevent the formation of a gel. The zeolite Beta synthesis mixture was stirred at high speed (600 rpm) for 1 h at room temperature. Gels of the following oxide molar composition were prepared for the synthesis: $46 \text{SiO}_2 : x \text{Al}_2\text{O}_3 : 11.4 (\text{TEA})_2\text{O} : (0.88 + 0.68x) \text{Na}_2\text{O} : 0.93 \text{K}_2\text{O} : 1.8 \text{HCl} : 710 \text{H}_2\text{O}$. The SiO$_2$/Al$_2$O$_3$ ratio was varied from
Chapter 5

24 to 46 (corresponding to Si/Al ratio of 12 - 23) by changing the alumina content ($x$) from 1.92 to 1. The ratio of $(K + Na)/SiO_2$ was varied from 0.054 to 0.068, and that of $K/(K + Na)$ from 0.30 to 0.37. The OH-/SiO_2, H_2O/SiO_2 and (TEA)_2O/SiO_2 ratios were kept constant at 0.45, 15.4 and 0.25, respectively.

5.2.2 Substrate modification

The experiments were carried out on $10 \times 10 \text{ mm}^2$ surface modified molybdenum (Mo, Aldrich, 99.9+ wt.%) substrates with a thickness of 100 $\mu$m. The substrates were boiled in xylene for 1 h to remove organic contaminations, dried at 140°C for 1 h, and treated by an etching mixture containing 4.3 vol.% H_2O_2 (Fluka) and 3.6 vol.% NH_4OH (Riedel de Haën) in distilled water to increase the surface roughness ($R_a$) to either 14 or 45 nm [18]. This is followed by atomic layer deposition (ALD) of a 170 nm Al_2O_3 film from Al(CH_3)_3 and water to prevent high temperature oxidation of the metal surface. A 50 nm TiO_2 layer was subsequently deposited on top of the alumina layer by ALD from TiCl_4 and water to reach better adhesion of the coatings to the substrate surface. Just before the zeolite synthesis, the titania layer was made super hydrophilic (> 15 OH groups nm$^{-2}$) by an UV treatment for 3 h at 20°C in a metal box (UV lamp: Hanovia 679A-36, 450 W, $\lambda$ range: 220 to 1400 nm) (c.f. details [18]). The Titania-Alumina-Molybdenum substrate will be referred to as TAMo-substrate hereafter.

5.2.3 Hydrothermal treatment

Directly after the UV irradiation step, the TAMo substrate was positioned in the synthesis mixture at 20 mm below the gas-liquid interface with the 10x10 mm$^2$ surfaces parallel to the gravity vector. The synthesis was carried out in the temperature range of 140-150°C at autogenic pressure for a time interval up to 48 h. A 50 mL PEEK insert filled with 35 mL solution was positioned in a stainless steel outer shell of the autoclave and closed. The heating of the precursor gel to the synthesis temperature was performed at initial heating rates of 1, 5, and 10°C min$^{-1}$, which will be referred to in the text as slow, moderate, and rapid heating, respectively. The bare stainless steel autoclaves were preheated to either 110 or 180°C to obtain initial heating rates of 5 or 10°C min$^{-1}$, respectively. The zero of synthesis time was taken as the time when the autoclave was placed in a convection oven maintained at the synthesis temperature. The syntheses were performed at static conditions. After the synthesis, the autoclave was quenched in water to room temperature. The composite samples were rinsed with demineralized water followed by a treatment in an ultrasonic bath (60 kHz, 120 W) for 1 h. Finally the samples were dried at 110°C overnight and calcined. During the calcination the coatings were positioned in an airflow of 50 mL min$^{-1}$ and the temperature was increased to 295°C with a heating rate of 1°C min$^{-1}$. At the end of
the dwell period of 2 h, the air flow was substituted by a helium flow and the temperature was increased to 500°C with a heating rate of 1°C min⁻¹ which was followed by another dwell interval of 2 h. The zeolite particles, which were obtained in the liquid phase, were filtered from the suspension (filters were obtained from Millipore with a pore size of 0.22 μm), washed with demineralized water, and dried for 24 h at room temperature.

5.2.4 Coating characterization

The weight difference of the TAMo-substrates before and the TAMo-substrate with the zeolitic coating after the hydrothermal synthesis was determined with an analytical mass balance (Mettler Toledo XS105) and was used to calculate the zeolite coverage. The Si conversion of the synthesis mixture is defined as follows:

$$\text{Si}_{\text{conversion}} = \frac{\text{mol}(\text{Si}_{\text{powder}} + \text{Si}_{\text{coating}})}{\text{molSi}_{\text{precursor}}} \times 100\%$$

(5.1)

where the molar amounts of $\text{Si}_{\text{powder}}$ and $\text{Si}_{\text{powder}}$, are calculated from both the as synthesized zeolite powder and coatings after correction for the amount of water, template, and cations present in the zeolite.

The synthesized coatings were examined by X-ray diffraction (XRD) for phase identification and crystal orientation. XRD data were collected on a Rigaku geigerflex diffractometer using Cu Kα radiation (1.5405 Å). XRD patterns were recorded in the range of 5 – 50° 2θ using step scanning at 0.02° 2θ per step and a counting time of 4 s for each step. The coating surface coverage and crystal morphology were examined by scanning electron microscopy (SEM) using a JEOL JSM-840A microscope. The average crystal size was determined from SEM images of various positions on the surface, where the total number of analyzed crystals was at least 300. The elemental composition of the coatings was analyzed by X-ray photoelectron spectroscopy (XPS) on a VG Escalab MKII spectrometer, equipped with a dual Al/Mg Kα X-ray source and a hemispherical analyzer with a five-channeltron detector. Spectra were obtained using the aluminum anode (Al Kα = 1486.6 eV) operating at 250 W and a constant pass energy of 20 eV with a background pressure of 2 × 10⁻⁹ mbar. Nitrogen adsorption isotherms were obtained on an ASAP-2020 Micromeritics instrument with a standard procedure after vacuum pretreatment at 300°C for 12 h up to a residual pressure <0.1 Pa. The surface area of the zeolitic coating was measured by the BET method at −196°C in the range of relative pressures within 0.001 and 0.4. The pore size distribution was obtained with the Horvath-Kawazoe method. The full pore volume was calculated from the maximum adsorption value obtained from the N₂ adsorption isotherm.
All coatings are referred to as C-xxx(Si/Al)-a-b according to the major zeolite phase present (xxx – three-letter abbreviation of the zeolite type), Si/Al ratio, synthesis temperature (a, °C), initial heating rate (b, °C min⁻¹). For example, a zeolite Beta coating with a Si/Al ratio of 23 obtained at 150°C at a heating rate of 5°C min⁻¹ will be referred as C-BEA(23)-150-5, while the corresponding precursor gel will be referred to as G-23-150-5 hereafter.

5.3 Results

5.3.1 Effect of Si/Al ratio and synthesis temperature on coating morphology

The gel composition with a Si/Al ratio in the range of 12–23 adapted from [27] was used as starting point for optimization of the synthesis procedure for zeolite Beta coatings. Silica sol was used as silica source instead of TEOS to accelerate the nucleation and crystallization rates [25]. The XRD patterns of the coatings obtained at 140 and 150°C are depicted in Figures 5.1(a, b), respectively. The patterns of the BEA [28], MER (Merlinoite) [29] type zeolite structures, and the TAMo substrate are given for comparison. The coatings obtained at 140°C from the gel with Si/Al ratios from 15 to 23 and at 150°C from the gel with Si/Al ratios of 20 and 23 showed very intensive Bragg reflections at 7.0, 7.7, 21.9, and 22.1° 2θ values corresponding to (100), (101), (205), and (302) planes of the zeolite Beta structure. The crystallinity of the zeolite Beta coatings obtained at 150°C from a gel with

![Figure 5.1](image_url)

**Figure 5.1** XRD patterns of zeolite Beta coatings obtained from precursor mixtures with Si/Al ratios of 12, 15, 17, 20, and 23 at (a) 140°C and (b) 150°C. The reference patterns of the Titania-Alumina-Molybdenum (TAMo) substrate, BEA [28], and MER [29] zeolite structures are given for comparison.
Si/Al ratios of 15 and 17 was considerably lower, while the coatings obtained both at 140 and 150°C from a gel with a Si/Al ratio of 12 consisted of MER zeolite with minor amounts of zeolite Beta.

As shown in Figure 5.2(a), the Si/Al ratio in the coatings was substantially lower than that in the precursor gel for the whole range of the gel compositions studied. In turn, the Si/Al ratio of coatings obtained at 140°C was lower than those obtained at 150°C for the range of Si/Al ratios of the gel above 18. This indicates that the efficiency of incorporation of framework elements is higher for aluminum than for silicon and increases even further at a lower synthesis temperature. The coating coverage of 1.7 g m\(^{-2}\) was obtained at both 140 and 150°C from a gel with the Si/Al ratio of 20 (Figure 5.2(b)). However, the coverage decreases as the Si/Al ratio increases in the synthesis mixture at 140°C, while the opposite trend is observed at 150°C. The coatings have a different morphology; viz. C-BEA(20)-140-5 consists of a continuous layer of crystals (Figure 5.3(a)), while the individual spherical crystals are seen in the SEM image of C-BEA(20)-150-5 (Figure 5.3(b)). In both cases, the coating coverage corresponds to an average layer thickness of 1.5 μm with a very

**Figure 5.3** SEM images of (a) C-BEA(20)-140-5, (b) C-BEA(20)-150-5, and (c) C-BEA(15)-150-5 selected from Figures 5.1 and 5.2.
narrow crystal size distribution (CSD) [18]. On the contrary, C-BEA(15)-150-5 showed a broad crystal size distribution with a coverage of 0.5 g m\(^{-2}\) (Figure 5.3(c)). This coverage is below a single monolayer of zeolite Beta crystals and the substrate is clearly visible in the SEM image. These results suggest that the temperature has to be optimized for a specific Si/Al composition in order to promote the crystallization process on the substrate.

5.3.2 Effect of heating rate and gravity on coating properties

The heating rate of the synthesis mixture has a profound effect on the level of

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**Figure 5.4** Heating profiles of zeolite Beta precursor mixtures. The solid and dotted curves indicate the temperature of the precursor mixture and the autoclave wall, respectively. The dashed lines show the initial heating rates of 1°C min\(^{-1}\) (△), 5°C min\(^{-1}\) (○), and 10°C min\(^{-1}\) (□), corresponding to the heating profiles of the precursor mixture.

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**Figure 5.5** The effect of heating of the precursor mixture with a Si/Al ratio of 17 (a and c) and 23 (b and d) on zeolite Beta coverage (a and b) and on Si conversion (c and d) at 140 and 150°C. The symbols correspond to heating rates of 1 (△), 5 (○), 10°C min\(^{-1}\) (□) (Fig. 5.4). MER formation is indicated by the dashed line in Fig. 4.5(a).
supersaturation in the synthesis mixture and therefore markedly affects the properties of the coatings [19]. The time required to reach the synthesis temperature is 4 h for low heating rate, 2 h for a moderate, and 30 minutes for a steep heating rate (Figure 5.4). The effect of the heating rate on the properties of zeolite coatings was investigated at 140 and 150°C. The initial heating rate virtually does not depend on the synthesis temperature in the range of 140-150°C. The zeolite coverage at various heating rates as a function of synthesis time is shown in Figures 5.5(a, b) for the Si/Al ratios of 17 and 23, respectively. The corresponding Si conversions are shown in Figures 5.5(c, d), respectively. The growth of the coatings at various conditions was monitored in time by SEM analyses for C-BEA(17)-140-1, C-BEA(17)-140-10 (Figures 5.6(a-h)) and C-BEA(23)-150-1, C-BEA(23)-150-10, C-BEA(23)-140-10 (Figures 5.7(a-f)).
The duration of the induction period at 140°C was not strongly affected by the initial heating rates (Figure 5.5(a); C-BEA(17)-140-1, C-BEA(17)-140-5, C-BEA(17)-140-10). At different Si/Al ratios of 17 and 23 at 140°C, the induction period increased from 24 to 30 h, respectively (Figures 5.5(a, b), Figures 5.6(a, b), and Figure 5.7(e)). A bimodal distribution of spherical zeolite Beta crystals with sizes of 0.15–0.25 and 0.5–1.0 μm was obtained from a synthesis mixture with a Si/Al ratio of 17 in the experiments with slow heating after 24 h (Figure 5.6(a)). A large population of smaller crystals (0.05–0.15 μm) was obtained in the experiments after rapid heating (Figure 5.6(e)). The highest coverage of 1.5 g m⁻² after 32 h synthesis time (Figure 5.5(a)) and also the highest level of Si conversion of 55% (Figure 5.5(c)) were obtained with slow heating. A closed layer of zeolite Beta crystals with a narrow CSD was already observed after 29 h (Figure 5.6(b)). Several smaller crystals were seen in the open spots on the substrate. Increasing the synthesis time to 48 h resulted in a higher Si conversion, which was approximately the same for slow, moderate and rapid heating. The zeolite Beta coverage increased only slightly in the experiments with moderate heating, while a mixture of BEA and MER type structures was formed after approximately 42 h synthesis time with slow heating (XRD pattern of Figure 5.8). The crystallization of the large MER

![Figure 5.7 SEM images of the growth of C-BEA(23)-150-1 (a, b), C-BEA(23)-150-10 (c, d), and C-BEA(23)-140-10 (e, f) which corresponds to Figure 5.5(b). The white arrows indicate some nanocrystals on the substrate surface.](image-url)
Figure 5.8 XRD patterns of C-BEA/MER(17)-140-1 after different synthesis times corresponding to Figures 5.5(a) and 5.6(a), which shows the appearance of the MER phase after approximately 42 h. The reference patterns of the substrate, BEA [28], and MER [29] zeolite structure are given for comparison.

Figure 5.9 Zeolite Beta coverage (-) as a function of initial heating rate (°C min⁻¹) of the precursor mixture after 48 h corresponding to Figures 5.5(a, b).

zeolite crystals (Figure 5.6(d)) is responsible for a further increase of the coverage for C-BEA(17)-140-1 in the course of the synthesis (Figure 5.5(a)). In case of rapid heating, the zeolite Beta coverage linearly increased to 0.8 g m⁻² after 48 h, which was still below a single monolayer. A large CSD was observed (Figure 5.6(h)).

The Si conversion as a function of the synthesis time at 150°C showed trends similar to that at 140°C (cf. Figures 5.5(c) and (d)). On the contrary, the coverage showed the opposite trend (Figure 5.9). The duration of the induction period at 150°C was increased from 13 to 20 or 24 h, respectively, when either moderate or rapid heating was applied instead of slow heating (Figure 5.5(b)). A single layer of zeolite Beta crystals with an average size of 0.7 μm was obtained already after 16 h in the experiments with slow heating (Figure 5.7(a)). After rapid heating, the first crystals in the range of 0.05–0.25 μm were formed on the substrate after 24 h and a closed layer with a narrow CSD was obtained after 48 h (Figures 5.7(c, d)). Average crystal sizes of 1.2 (Figure 5.7(b)) and 1.6 μm (Figure 5.7(d)) were obtained at slow and rapid heating, respectively.

A substrate with a low surface roughness of 14 nm was used to distinguish the contribution to the coverage between the crystals in-situ grown on the surface and
Figure 5.10  (a) Positioning of the substrate ($R_s = 14$ nm) in the zeolite precursor mixture directly below a cover. The black dots on the substrate indicate the position on the coating of the SEM analysis at 100 μm (b and c) and 10 mm (d and e) below the cover. The scale bar (in mm) next to the autoclave indicates the height and length of the separate parts. SEM images are shown of the surface (b and d) and of the cross section (c and e, tilting angle = 30°) of C-BEA(23)-150-10. The insets in the separate figures show a close up of the SEM images.

of those evolved or deposited by other mechanisms. A protective cover was fixed above the substrate to avoid the contribution from gravitational aided precipitation of amorphous gel particles and zeolite nanocrystals from the volume above the substrate (Figure 5.10(a)). At a distance of 0.1 mm below the cover, C–BEA(23)-150-10 consists of a single layer of crystals grown directly on the substrate with a bimodal CSD and an average crystal size of 0.7 μm (Figure 5.10(b)). A few larger crystals with an average size of 1.6 μm on top of the inner layer can also be seen. However, a closed layer of crystals of ca. 1.6 μm in diameter was obtained at a distance of 10 mm below the cover (Figure 5.10(d)). In the latter case, the crystals from the inner layer cannot be seen. The SEM images of the cross section at both positions show a coating thickness of 2 μm with the presence of a layer of smaller crystals attached to the substrate and an outer layer of large crystals (Figures 5.10(c, e)).
5.4 Discussion

5.4.1 Growth model of continuous zeolite Beta coatings

The small crystal size distribution (CSD) of the coatings C−BEA(20)-140-5, C−BEA(20)-150-5 (Figures 5.3(a, b)), C−BEA(17)-140-1, (Figure 5.6(c)), and C−BEA(23)-150-1, C−BEA(23)-150-10, C−BEA(23)-140-10 (Figures 5.7(b, d, f)), indicates that these are grown from a gel layer initially deposited at the surface of the substrate. Initially, all crystals grew fast due to the very high concentration of nutrients both in the gel layer and in the liquid phase. The crystal growth rate reduced drastically as the concentration of the nutrients was depleted in the gel layer after the crystallization period. Therefore, zeolite crystals with rather the same size at the end of the crystallization could be formed [30]. The steep increase of the crystallization curves after the induction period for all coatings except for C−BEA(17)-140-10 (Figures 5.5(a, b)), confirms the fast crystallization on the substrate. The gel layer with embedded crystals of C−BEA(23)-150-1 is still partly visible after 16 h in Figure 5.7(a).

Various steps in a proposed growth mechanism of zeolite Beta coatings are schematically shown in Figures 5.11(a, b), which are to a certain extent overlapping events. Figure 5.11(b) illustrates the heterogeneous nucleation and growth of zeolite Beta crystals on C−BEA(17)-140-10, which will be discussed in the next section. In this section the separate steps in the growth of zeolite Beta coatings from a gel layer will be illustrated by the evolution of C−BEA(23)-150-10 in Figure 5.11(a). In the initial stage of the synthesis, the dissolution and rearrangement of the precursor mixture into amorphous gel particles dominates (step I and II) [31, 32]. The thermodynamic potential and liquid motions cause transport of these gel particles from the liquid phase to the substrate [33] forming a discontinuous layer of primary particles on its superhydrophilic surface [18]. At low supersaturation, these particles agglomerate into a thin homogeneous gel layer [33-39]. Heterogeneous nucleation at the substrate/gel interface yields the nanocrystals of zeolite Beta (step II, and see also the SEM image taken after 24 h in Figure 5.7(c)). At the same time, primary sub-colloidal gel particles of ca. 3 nm in diameter can assemble in the liquid phase [40] and aggregate to give amorphous clusters up to 10 nm in size [32, 40-45]. In the concentrated synthesis mixture, these clusters can further aggregate to amorphous aluminosilicate particles up to 50 nm in size, which are strongly enriched in aluminum, sodium, and potassium [32, 43, 44, 46-48]. These particles precipitate slowly due to the gravity and can only attach to the substrate, if being formed in the vicinity of the substrate surface (step a-III). Indeed, only a very limited number of large gel particles were attached to the top part of the substrate, which was isolated from the upper volume, yielding a discontinuous layer of zeolite crystals after 48 h (Figures 5.10(b, c)). On the contrary, a closed
Two different growth mechanisms of zeolite Beta coatings, originating from a gel layer and from a diluted precursor mixture, which is illustrated by the evolution of (a) C-BEA(23)-150-10, and of (b) C-BEA(17)-140-10, respectively. The super hydrophilic surface of the substrate has a good interaction with the precursor mixture (step I). A thin homogeneous amorphous aluminosilicate gel layer is deposited on the surface of the substrate in the initial stage of the synthesis process (step II). Furthermore, heterogeneous nucleation occurs at the substrate/gel interface depending on the synthesis conditions. In case of C-BEA(23)-150-10 (a), the agglomeration of the gel particles continues in the bulk liquid, which also results in the growth of the gel layer at the surface (a-III and a-IV). Furthermore, nuclei are formed at the gel/liquid interfaces of both the gel layer at the substrate and the nanoparticles in the bulk liquid (a-III and a-IV). Fast crystallization occurs at the gel/liquid interface, while a relatively slow crystallization occurs at the substrate/gel interface (a-V). The crystals in the coatings show a narrow crystal size distribution. In case of C-BEA(17)-140-10 (b), the nucleation and crystallization process is enhanced in the bulk liquid, which prevents the formation of a stable gel layer at the substrate and results in a discontinuous coating (b-III, b-IV, and b-V). The crystals at the substrate show a large crystal size distribution (b-V).

A layer of crystals was obtained at the bottom part of the substrate due to reduced hindrance for the deposition of the amorphous nanoparticles (Figures 5.10(d, e)).

In the fourth step (a-IV), zeolite Beta nuclei are formed via a reaction between dissolved aluminum and silicon with TEA-silicate species. This reaction has the
highest rate at the gel/liquid interface because the gel layer is enriched in aluminum, while the bulk liquid is enriched in silicon and TEA species [49, 50]. The aluminum concentration in the liquid is regulated by the total content of alkali cations [26, 50]. In the last step, the nucleation is followed by fast crystallization via condensation reactions of the precursors into the zeolite Beta framework at both the substrate/gel and gel/liquid interfaces (step a-V). As a result, a continuous coating of zeolite Beta crystals was formed after 48 h (Figure 5.5(b) and 5.7(d)). The presence of two layers of crystals can be clearly seen in Figures 5.10(b, c). The bimodal crystal size distribution is related to a higher crystallization rate at the gel/liquid interface due to enhanced mass transfer of silicon and TEA species. The crystals in the top layer are considerably larger than those crystallized at the substrate/gel interface. Nevertheless, the crystals at the substrate/gel interface could slowly grow further in size in the course of the synthesis process due to the porous nature of the gel layer [37].

5.4.2 Effect of heating

According to the proposed mechanism, heterogeneous nucleation at the substrate can occur either from a thin layer of primary sub-colloidal particles [35, 36], or directly from the synthesis mixture [51], the latter being more likely in a mixture with a low degree of supersaturation. Aggregates are more essential for nucleation, while primary units are involved in the crystal growth [32, 40, 43]. The availability of the gel particles in the liquid phase, which depends on the nucleation and crystallization kinetics, determines the rate of formation and the thickness of the gel layer. A high ratio between the primary units and aggregates is achieved at a high degree of solubility of the nutrients. In this case, condensation occurs rather quickly, slowing down or even preventing the gel rearrangement [52]. Such conditions can be realized during rapid heating of the precursor mixture at 150°C. This doubles the duration of the induction period compared to slow heating when the nutrients from the precursor mixture have sufficient time to rearrange into the amorphous gel aggregates (Figure 5.5(b)). Furthermore, the rate of heterogeneous nucleation on the substrate increased during rapid heating as can be seen from the larger number of small nanocrystals present on the surface in the initial stage of the crystallization process (Figures 5.6(e), and 5.7(c, e)). On the contrary, only a few nanocrystals are attached to the substrate at the end of the induction period under slow heating conditions (Figure 5.6(a)).

A stable gel layer surface cannot be formed under rapid heating conditions on the substrate at Si/Al ratios below 17 due to the low degree of supersaturation. This results into a low rate of formation of gel particles (Figure 5.11, step b-III), while their consumption rate towards nucleation and crystallization of zeolite crystals in the liquid phase is rather high due to higher concentrations of both aluminum and
sodium [53] (steps b-IV and b-V). Therefore, the formation of coatings proceeds through heterogeneous nucleation and growth on the substrate resulting in a discontinuous coating with a large CSD which coverage increased linearly in time (Figure 5.5(a)). This mechanism was pronounced at Si/Al ratios between 12 and 17 at rapid and moderate heating (Figures 5.2(b) and 5.3(c)).

Since the aluminosilicate gel particles were deposited on the substrate from the liquid phase, it can be expected that the nucleation and crystallization rates controlling the coating resemble that in the liquid phase. Nevertheless, the induction period for the crystallization on the substrate is much longer than in the liquid phase, \textit{viz.} the Si conversion at the beginning of crystallization on the substrate was 30-45% (Figures 5.5(c, d)). Although a complex phenomenon to understand, it might be due to the low overall gel/liquid interface area of the static gel layer on the substrate as compared to that of the mobile spherical gel particles in the liquid phase. The large interface area stimulates the nucleation of zeolite Beta. Rapid heating of the precursor mixture resulted in a lower nucleation rate compared to slow heating (Figures 5.5(a-d)), while a lower reaction temperature especially reduced the crystallization rate (cf. G-BEA(23)-140-10 and G-BEA(23)-150–10 in Figure 5.5(d)). As a result, the average crystal size increases with temperature and decreases with increasing heating rate.

5.4.3 Effect of Si/Al ratio

The crystallization of zeolite Beta was stopped after 48 h when the liquid phase was exhausted in aluminum, although an incomplete conversion of the silicon was observed (Figures 5.5(c, d)). Due to the incomplete use of silicon, the synthesis inefficiency increases as the aluminum concentration of the precursor gel decreases [50]. Si conversions of 55% and 65% were reached at Si/Al values of 23 and 17, while a conversion of 80% was obtained from a precursor mixture with a Si/Al ratio of 15. Figure 5.2(a) shows approximately 30% lower values for the Si/Al ratios of C-BEA(17)-140-5 and C-BEA(23)-150–5 compared to the Si/Al ratio in the precursor mixture. This value corresponds rather well with a Si conversion in the bulk phase in the range of 55–65%.

The successive transformation of a metastable phase to a more stable one can occur if the composition of the synthesis mixture allows nucleation of a new phase [54]. Several aluminum-rich phases were formed next to zeolite Beta at Si/Al ratios below 9.7 (6 Al/unit cell) [50, 55]. Zeolite MER was hydrothermally synthesized from the same synthesis mixture with a Si/Al ratio close to 5 [56]. A high local aluminum concentration can be achieved at the interface of the coating and the liquid phase due to the dissolution of zeolite Beta crystals after 32 h (Figure 5.5(a)). Electrostatic forces induced by the substrate enrich the gel phase at its surface with negatively charged Al species resulting in a lower Si/Al ratio closer to the substrate.
surface [51]. The initial deposition of an Al-rich aluminosilicate gel layer at the substrate can explain the formation of MER type zeolite in C-BEA(12)-140-5 and C-BEA(12)-150-5 (Figures 5.2(a, b)), while zeolite Beta was analyzed as the only crystalline product in the bulk phase.

5.5 Conclusions

Zeolite Beta coatings are crystallized \textit{in-situ} on a Mo substrate in the Si/Al range of 10 – 25. It was shown that the synthesis temperature and heating rate have to be optimized at different Si/Al ratios. Continuous coatings are obtained with an average layer thickness of approximately 2 \mu m. A growth mechanism for the synthesis of continuous zeolite Beta coatings is proposed, which demonstrates the importance of the formation of an amorphous gel layer at the surface of the substrate prior to the crystallization process. The formation of this gel layer can be stimulated by controlling the level of supersaturation within the synthesis mixture. Slow heating (1°C min\(^{-1}\)) and a low synthesis temperature of 140°C is required at low Si/Al values of the precursor mixture, while rapid heating (10°C min\(^{-1}\)) at 150°C is favored at relatively high Si/Al ratios. The crystallization process has to be quenched when the precursor mixture is depleted in aluminum to prevent the transformation of zeolite Beta in other phases such as MER zeolite.

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References

Hydrothermal Synthesis and Characterization of ZSM-5 Coatings on a Molybdenum Support and Scale-up for Applications in Microreactors

This Chapter has been published as:

Abstract
A procedure has been developed to grow ZSM-5 crystals in-situ on a molybdenum (Mo) support. The high heat conductivity (138 W m⁻¹ K⁻¹) and high mechanical stability at elevated temperatures of the Mo support allow the application of ZSM-5 coatings in microreactors for high temperature processes involving large heat effects. The effect of the synthesis mixture composition on ZSM-5 coverage and on the uniformity of the ZSM-5 coatings was investigated on plates of 10 × 10 mm². Ratios of H₂O/Si = 50, Si/Al = 25, and TPA/Al = 2.0 were found to be optimal for the formation of uniform coatings of 6 g m⁻² at a temperature of 150°C and a synthesis time of 48 h. Scaling up of the synthesis procedure on 72 Mo plates of 40 × 9.8 × 0.1 mm³ resulted in a uniform coverage of 14.8 ± 0.4 g m⁻². The low deviation per individual plate (< 3%) indicates the uniformity of the synthesis conditions in the scale-up procedure.
6.1 Introduction

The interest in the preparation of zeolitic coatings has increased enormously during the last decade due to their versatile applications as membranes [1], chemical sensors [2], and catalytic coatings [3, 4, 5]. In the latter case, both the framework and charge compensating cations can be easily substituted by other elements creating an active catalyst. Recent developments show the potential of zeolitic coatings in chemical synthesis, e.g. Fe-ZSM-5 for benzene to phenol oxidation [6], Mo-ZSM-5 for methane dehydrogenation [7], and Co-ZSM-5 for ethane ammoxidation to acetonitrile [8, 9]. Many processes can be considerably intensified by combination of the high intrinsic surface area of zeolites (400 – 700 m$^2$ g$^{-1}$) with a large geometrical surface area of microstructured reactors (5000 - 10000 m$^2$ m$^{-3}$). Furthermore, implementation of zeolitic coatings in microreactors has several advantages such as a low-pressure drop, a narrow residence time distribution, high heat and mass transfer rates, and a possibility to carry out the reaction in the explosive regime [10]. Finally, microreactors can be regarded as the natural platform for the high-throughput screening of zeolitic coatings [11].

Microreactors are typically built up from several dozens up to several hundreds of individual reactor plates or channels on which the catalytic coating is deposited. Another important characteristic of microstructured reactors is that they are amenable to scale-out [12]. So, the production can be increased by increasing the number of reactors, and thus the number of reactor plates, rather than the size. The performance of reactors, especially microreactors, depends on the uniformity of the catalytic coatings. A non-uniform composition of the catalytic coatings as well as variations in coating thickness [13, 14], will affect the conversion and selectivity of the chemical process adversely. Therefore, the implementation of zeolitic coatings in microreactors requires the development of a scale-up procedure to simultaneously synthesize identical coatings on a large number of reactor plates or channels. Non-uniformities between the coatings can be avoided when all reactor plates are treated in one single deposition step, e.g. a large volume of a synthesis mixture in case of the in-situ growth of zeolitic coatings on a multitude of reactor plates.

Despite the opportunities of zeolitic microreactors, this field has been scarcely explored so far [15]. Hydrothermal synthesis of zeolites on various substrate materials as metals [16, 17, 18] and ceramics [19, 20, 21] has been thoroughly investigated. Recently, we demonstrated that stable layers of ZSM-5 crystals can be in-situ grown from the synthesis mixture on the surface of the channels and thin walls of a microreactor made of AISI-316 stainless steel [22]. However, this material is not the best choice for the application in high temperature microreactors because of the low thermal conductivity and corrosion resistance at elevated temperatures.
On the contrary, refractory metals have high melting points, an improved corrosion resistance [23], and low thermal expansion coefficients. Furthermore, some of them (e.g. molybdenum) have a high heat conductivity. Therefore, the application of zeolitic coatings in microstructured reactors made in refractory metals [11, 24] requires the development of a synthesis procedure on these advanced materials.

In our previous work, we presented the design of a molybdenum microreactor for the screening of catalytic coatings [11]. This reactor can be used especially in high temperature gas phase reactions involving large heat effects. The ammoxidation of light paraffins over cobalt exchanged ZSM-5 zeolites is an example of such a process [8, 9]. In this paper, a procedure is developed for the hydrothermal synthesis of ZSM-5 coatings on molybdenum plates of 10 × 10 mm². The synthesis parameters have been optimized in order to obtain coatings with a zeolite coverage between 2 and 15 g m⁻², where the latter value corresponds with an average thickness of the coating of 12 μm. The lower limit corresponds to a single layer of zeolite crystals [22], while the upper limit is set due to the physical dimensions of the microstructures in the walls of the high-throughput microreactor (130 μm) and the thickness of the molybdenum plates (100 μm). The design of the reactor requires a multitude of identical sets of eight coatings of 40 × 9.8 mm². These coatings can be loaded with a series of active species of various contents in separate ion exchange procedures in order to optimize the zeolitic coating activity and selectivity. Therefore, a scale-up procedure is developed to simultaneously synthesize ZSM-5 coatings on 72 molybdenum reactor plates. In the following we describe the synthesis and characterization of ZSM-5 coatings on a molybdenum support and the scale-up of the synthesis procedure.

6.2 Experimental

6.2.1 Materials

Molybdenum foil (Aldrich, 99.9+ %) of 100 μm in thickness was cut in plates of 10 × 10 mm² and 40.0 × 9.8 mm² for experiments for the optimization of the ZSM-5 synthesis procedure and for the development of the scale-up procedure, respectively. In this study experiments for the optimization of ZSM-5 synthesis were conducted on molybdenum (Mo) as well as on surface modified Titania-Alumina-Molybdenum (TAMo). The pretreatment procedures for both plates are summarized in Table 6.1.

Mo plates were pretreated according to steps 1 to 4 of Table 6.1. Steps 1 to 3 are cleaning and etching steps according to a procedure described in [17]. Before synthesis, the Mo plate was dipped in a solution of the templating agent (step 4),
Table 6.1  Pretreatment procedures of molybdenum (Mo) and Titania-Alumina-Molybdenum (TAMo) plates.a

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Procedure</th>
<th>Conditions</th>
<th>Plates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Xylene</td>
<td>140°C, 1 h.</td>
<td>Mo: +</td>
</tr>
<tr>
<td>2</td>
<td>NH4OH/H2O2/5H2O</td>
<td>80°C, 45 sec.</td>
<td>Mo: +</td>
</tr>
<tr>
<td>3</td>
<td>HCl/6H2O2/6H2O</td>
<td>80°C, 45 sec.</td>
<td>TAMo: -</td>
</tr>
<tr>
<td>4</td>
<td>10 wt.% TPAOH e</td>
<td>25°C, 60 sec.</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>ALD of 170 nm Al2O3</td>
<td>250°C</td>
<td>TAMo: +</td>
</tr>
<tr>
<td>6</td>
<td>ALD of 50 nm TiO2</td>
<td>500°C</td>
<td>-</td>
</tr>
</tbody>
</table>

ALD denotes atomic layer deposition, which was performed at Nanoscale Oy, Finland (http://www.nanoscale.fi/)

a  Dimension of plates: 10 × 9.8 × 0.1 mm³ and 40 × 9.8 × 0.1 mm³
b  Riedel de Haën (25 wt.%)
c  Fluka (30 wt.%)
d  Aldrich (37 wt.%)
e  Merck (20 wt.%)

and then dried for 1 h at 110°C. TAMo plates were obtained after deposition of thin layers of Al2O3 and TiO2 (steps 5 and 6, respectively) on an etched surface of molybdenum (after steps 1 and 2) by atomic layer deposition (ALD, Nanoscale Oy, Finland). Molybdenum plates were cleaned in a concentrated HCl solution prior to the ALD process. The Al2O3 film was deposited on the Mo surface by ALD with TMA (trimethylaluminium) as the metal precursor and H2O as oxidation precursor at a temperature of 250°C. The growth of the TiO2 film on the Al2O3 film was performed from TiCl4 (titaniumchloride) and H2O sources at 500°C. Every precursor pulse in the tubular glass ALD reactor is alternated with an inert nitrogen pulse. The Al2O3 film protects the molybdenum plate from oxidation at reaction conditions while the TiO2 film can be made hydrophilic by UV irradiation. TAMo plates were treated by UV radiation with wavelengths in the range of 220 to 1400 nm for 3 h (Hanovia 679A-36 equipment, 450 W) prior to the zeolite synthesis procedure.

6.2.2  Small scale synthesis of zeolitic coatings

The synthesis mixtures were prepared by adding tetraethylorthosilicate (TEOS, >98%, Merck) as the silica source to a mixture of sodium aluminate (NaAlO2, 95%, technical grade, Riedel de Haën) as the alumina source, tetrapropylammonium hydroxide (TPAOH, 40 wt.% , Merck) as the template agent, and demineralized water. In this study the synthesis mixtures were prepared within the following composition range: (32 – 100) SiO2 : 1 Al2O3 : (2.0 – 5.5) TPA2O : 0.5 Na2O : (960 – 10000) H2O. Before the synthesis, the solution was hydrolyzed for 23 h at 47°C under continuous stirring. Then, demineralized water was added to the synthesis mixture to compensate for the extra weight loss of water after the aging procedure.
Directly after the UV irradiation, the plate was positioned in the synthesis mixture at 20 mm below the gas-liquid interface with the $10 \times 10 \text{mm}^2$ surfaces parallel to the gravity vector. The synthesis was carried out in a 50 ml PEEK insert filled with 35 mL solution under hydrothermal conditions at autogenic pressure, and at 140-160°C for 2 – 96 h. The stainless steel outer shell of the 35 mL autoclave was preheated to the reaction temperature before insertion of the PEEK inserts. After the synthesis time, the autoclave was quenched in water to room temperature. The composite samples were rinsed with demineralized water followed by an ultrasonic treatment (60 Hz, 120 W) for 1 h. The samples were dried at 110°C overnight. Calcination was carried out in an air flow of 50 mL min$^{-1}$ with a heating rate of 1°C min$^{-1}$ from 20 to 500°C followed by a dwell interval for 10 h.

### 6.2.3 Large scale synthesis of zeolitic coatings

The synthesis mixture was prepared according to the procedure described for the small scale synthesis. The large scale synthesis was carried out in a 3.7 L PEEK (poly-ether-ether-ketone) insert (ID = 0.2 m) filled with a 3 L zeolite synthesis solution. The temperature of the stainless steel outer shell of the 3 L autoclave was heated with a 2000 W band heater, which was controlled by a 8200 West controller. During the initial period of 2 h, required to heat up the solution from room temperature to the synthesis temperature, the solution was continuously stirred using a magnetic stirrer to avoid temperature gradients within the autoclave. After this period the synthesis proceeded under static conditions as in the 35 mL autoclaves. After the synthesis, the 3 L autoclave was cooled down to room temperature by circulating cold water through a cooling unit in the stainless steel outer shell. The post-treatment procedure of the composite samples was similar as for the small scale synthesis procedure.

Figure 6.1(a) shows a 3D image of the PEEK holder, which was applied in the large scale synthesis procedure. The holder consists of two identical layers referred to as layers A and B, which are the top and bottom layers, respectively. Each layer consists of three symmetrical sets of 12 identical positions, which are indicated in Figure 6.1(b). In Table 6.2 all of the 72 plates are numbered according to their position in the holder.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Symmetry set</th>
<th>Plate numbers</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>I</td>
<td>1 – 12</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>13 – 24</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>25 – 36</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>37 – 48</td>
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<tr>
<td>B</td>
<td>II</td>
<td>49 – 60</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>61 – 72</td>
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</tbody>
</table>
Figure 6.1  Holder for the scale-up procedure for the in-situ synthesis of zeolitic coatings on 72 plates of $40 \times 9.8 \times 0.1 \text{ mm}^3$. (a) The holder consisting of two identical layers (A and B), which are positioned on top of each other. (b) Schematic top view of the holder geometry (an enlargement of the triangle indicated in Figure 6.1(a); $30^\circ$ of the holder is depicted), in which three different symmetry positions of the plates (I, II, and III) are indicated. Table 6.2 summarizes the numbering of the 72 positions for the plates in the holder, which can be divided in six symmetrical sets of 12 plates.

6.2.4 Characterization

The plates were weighted before the synthesis with an analytical mass balance. The weight gain of the plates after the synthesis procedure was used to calculate the zeolite coverage. The Si conversion is defined as:

$$
\text{Si conversion} = \frac{\text{mol} (\text{Si}_{\text{ZSM-5 powder}} + \text{Si}_{\text{ZSM-5 coating}})}{\text{mol Si}_{\text{synthesis mixture}}} \times 100\%  \tag{6.1}
$$

The coatings were examined by X-ray diffraction (XRD) for phase identification and crystal orientation. XRD data were collected on a Rigaku geigerflex diffractometer using Cu Kα radiation ($1.5405 \text{ Å}$). XRD patterns were recorded in the range of $5 – 50^\circ 2\theta$ using step scanning at $0.02^\circ 2\theta$ per step and a counting time of 4 s for each step. The degree of preferred orientation perpendicular to the c-axis of the hexagonal crystals was calculated using the following equation:

$$
D_{p2} = \frac{\text{sums of intensities (200) and (020) XRD peaks}}{\text{intensity of (002) XRD peak}}  \tag{6.2}
$$

The surface coverage and morphology as well as the layer thickness of the ZSM-5 coatings were examined by SEM on a JEOL JSM-840A.

N₂ adsorption isotherms were obtained on an ASAP-2000 Micromeritics instrument with a standard procedure after vacuum pretreatment at $300^\circ \text{C}$ for 30 h up to a residual pressure <0.1 Pa. The surface area of the zeolitic coating was
measured by the BET method at $-196^\circ$C in the range of relative pressures within 0.005-0.20, with N$_2$ as the adsorbent. The pore size distribution was obtained with the Horvath-Kawazoe method. The full pore volume was calculated from the maximum adsorption value obtained from the N$_2$ adsorption isotherm. The layer thickness of the coatings ($l$) was calculated, based on measured surface areas ($S$) assuming the BET surface for ZSM-5 crystals ($S_{BET}$) to be 435 m$^2$ g$^{-1}$ [21], an apparent density of 0.9 g cm$^{-3}$ ($d$), and a substrate geometrical area ($A$):

$$l = \frac{S}{A \cdot S_{BET} \cdot d}$$

(6.3)

Laser Scanning Confocal Microscopy (LSCM) was applied to estimate the layer thickness of the coatings at the interface of the coated and non-coated parts of the surface. In order to protect a part of the plate from the synthesis mixture, teflon tape was fixed on it. This creates a sharp edge in the zeolitic layer, which was used to determine a layer thickness from a two-dimensional LSCM height profile.

### 6.3 Results and discussion

#### 6.3.1 ZSM-5 coating optimization

It was demonstrated that dipping in a template solution just before the synthesis enhances the zeolite growth rate on metal surfaces [19, 25]. In case of a multilayer TAMo substrate, the hydrophilicity of an external TiO$_2$ surface and, as a result, the zeolite nucleation rate on it, are considerably enhanced by UV pretreatment [26]. The effect of H$_2$O/Si, Si/Al, and TPA/Al ratios on ZSM-5 coverage was investigated after these pretreatments on Mo and TAMo substrates, respectively (Figure 6.2). In series A, B and C the influence of the dilution ratio

![Figure 6.2](image-url)  
**Figure 6.2** Effect of the H$_2$O/Si ratio on the ZSM-5 coverage on Mo (series A) and TAMo (series B, C and D) substrates. Series B and C show the effect of the TPA/Al ratio on the ZSM-5 coverage. The effect of the Si/Al ratio is shown Series D. The dashed horizontal lines represent the upper and lower limits of the ZSM-5 coverage.
(H₂O/Si) was investigated. Series A was performed on Mo substrates, while series B and C were performed on TAMo substrates at different TPA/Al ratios. Furthermore, series D indicates the effect of the Si/Al ratio on ZSM-5 coverage.

Figure 6.2 shows that the dilution ratio has the largest influence on the zeolite coverage. Therefore, this parameter was optimized first, while other parameters being the same, unless otherwise stated. When the H₂O/Si ratio is increased from 24 to 100, a major decrease in ZSM-5 coating thickness was observed from about 45 μm to a single crystal layer. Figures 6.3 and 6.4 show SEM images of ZSM-5 coatings obtained on Mo (series A) and TAMo (series B) substrates, respectively. At a H₂O/Si ratio of 25 and a reaction temperature of 160 °C, a continuous ZSM-5 coating with an average layer thickness of about 45 μm was obtained on a Mo surface. The non-uniform morphology of the coating and the absence of developed crystal faces indicate fast ZSM-5 growth (Figure 6.3(a)). High nucleation and crystallization rates are achieved when high supersaturations are used. This results in a large number of small, irregularly shaped crystallites showing roughened growth [3]. At higher dilution ratios a more controlled growth of ZSM-5 crystals is obtained. The crystals are oriented parallel to the Mo surface (Figure 6.3(c)). The average sizes of the ZSM-5 crystals in the direction of the crystallographic axes a, b and c are 7, 2, and 11 μm, respectively. The relatively large crystals with well-developed crystal faces cause discontinuity in the oriented crystal layer [3]. Pinholes in the ZSM-5 coatings are observed in Figure 6.3(b, c).

For catalytic applications, the presence of framework Al can be essential, since it determines the acidity as well as the ion-exchange ability of the zeolite. The decrease in the Si/Al ratio from 50 to 25 decreased the average size of the ZSM-5 crystals to 3.5 x 1 x 4 μm³ in the direction of the crystallographic axes a, b and c, respectively (Figure 6.4). This is in line with earlier reported data that aluminum rich crystals are smaller in size than the more siliceous ones [20]. The H₂O/Si ratio has no profound effect on the crystal sizes on the TAMo substrate, which is in contrast to a study performed on a stainless steel substrate [22]. The ZSM-5 crystals

Figure 6.3  Scanning electron micrographs of ZSM-5 coatings at different dilution ratios on a Mo substrate (series A of Figure 6.2). Conditions: 160°C, 48 h, Si/Al = 50, TPA/Al = 5.5 at H₂O/Si ratios of (a) 25, (b) 50, and (c) 100.
preferentially grow on crystals already connected to the surface (Figure 6.4(c)), although there are still uncovered areas on the TAMo surface. This suggest that the growth process under these conditions is determined by diffusion of the reactants to and not by formation of the zeolite crystals [20]. Oudshoorn reported relatively low activation energies for nucleation and for crystal growth, which are characteristic for diffusional limited systems. Nevertheless, a uniform ZSM-5 coating was obtained on the TAMo substrate at a H₂O/Si ratio of 50. Ten similar experiments confirmed a good synthesis reproducibility producing a coverage of 6.2 ± 0.5 g m⁻². Several cracks in the coatings were seen after calcination (Figure 6.4(a)), which indicates a strong chemical attachment of the coating to the surface of the TAMo substrate. Further decreasing of the Si/Al ratio resulted in a considerable decrease both in coverage (series D of Figure 6.2) and in crystal size. Although still a substantial coverage was obtained at a Si/Al value of 22, the lower value of 16 reduced the ZSM-5 coverage below 0.5 g m⁻².

The template concentration determines the pH of the synthesis mixture and therefore the zeolite nucleation and crystallization kinetics, which increases at higher pH. However, too fast crystallization leads to low crystallinity. Furthermore, dissolution of the support has to be prevented during the time needed to form a crystalline phase [3]. Therefore, the TPA/Al ratio was also optimized. When a TPA/Al ratio of 5.5 was applied on the TAMo substrate, especially at a low surface roughness, the TiO₂ film partly dissolved as a result of the high pH of 13.5. At lower TPA/Al values of 2.8 and 2.0 (series B and C in Figure 6.2), no dissolution of the TiO₂ layer was observed, and ZSM-5 crystals were successfully grown on the TAMo surface. At the higher template concentration (series C), higher coverages were obtained and small crystals were formed. The average crystal volume was reduced from about 15 μm³ to 3 μm³ when the TPA/Al ratio was increased from 2 to 2.8.

Figure 6.4 Scanning electron micrographs of ZSM-5 coatings at different dilution ratios on a TAMo substrate (series B of Figure 6.2). Conditions: 150°C, 48 h, Si/Al = 25, TPA/Al = 2.0 at H₂O/Si ratios of (a) 50; crack in the ZSM-5 crystals indicates the coating stability (circle), (b) 65, and (c) 100.
Figures 6.5(a, b) show typical XRD patterns of as-synthesized ZSM-5 coatings on a TAMo substrate. All peak locations correspond to the ZSM-5 reference in Figure 6.5(e) [27]. The XRD pattern of a calcined ZSM-5 coating on a TAMo substrate is shown in Figure 6.5(c). Removal of the template from the zeolitic coatings occurs at 350 – 500°C and is accompanied by a substantial shrinkage in the zeolite framework [28]. The \( a \)-, \( b \)- and \( c \)-axis contraction is non-uniform in MFI zeolite crystals, which changes the relative intensities of the diffraction peaks as can be seen in Figure 6.5(c). MoO\(_3\) peaks were not observed, which proofs the stability of the ZSM-5 coating and the protective effect of the Al\(_2\)O\(_3\) film. However, Mo-oxides (especially MoO\(_3\) phase) were identified by XRD after calcination of ZSM-5 coatings on regular Mo substrates. The oxide layer on the Mo surface deteriorates the coating stability, which eventually causes delamination of the zeolitic layer.

The XRD patterns of the zeolitic coatings are consistent with the ZSM-5 structure, however, the relative peak intensities are different from those of zeolite powders. Strong peaks are observed at \( 2\theta \) of 7.49, 8.80, 8.90, 23.10 and 23.98°, corresponding to diffraction of (011), (020), (200), (051), and (033), respectively [27].
Values of $D_{P2}$ were calculated for the ZSM-coatings of series B and C (Figure 6.2). Figure 6.6 shows the dependence of the $D_{P2}$ values on the zeolite coverage. The relatively high values of $D_{P2}$ at a low ZSM-5 coverage, corresponding to a coating thickness of less than one single crystal layer, reveal a more profound alignment with the $c$-axis parallel to the substrate surface. At a higher coverage, the preferred orientation disappears when $D_{P2}$ values reduce to unity. In ZSM-5 coatings with a thickness larger than 2 $\mu$m most of the crystalline material has adapted an orientation with both the $a$ and $b$ axes pointing away (but not perpendicular to) from the substrate surface [29]. In thin ZSM-5 films, the crystals are preferentially oriented with the $a$-axis (sinusoidal channels) or the $b$-axis (straight channels) perpendicular to the substrate surface [19, 30]. Orientation is caused by the preferential growth of the $ac$-plane of the crystallites in the plane of the substrate surface [31].

The ZSM-5 coverage is a function of the feed-to-support area ratio [20, 21]. The influence of this ratio was investigated by varying the amount of support, that is the total surface area of the support, while keeping the amount of synthesis mixture the same. Figure 6.7 shows that the coverage on the TAMo substrate is independent of the feed-to-support area ratio at values above 30 mol Si m$^{-2}$support for the specific synthesis conditions. Based on this value it was decided to fix the volume of the autoclave at 3 L for the scale-up synthesis, which resulted in a feed-to-support area ratio of 47 mol Si m$^{-2}$support.

![Figure 6.7](image1.png)  
**Figure 6.7** Effect of the feed ratio on ZSM-5 coverage. Conditions: 150°C, 48 h, Si/Al = 25, TPA/Al = 2.0, and H$_2$O/Si = 50.

![Figure 6.8](image2.png)  
**Figure 6.8** Liquid temperature as a function of synthesis time during heating of the 35 mL (run nr. S1) and the 3 L (run nr. L1) autoclaves. The shaded area indicates the estimated induction period. See Table 6.3 for conditions.
6.3.2 Scale-up of in-situ synthesis

The main goal of the scale-up procedure is to obtain the same and uniform ZSM-5 coverage on all plates of $40.0 \times 9.8 \times 0.1 \text{ mm}^3$. A dedicated plate holder for 72 plates was designed to maximize the distance between the plates, within a total volume of 3 L (Figure 6.1). The open structure of the holder provides equal accessibility of the nutrients to the substrate surfaces during the crystallisation process. The reaction conditions as well as the synthesis mixture composition have to be chosen such that neither heat nor mass transfer limitations will be present in the synthesis volume. The synthesis conditions were optimized at a $\text{H}_2\text{O}/\text{Si}$ ratio of 50 to provide a feed-to-support area ratio of 47 mol Si m$^{-2}$support. This ratio gives a Si-conversion below 50%, which will ensure that the synthesis mixture will not be locally depleted, preventing concentration gradients. The effect of the different heating rates in the 35 mL and 3 L autoclaves as well as the effect of stirring was investigated (Table 6.3).

The effect of the different heating rates on the ZSM-5 coverage was examined in experiments S1 and L1. The temperature of the synthesis mixture in the 3 L autoclave approaches the set-point much faster due to direct contact of the autoclave with a heating cartridge, while the 35 mL autoclave is heated by a convection oven (Figure 6.8). As a result the temperature of the synthesis mixtures in the 35 mL and 3 L autoclaves reached the set-point with different average rates of 0.6 and 1.3°C min$^{-1}$, respectively. When a similar batch composition was used for the synthesis, coverages of 6.2 and 8.9 g m$^{-2}$, and a Si conversion of 40 and 33%, were obtained in the 35 mL and 3 L autoclaves, respectively (Table 6.3). These results can be attributed to the higher heating rate in the 3 L autoclave.

The primary event during the temperature raise of the reaction mixture from the aging to the synthesis temperature, that is from 47°C to 150°C, is the accelerated dissolution of the (alumino)silicate gel phase, resulting in higher concentration and mobility of monomeric silicate and aluminate species [32]. Zeolite crystallization is expected after an induction period in which nucleation

<table>
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<th>Run no.</th>
<th>$T_{\text{rate}}$</th>
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<th>BET</th>
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<td>g m$^{-2}$</td>
<td>%</td>
<td>m$^2$ g$^{-1}$</td>
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</tr>
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<td></td>
<td></td>
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</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>370</td>
</tr>
</tbody>
</table>

*a Synthesis condition; 50 SiO$_2$: 1 Al$_2$O$_3$: 2 TPA$_2$O: 0.5 Na$_2$O: 2500 H$_2$O, 150°C, 48 h.
*b S denotes 35 mL autoclave; L denotes 3 L autoclave.
*c The heating rate ($T_{\text{rate}}$) was determined according to the period that was required to increase the temperature of the liquid from 90°C to 140°C.
occurs. Nucleation of Si-TPA-ZSM-5 particles from clear solutions occurs via association of secondary amorphous particles and monomeric silicate in a TPA mediated synthesis [33, 34]. When the solubility of the amorphous particles increases, the presence of secondary particles decreases, which results in a reduced nucleation rate. Since the total amount of ZSM-5 crystals formed during the synthesis experiment is dependent on the nucleation rate, zeolite formation in the bulk was considerably reduced as the Si conversion decreased from 40 to 33%.

The higher temperature increase of the liquid in the 3 L autoclave resulted in an increased ZSM-5 coverage on the support. Koegler et al. proposed a Si-ZSM-5 thin film growth model on a support [31]. At the start of the synthesis the silica gel is deposited on the support, forming a thin, low-density silica surface. At a stage where the gel layer formation is reduced, nucleation will occur at the interface of the gel and the synthesis solution, where the template and silica source are present in abundance. The rate of nucleation is dependent on the availability of soluble silicate. The use of a monomeric silica source as TEOS and the presence of sodium in the synthesis mixture [34] as well as an elevated reaction temperature facilitates the dissolution of a condensed silica precursor. Nucleation and crystallization of ZSM-5 crystals on stainless steel already occurs at 110°C [20]. In the synthesis of Si-TPA-MFI at 125°C a nucleation period of approximately 200 minutes was reported [35, 36]. The shaded area in Figure 6.8 indicates the period in which the liquid temperature in the 3 L autoclave is higher than in the 35 mL autoclave yielding a higher nucleation rate on the corresponding substrates. Similar findings were reported for the in-situ synthesis of zeolite A on stainless steel. When the substrate was directly heated, zeolite nucleation and crystallization in the bulk was suppressed and promoted that on the substrate [37].

Experiment L1 resulted in a relatively large variation in coverage between different symmetrical positions in the holder. The coverage decreased from 9.1 to 8.6 g m⁻² for plates positioned near the wall of the PEEK inserts to plates positioned in the center of the synthesis mixture. The difference between symmetry sets I, II, and III can be attributed to the initial temperature gradient in the liquid volume, being higher near the wall of the insert. This initial temperature gradient in the synthesis volume during the heating period can be avoided by stirring of the mixture.

The effect of stirring during the heating period was investigated in experiment L2. The average coverage per symmetry set (Table 6.2) and the deviation in coverage from the average value for each of the 72 coatings (Figure 6.1) are depicted in Figure 6.9. The average ZSM-5 coverage is 14.8 g m⁻² and the standard deviation over all 72 plates is ±0.4 g m⁻². The average values for the coverage of the six symmetrical sets of coatings are within this standard deviation (run L2 of Table 6.3). The relatively small and non-systematic differences between the
Figure 6.9  Scanning electron micrographs of ZSM-5 coatings at different dilution ratios on a TAMo substrate (series B of Figure 6.2). Conditions: 150°C, 48 h, Si/Al = 25, TPA/Al = 2.0 at H₂O/Si ratios of (a) 50; crack in the ZSM-5 crystals indicates the coating stability (circle), (b) 65, and (c) 100.

separate sets prove that neither axial nor radial concentration gradients were present in the liquid volume during the zeolite synthesis procedure in the 3 L autoclave. Furthermore, one may conclude that the formation of crystallites, formed in the homogeneous bulk phase, and the effect of gravity play no role in the scale-up synthesis procedure, when the Si conversion is below 50%. Figures 6.5(b, c) show the XRD patterns of both the as-synthesized and calcined ZSM-5 coatings, respectively, obtained in the scale-up procedure. The coverage on the TAMo substrates after scale-up experiment L2 is about 1.7 times higher than that obtained in scale-up experiment L1, in which no stirring was applied. This difference can be explained by the effect of stirring during the initial heating period of 2 h. Stirring of the liquid increases the opportunity that nuclei or crystals, which are formed in the homogeneous liquid phase, away from the support surface, collide with, or are carried onto, the surface of the substrate or the zeolitic coating. A doubling of the coverage was reported for the in-situ synthesis of ZSM-5 coatings on stainless steel monoliths in case of stirring of the synthesis mixture [25].

6.4 Conclusions

ZSM-5 coatings with a wide range of Si/Al ratios between 16 and 50 have been prepared on Mo and surface modified TiO₂/Al₂O₃/Mo substrates by hydrothermal synthesis. The effect of the synthesis mixture composition on ZSM-5 coverage was
investigated. The thickness of the coatings can be adjusted from a single crystal layer to a multi layer with a thickness of 45 μm by applying different H₂O/Si ratios.

A scale-up procedure has been developed for hydrothermal synthesis of uniform ZSM-5 coatings on a set of 72 molybdenum plates of 40 × 9.8 × 0.1 mm³ in a 3 L autoclave. A coverage of 14.8 ± 0.4 g m⁻² was obtained on all plates in the scale-up procedure. The deviation in coverage on the separate plates did not exceed 3%. In the scale-up procedure, the positive effect of the fast heating of the synthesis mixture on the enhancement of ZSM-5 coverage was demonstrated. At higher temperatures, the solubility of chemicals in the mixture increases, which decreases the nucleation rate in the bulk volume of the autoclave, while the ZSM-5 growth at the surface of the substrate is enhanced. The ZSM-5 coverage can be increased further by stirring of the synthesis mixture. Stirring of the liquid increases the opportunity that nuclei or crystals, formed in the bulk liquid, collide with, or are carried onto, the substrate surface or the zeolitic coating.

Acknowledgement

The financial support by the Dutch Technology Foundation (STW, project no. EPC.5543), Shell International Chemicals B.V., Akzo Nobel Chemicals B.V., and Avantium Technologies B.V. is gratefully acknowledged. The authors would also like to thank Dr. Milja Mäkelä from Nanoscale Oy (Finland) for her co-operation in the optimization of the ALD procedure.

Bibliography

High-Throughput Screening of Co-BEA and Co-ZSM-5 Coatings in the Ammoxidation of Ethylene to Acetonitrile in a Microstructured Reactor

This Chapter has been submitted as:

Abstract
The activity and selectivity of Co-ZSM-5 and Co-BEA coatings (Si/Al = 15-23) with a thickness of 1 micron deposited on a Mo substrate were determined in the ammoxidation of ethylene in a microreactor. Zeolite Beta coatings were more than twice as selective towards the acetonitrile formation than ZSM-5 coatings. The rate of acetonitrile formation increased by a factor of 6 by increasing the aluminum content in the coatings from a Si/Al ratio of 23 to 15. The effect of the Co/Al ratio was less pronounced. The addition of small amounts of boron decreased the selectivity to acetonitrile in the whole range of Si/Al ratios studied. A maximum TOF of 0.8 s⁻¹ was obtained at a reaction temperature of 500°C, with a selectivity of 58% to acetonitrile. The optimized zeolitic coatings show higher reaction rates than a pelletized Co-ZSM-5 catalyst.
7.1 Introduction

There is a growing interest in gas to liquid (GTL) conversion to transform cheap and abundant hydrocarbons from natural gas to liquid fractions, which can be easily stored and transported. The highly exothermic ammonoxidation of ethane (or ethylene) to acetonitrile represents one of possible ways for GTL conversion. Li and Armor reported significantly improved yields of acetonitrile of 26% over a catalyst comprised of Co exchanged into Beta zeolite [1]. Previously the best oxide catalysts for this reaction achieved a yield of 2.6%. In addition, the productivity of the catalyst as measured by the molar rate of acetonitrile production per gram of catalyst was also larger by a factor of 20 than for the best complex oxide catalysts. Metal cations exchanged into zeolites provide unique catalytic centers, with a higher site density than can be achieved with conventional oxides [2-4]. The acetonitrile yield over Co-zeolites was further improved by addition of small amounts of boron [5].

The process can be further intensified by depositing a zeolite catalyst as a thin layer on a highly conductive microstructured metal substrate, which facilitates heat removal from the reaction zone to the environment [6-8]. Due to the absence of macropores in thin zeolitic coatings, all the catalyst material is available for the reaction, which is often not the case in relatively large catalyst pellets or extrudates with a low effectiveness factor in fast catalytic processes. Furthermore, application of microstructured reactors allows the reaction to be performed with high concentrations of the reactants in the explosive regime, and provides a tool for the easy handling and on-the-spot manufacturing of toxic or hazardous chemicals.

In this study, ZSM-5 and zeolite Beta coatings were grown on molybdenum substrates by hydrothermal synthesis, having a different topology and content of aluminum in their framework. Subsequently, the cobalt content was systematically altered in the coatings, and in some cases boron was added as a promoter. A high-throughput screening of the coatings was performed in a microreactor in a wide range of reactant partial pressures and temperatures to optimize the coating composition and the reaction conditions.

7.2 Experimental

ZSM-5 and zeolite Beta coatings were in-situ grown on surface modified molybdenum substrates (platelets of $40 \times 10 \times 0.1 \text{ mm}^3$). We have previously reported on the synthesis protocols [8-10] and the scale-up procedure to obtain identical coatings on a large number of substrates [9]. Three series of Beta coatings with Si/Al ratios of 15, 17, and 23, and one series of ZSM-5 coatings with a
Si/Al ratio of 20, were prepared (Table 7.1). After calcination at 500°C, these four series of coatings were three times treated with a 1.0 M aqueous NH₄NO₃ solution to produce the H-form of the corresponding zeolites. Finally, the samples were dried at 110°C overnight and calcined in an air flow of 50 mL min⁻¹ while the temperature was increased to 300°C at a heating rate of 1°C min⁻¹. At the end of the dwell period of 2 h, the air flow was substituted by a helium flow, and the temperature was increased to 500°C at a heating rate of 1°C min⁻¹, which was followed by another dwell period of 2 h. Then, each of the four series was divided in eight sets in order to be loaded with various contents of cobalt and boron.

The H-form of the zeolites was ion-exchanged with a cobalt acetate solution [8]. Boron was subsequently introduced by impregnation with an ammonia borane solution at room temperature for 1 h, followed by a calcination at 500°C in helium. The various conditions and properties of the zeolitic coatings are listed in Table 7.2. The Co/Al ratios were calculated assuming that all Al single sites were balanced by (Co-OH)⁺ species and all Al pairs by Co²⁺ cations. This distribution of the single sites and pairs as a function of the Si/Al ratio is reported in the literature [11-13] and confirmed by XPS analysis in this study. The coatings are referred to as xxx-Si/Al-Co/Al according to the zeolite phase (xxx - the abbreviation of the zeolite type BEA or ZSM5), the Si/Al ratio, and the Co/Al ratio of the zeolitic coating.

Table 7.2  Ion exchange conditions and properties of the various zeolitic coatings used for catalyst screening (see Table 7.1 for definition of Series A – D).

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<th>Series A</th>
<th>Series B</th>
<th>Series C</th>
<th>Series D</th>
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<td>100</td>
<td>10</td>
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<td>VI</td>
<td>100</td>
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<tr>
<td>VII</td>
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<td>VIII</td>
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<td>2.8</td>
<td>3.7</td>
<td>3.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

² Each set in series A consist of three platelets, and in series B, C and D of four platelets.
The microstructured reactor for the high-throughput screening of the coatings consists of eight compartments, in which eight different sets of coated platelets, i.e. one complete series in Tables 7.1 and 7.2, can be tested simultaneously in the differential mode [14, 15]. The coatings were pretreated in a helium flow of 200 mL min\(^{-1}\) for 1 h at 530°C. Blank experiments were carried out on inert titanium plates to exclude the contribution of the reactor material to reactant conversion. The reaction conditions were optimized by varying ammonia, ethylene, and oxygen concentrations in the range 1 - 10 vol.%, the reaction temperature in the range 350 – 500°C, and the inlet flow rate in the range of 100 - 500 mL min\(^{-1}\) (STP). The screening experiments were carried out at 450°C and 250 mL min\(^{-1}\) (STP) in a mixture of ethylene (2 vol.%), ammonia (2 vol.%), and oxygen (2 vol.%), balanced by helium. The products were analyzed at steady state conditions on a CP-4900 micro-GC (Varian). Oxygen and nitrogen were analyzed using a molsieve 5A column, while carbon dioxide, ethylene, ammonia, water, methanol, and acetonitrile were analyzed using a poraplot U column and TCD detectors. Trace amounts of CH\(_4\), NO\(_x\), and several unidentified products were also present. It was assumed that methanol was formed from the dissociation of acetonitrile together with another \(C_1\) containing component, most likely hydrogen cyanide [16], which could not be analyzed separately with the micro-GC applied. The carbon and nitrogen mass balances were closed within 95%.

The reaction rate is expressed either in terms of the acetonitrile formation rate per gram of zeolite per second (see Table 7.2) or in terms of the turn over frequency per single Co atom (TOF, s\(^{-1}\)). Carbon selectivity \(S_{C_i}\) to a carbon containing product \(P_i\), and nitrogen selectivity \(S_{N_j}\) to a nitrogen containing product \(P_j\), are defined as:

\[
S_{C_i} = \frac{y_{C_i} \cdot n_{C_i}}{\sum_j y_{C_i} \cdot n_{C_i}} \cdot 100\% \tag{7.1}
\]

\[
S_{N_j} = \frac{y_{N_j} \cdot m_{N_j}}{\sum_j y_{N_j} \cdot m_{N_j}} \cdot 100\% \tag{7.2}
\]

where \(y_{C_i}\) and \(y_{N_j}\) are the molar fractions, and \(n_{C_i}\) and \(m_{N_j}\) are the number of carbon and nitrogen atoms in the product molecule, respectively.
Figure 7.1 Reaction rate on Co-ZSM-5 and Co-BEA coatings in the ammoxidation of ethylene to acetonitrile. The coating properties are listed in Table 7.1. The dashed vertical lines separate the sets with different cations: Co (I-IV), Co and B (V-VII), Na and K (VIII) (see Table 7.2). The coatings were tested at 450°C at a total flow rate per compartment of 31 mL min⁻¹ (STP) consisting of 2 vol.% of ethylene, 2 vol.% ammonia and 2 vol.% oxygen, He-balance.

7.3 Results and Discussion

Figure 7.1 shows the reaction rates of all 32 sets of coatings (Table 7.2), which are divided in the four series (A, B, C, and D) specified in Table 7.1. The highest rate of reaction of 250 µmol g⁻¹ s⁻¹ was obtained on zeolite Beta coatings with a Si/Al ratio of 15, which corresponds to the highest aluminum content. Isolated Co²⁺ ions, located at aluminum pairs in the zeolite framework, are the most active sites in the formation of acetonitrile [17, 18]. The number of aluminum pairs in the ZSM-5 and zeolite Beta structures increases from 30 to 80% with decreasing Si/Al ratio from 23 to 13, while their relative number of Al single sites correspondingly decreases [4, 13]. The activity of the coatings of sets I – IV (Table 7.2) for all four series appear to be independent on the cobalt concentration in the ion exchange solutions, i.e. the Co/Al ratio. These results suggest that all available sites in the coatings were occupied by Co ions already after exchange with the lowest cobalt concentration of 7.5 ·10⁻⁵ M (Set I of Figure 7.1). This concentration is more than two orders of magnitude smaller than that in solutions used for pelletized catalysts with a similar degree of ion-exchange.

Figure 2 shows the TOF values of the coatings of series A – D after an ion exchange procedure with a cobalt concentration of 7.5 ·10⁻⁵ M (Set I). The lower TOF value of Co-ZSM5-20-0.78 compared to Co-BEA-23-0.85 may be due to both the larger average crystal size (Table 7.1) and the lower diffusivity of the reactants in ZSM-5 micropores as compared to the large pore sized zeolite Beta crystals. Moreover, different local cobalt environments are obtained in the ZSM-5 and zeolite Beta crystal lattice, that is the specific cobalt coordination in the negatively charged framework, which affects the cobalt-ligand interaction and consequently its turnover frequency in acetonitrile formation. The activity of the Co sites increases with decreasing Si/Al ratios from 23 to 15 in the zeolite Beta coatings.
Figure 7.2 TOF values of the Co-BEA and Co-ZSM-5 coatings of set I (see Figure 7.1) of series A – D. Conditions are the same as those in Figure 7.1.

(Series A, B, C in Figure 7.2). The opposite trend in the yield of acetonitrile was observed on cobalt exchanged pelletized zeolite catalysts at lower Si/Al ratios between 12 and 2 [3]. Zeolite Beta with Si/Al ratios below 10 has a relatively large number of crystallographic defects, yielding the undesired Al Lewis acid sites for the ammoxidation reaction [19]. Therefore, an optimum Si/Al ratio for zeolite Beta in ethylene ammoxidation is expected to be between 10 and 15. In this range, the formation of cobalt-ligand species required for the ammoxidation reaction is maximized by providing an optimal interaction between the Co$^{2+}$ ions and the negative framework oxygen ions [20].

This optimal interaction seems to be distorted by addition of the electron deficient boron cations. Boron ions partially compensate the negative charge of the zeolite lattice and decrease the bonding of the cobalt ions to the zeolite framework. As a result, the acetonitrile yield decreases (compare sets V-VII with I-IV in Figure

Figure 7.3 Activity and product selectivity of the Co-BEA-15-0.65 coating (set I, series B) as a function of the reaction temperature. Product Y denotes an unknown C$_1$ containing product. Conditions: see Figure 7.1.
A rather strong cobalt bonding is required for zeolite Beta with Si/Al above 15, whereas a weaker cobalt bonding is desirable at Si/Al ratios below 12 [3].

The effect of reaction temperature and contact time on reaction rate and selectivity was investigated on Co-BEA-15-0.65 (Figure 7.3). The maximum reaction rate of 530 μmol g⁻¹ s⁻¹ (TOF = 0.8 s⁻¹) was observed at 500°C, which is higher than that reported on Co-ZSM-5 pellets (488 μmol·g⁻¹·s⁻¹) at this temperature [21]. The higher activity is due to the absence of macropore diffusion limitations in the coatings [7]. However, the highest C-selectivity (S_c) to acetonitrile was only 58% which is 1.4 times lower than that reported by Li and Armor [2]. Furthermore, methanol was formed on the coatings with a selectivity of 15%, which was not observed as a product on pelletized Co-Beta catalysts. In the presence of water, methanol can be formed by reaction (7.3) on two adjacent bivalent cations [16]:

\[
\text{CH}_3\text{CN} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCN} \tag{7.3}
\]

The C-selectivity to acetonitrile was rather constant over a large range of contact times, while an optimal activity was observed at a GHSV of 5·10⁵ h⁻¹ (Figure 7.4). A constant N-selectivity (S_N) to nitrogen of 80% was obtained confirming selective oxidation of ammonia at the applied reaction conditions.

### Conclusions

Optimal compositions of Co- and Co-B-exchanged zeolitic coatings were found for the ammoxidation of ethylene to acetonitrile. Zeolite Beta is preferred over ZSM-5 because of the better accessibility of the active Co²⁺ sites. By increasing the Al content of the zeolite Beta coatings from a Si/Al ratio of 23 to 15, the catalyst...
activity improved by a factor of 6. The addition of small amounts of boron negatively affected the catalyst performance.

The zeolitic coatings showed remarkable differences with pelletized zeolite catalysts. The concentrations of the ion exchange solutions used for Co-zeolitic coatings was typically a factor of 100 smaller than used for pelletized Co-zeolite catalysts. A maximum TOF of 0.8 s\(^{-1}\) and C-selectivity to acetonitrile of 58% were obtained on coating Co-BEA-15-0.65 at 500°C. The Co-zeolitic coatings showed a reaction rate, which was 8% higher than that of a pelletized catalyst. Finally, a selectivity to methanol of 15% was observed for Co-zeolite coatings, while pelletized catalysts did not show methanol formation.

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Bibliography

Conclusion

8.1 Conclusions

In this thesis, a microreactor was developed for the high-throughput screening of catalytic coatings for potential microreactor applications. The reactor was applied in the screening of Co-Beta and Co-ZSM-5 coatings in the highly exothermic ethylene ammoxidation.

A microreactor is a device that enables chemical reactions to be performed on the micro- to milliliter scale. The extremely large surface area-to-volume ratio within microreactors is the main contributor to their intrinsic benefits, as high heat and mass transfer rates, a well defined laminar fluid flow profile, and a close contacting of the chemical reactants with the catalytic coatings at the walls of the reactor channels. Therefore, microreactors are in particular suited for highly exothermic and fast reactions allowing temperature control and isothermal operation in contrast to conventional reactor systems. Consequently, microreactors can be used as a tool for intrinsic kinetic measurements and complex mechanistic studies. Moreover, the small reactor volume provides fast response and analysis times, and inherently small amounts of waste, which make microreactors a natural platform for high-throughput screening studies of catalysts. In such rapid catalyst development and optimization trajectories, the time-to-market of novel chemical products or improved chemical processes can be reduced considerably.

The molybdenum based high-throughput microreactor (HTMR) consists of eight microstructured compartments, in which different catalytic coatings can be screened in parallel at realistic process conditions. All essential reactor design issues of a microreactor as fluid flow distribution, isothermal reactor conditions, and sampling of product gases as well as the geometries of the separate reaction sections were optimized using three-dimensional computational fluid dynamics (CFD) simulations. The results of the CFD simulations of fluid flow, temperature,
and concentration distributions used in the design show a good agreement with experimental data in all cases. A novel concept of a low-pressure drop fluid flow distribution header was applied for flow equalization in the reactor compartments. The flow distributor has a structured geometry, *viz.* a thick walled screen, of which the elongated rectangular channels are positioned with a 90° turn relative to the reactor compartments. The flow non-uniformity is below 2% in the range of Reynolds numbers of 6 – 113, which was validated by Laser Doppler Anemometry. The axial and radial temperature non-uniformity in the HTMR was below 3 K in ethylene oxidation at 425°C over CuO/Al₂O₃/Al coatings. Furthermore, a deviation of only 2.3% was obtained in the average rate of reaction at realistic screening conditions in ethylene ammoxidation over identical Co-ZSM-5 coatings in all reactor compartments. Finally, the cross talking noise of product gases in the adjacent reactor compartments was minimized below 0.1% according to the CFD model when the sampling capillaries were positioned at least 4 mm inside the reactor compartments, and the gas flow profile in the reactor outlets was not disturbed (iso-kinetic suction intake).

Generally, this microreactor development trajectory illustrates the importance and relevance of a proper design prior to the actual microfabrication of the reactor’s parts and their assembling. It shows that full 3D CFD design of the reactor allows for a proper evaluation of all relevant design issues (choice of reactor material, geometries, length of sampling capillaries, etc.) as well as for a detailed study of all relevant physical phenomena (flow distribution, mass and heat transport, axial dispersion, etc.). The clear advantage of CFD-based microreactor design is that it allows taking full advantage of the microscale in optimizing the reaction conditions. This work also illustrates that a proper in-depth study of the mass and heat transport taking place in the reactor provides guidelines for the actual required micromachining precision. Most often it will be needed to design tailor-made microreactors for each particular reaction or microprocessing application. Using off-the-shelf available parts (flow distributors, mixers, reaction compartments, etc.) for assembling a complete microreactor for a particular reaction may not provide the optimum configuration, leading to lower selectivities and yields.

The HTMR concept was demonstrated in the screening of zeolitic coatings in ethylene ammoxidation to acetonitrile. The hydrothermal synthesis of zeolites on a substrate is an elegant method to obtain thin zeolitic coatings, which are chemically bonded to the surface of the substrate. A general method was developed for the *in-situ* crystallization of zeolite crystals on a metal substrate, which was applied for zeolite Beta and ZSM-5 coatings on a molybdenum (Mo) substrate. Prior to the hydrothermal synthesis, the surface of the substrate was modified by an etching procedure which increases the roughness at the nanoscale
level. The larger number of irregularities on the surface increases the positions where zeolite crystals can nucleate or anchor. Subsequently, thin films of Al$_2$O$_3$ (170 nm) and TiO$_2$ (50 nm) were successively deposited by atomic layer deposition (ALD) on the substrate. The internal Al$_2$O$_3$ film protects the Mo substrate from oxidation up to 550°C in an oxidative environment. A high wettability of the external TiO$_2$ film after UV irradiation increases zeolite nucleation on its surface. A superhydrophilic behavior for at least 3 h was obtained after UV irradiation of the TiO$_2$ surface.

Highly crystalline zeolite Beta coatings in a range of Si/Al ratios of 10 – 25 were synthesized on the surface modified molybdenum substrate by hydrothermal synthesis. The coatings were obtained from a viscous Na, K, and TEA containing aluminosilicate precursor mixture with silica sol as reactive silicon source. A mechanism for the *in-situ* growth of zeolite Beta coatings was proposed. According to this mechanism, the deposition of an amorphous gel layer on the substrate surface in the initial stage of the synthesis is an important step for the crystallization of continuous zeolite Beta coatings. The heating rate of the precursor mixture and the synthesis temperature were optimized to control the level of supersaturation and to stimulate the initial formation of a gel layer. The synthesis conditions were optimized to obtain coatings varying from a single layer of zeolite Beta crystals up to a layer thickness of 5 μm in the whole range of Si/Al ratios studied. ZSM-5 coatings in a range of Si/Al ratios of 16 – 50 were also synthesized on TiO$_2$/Al$_2$O$_3$/Mo substrates from a Na, TPA containing synthesis solution with TEOS as silicon source. The thickness of the ZSM-5 coatings can be adjusted from a single crystal layer to a multi layer with a thickness of 45 μm by applying different H$_2$O/Si ratios.

The application of zeolitic coatings in the HTMR required a scale-up of the hydrothermal synthesis procedure to obtain a large number of identical zeolitic coatings. The scale-up procedure was demonstrated for the *in-situ* synthesis of ZSM-5 coatings on a set of 72 TiO$_2$/Al$_2$O$_3$/Mo substrates with dimensions of 40 × 9.8 × 0.1 mm$^3$ in a total synthesis volume of 3L. A coverage of 14.8 ± 0.4 g m$^{-2}$ was obtained on all plates in the scale-up procedure. The low deviation per individual plate (< 3%) indicates the uniformity of the synthesis conditions in the scale-up procedure.

Finally, the activity and selectivity of various series of Co-ZSM-5 and Co-BEA coatings (Si/Al = 15 – 23) with a thickness of 1 μm were determined in ethylene ammoxidation. A high-throughput screening of the zeolitic coatings was performed in the HTMR in a wide range of reactant partial pressures and temperatures to optimize the coating composition as well as the reaction conditions. Zeolite Beta coatings are more than two times as selective towards the acetonitrile formation than ZSM-5 coatings at Si/Al ratios of approximately 23. The
rate of acetonitrile formation increased by a factor of 6 by decreasing the Si/Al ratio from 23 to 15. The effect of the Co/Al ratio was less pronounced. The addition of small amounts of boron decreased the selectivity to acetonitrile in the whole range of Si/Al ratios studied.

Generally, the zeolitic coatings showed remarkable differences with pelletized zeolite catalysts. The concentrations of the ion exchange solutions used for Co-zeolitic coatings was typically a factor of 100 smaller than used for pelletized Co-zeolite catalysts. A maximum TOF of 0.8 s\(^{-1}\) was obtained at 500°C on zeolite Beta coatings with Si/Al and Co/Al ratios of 15 and 0.65, respectively. This rate of reaction is about 10% higher than that of a pelletized Co-zeolite catalyst, which is attributed to the absence of transport limitations in the thin zeolitic coatings. Decreasing the Si/Al ratio further in the range of 12–15 will result in an optimum activity of the coatings. Finally, a selectivity to methanol of 15% was observed for Co-zeolite coatings, while methanol formation was not observed on pelletized catalysts.

### 8.2 Outlook

Today, microreactor engineering is becoming a mature scientific exponent of chemical engineering. Although related topics can be traced back sporadically almost half a century ago, the discipline of microreactor engineering is in increasing extent in development for approximately a decade now. The International Conference on Microreaction Technology (IMRET) was organized for the first time in 1997, and because of its success, in 2007 the 10\(^{th}\) edition will take place. Research in this area is still expanding (Figure 8.1), because of the unique characteristics of microreactors, and their potential in versatile applications.

![Figure 8.1](image_url)  
**Figure 8.1** The total number of publications and patents on microreactors in the period of 1990 to 2006. Search engine: Scifinder.
Currently the research tends to shift from the explorative and characterizing field to more industrial relevant research topics and a stronger focus on commercialization and real applications. The increasing number of patents in this field clearly shows the commercial interest (Figure 8.1). A recent industrial example is the design and cost analysis of a new site for the production of hydrogen peroxide of 150,000 tons per year, which is based on the direct contacting of hydrogen and oxygen in the presence of a heterogeneous noble metal catalyst in microstructured mixing units [1].

The use of microreactors in future can be divided hypothetically in two areas, *vūz.* (1) as a measurement instrument in laboratories, and (2) as production units for chemicals manufacturing or processing for specific applications. As laboratory tools, microreactors can be used for example in kinetic studies, the screening of catalysts or catalytic coatings, and exploration of novel reaction pathways for economically and environmentally benign solutions to chemical manufacturing. For such applications complex and innovative microreactor designs are often required to access the chemical or physical regimes of interest or to match the specific practical demands of the application. For example, reaction and cooling channels were integrated in an aluminum block to obtain near isothermal reaction conditions required for a kinetic study of the strongly exothermic ammonia oxidation over a Pt-Al₂O₃ catalyst [2, 3], or the development of a high-throughput microreactor for the screening of catalytic coatings described in this thesis. With respect to the development of microreactors for production purposes the trend should be more towards the design and fabrication of simpler devices, which are robust, cheap, easily exchangeable after failure during operation, and stable in time. Microreactors have to be constructed of materials which are not sensitive to corrosion or erosion and of which the surfaces and the interior volume can be treated with ultra-precision microfabrication tools. Furthermore, microreactors have to be integrated with sensors and actuators for process control purposes, and the lack of experience with respect to their long-term operation has to be dealt with. Finally, methods have to be further developed and/or optimized to deposit catalytic coatings that preserve their activity during operation and that remain firmly attached to the walls of the microchannels to prevent pore-plugging and loss of microreactor performance. Therefore, a multi-disciplinary approach is desired for a successful route to real applications, in which material, electrical, and chemical engineers and chemists work closely together. In such an approach the transition from research objectives to practice becomes feasible in case microreactors offer a clear benefit over convention reactor types.

Reactor modeling and analysis remains of eminent importance to provide in-depth insights of the operating characteristics of microreactors, as well as to evaluate the “pro and cons” associated with innovative microreactor designs.
Computational fluid dynamics (CFD) software packages are commercially available, which can be used both for quantification of the various aspects of microstructured reactors in the design phase, and for interpretation of data in the experimental phase. Even though idealized assumptions have to be made in the three-dimensional CFD models, a good correspondence with experimental observations should be obtained in practice, since all physical parameters are known and the basic transport equations for laminar flow inside the microchannels are well established. Various studies [4 – 6] proved the importance of the design of microreactors through simulation prior to fabrication and experimentation as was also demonstrated in this thesis (Chapters 2 and 3). Such a design approach can avoid costly, iterative experimental design processes where components are fabricated, tested and then redesigned to improve performance. Finally, a successful fabrication and operation of microreactors can only be obtained when both these processes are in agreement with the boundary conditions set in the CFD models, i.e. avoid interfaces or specify the machining characteristics, and have a full control of the reactor conditions as well as its interaction with the environment, respectively.

Despite the development of innovative microreactor design and its fabrication, the microreactor performance is often limited by the activity of the state-of-the-art catalysts. In principle the catalysts remain the workhorse in heterogeneous chemical processes, independent of the reactor size and its sophistication. Therefore, methods need to be developed and optimized for both the deposition of the thin catalyst support layers and the incorporation of active elements within these layers, i.e. catalytic coatings. Subtle differences in the properties of the catalytic coating, such as the elemental composition, the porosity, and the crystallinity of the catalyst support layer as well as the amount, ratio and oxidation state of the active elements, can change its performance dramatically. In this sense high-throughput screening studies at realistic process conditions are of prime importance in microreactor engineering in order to investigate a large number of catalytic parameters in a systematic approach focused on microreactor performance. Furthermore, the effect of the substrate on the catalytic coating properties has to be investigated in more detail. Numerous parameters may affect the coating properties in the preparation phase, such as the purity of the substrate and thus the amount of trace elements, the size and scale of the substrate, electrostatic forces in ionic solutions, gravitational forces in dispersions or gels, electric and heat conductivity of the substrate material, surface hydrophilicity and roughness, etc. Moreover, the substrate may also affect the catalytic activity of the coatings in numerous ways, such as by having an electron deficient or donating nature, the porosity and roughness of the substrate, the occasional use of additives to obtain a strong bonding with the substrate, etc. In addition also the long-term
activity of the catalytic coatings is an important issue, since a slow migration of elements from the underlying substrate into the catalytic coating can occur, e.g. in silicon based microreactors at elevated temperatures. Finally, the effects of the physical properties of the coatings on the fluid flow in microchannels have to be addressed. The high surface area-to-volume ratio within microchannels induce that surface acting forces, as surface tension, become dominant over volume acting forces, as inertial forces. Therefore, especially for liquid phase processes, the hydrophilic or hydrophobic nature of the catalytic coatings determines the fluid flow profile in- and filling of the microreactor channels.

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List of publications

Patents

Publications


Oral presentations


6th European Conference on Catalysis (Europacat VI), Innsbruck, Austria, September 2003.

Poster Presentations
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Martijn Mies was born on the 2nd of February 1976 in Oudenbosch. In 1994 he received his diploma of the secondary grammar school “Thomas More College” in Oudenbosch. In September of that year he started with his chemical engineering studies at the “Hogeschool West-Brabant” in Breda, where he received his B.Sc. degree in 1998. He continued his education at the Eindhoven University of Technology for a study in Chemical Engineering and Chemistry, where he received his M.Sc. degree in 2001 on the topic “Liquid Phase Phenol Oxidation over Platinum Supported Catalyst”. In November 2001 he started his Ph.D. research at the Laboratory of Chemical Reactor Engineering of the Eindhoven University of Technology under supervision of dr. E.V. Rebrov, dr. M.H.J.M. de Croon, and prof.dr.ir. J.C. Schouten. Since March 1st 2006 he works as a research scientist at Albemarle Catalysts in Amsterdam.