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Miniaturization of Heterogeneous Catalytic Reactors: Prospects for New Developments in Catalysis and Process Engineering

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Abstract: This paper gives an overview of the research done since 1999 at Eindhoven University of Technology in the Netherlands in the field of miniaturization of heterogeneous catalytic reactors. It is described that different incentives exist for the development of these microstructured reaction systems. These include the need for efficient research instruments in catalyst development and screening, the need for small-scale reactor devices for hydrogen production for low-power electricity generation with fuel cells, and the recent quest for intensified processing equipment and novel process architectures (as in the fine chemicals sector). It is demonstrated that also in microreaction engineering, catalytic engineering and reactor design go hand-in-hand. This is illustrated by the design of an integrated microreactor and heat-exchanger for optimum performance of a highly exothermic catalytic reaction, *viz*. ammonia oxidation. It is argued that future developments in catalytic microreaction technology will depend on the availability of very active catalysts (and catalyst coating techniques) for which microreactors may become the natural housing.

Keywords: Catalytic coating · Integrated microreactor/heat-exchanger · Micro fuel processing · Micro reaction systems · Process intensification

1. Introduction

In recent years microfabrication technologies have been introduced in the fields of chemistry and chemical process engineering to realize microchannel devices, *e.g.* mixers and reactors, with capabilities considerably exceeding those of conventional macroscopic systems [1][2]. Microreactors have reaction channels with diameters of the order of 100 μm and channel lengths of about 1–10 mm with an inherently large channel surface-area-to-volume ratio. These properties offer clear advantages such as high mass and heat transfer rates (beneficial for high selectivities and conversions and good heat control) and low hold-ups (excellent controllability, small safety risks and low environmental impact). This makes these microreaction devices specifically suitable for highly exothermic reactions, short contact time reactions, and for the on-demand and safe production of *e.g.* toxic and hazardous chemicals.

There are very challenging opportunities for applications of microchemical systems and reactors [3]:

i) **High-throughput Catalyst Screening:**
Microreactors are the natural platforms for parallel screening and high-throughput testing of large numbers of new catalysts, catalyst compositions (combinatorial catalysis), and catalyst coating techniques, while they also provide efficient tools for generation of intrinsic kinetic data needed for process development and design. In this application microreactors are considered as efficient research instruments that can be used in the laboratory to explore the optimum operation conditions for a certain reaction system.

ii) **Microfuel Processing:**
Recent developments show that microchemical systems offer clear opportunities for small-scale fuel processing and portable power generation, for example to replace battery packs in laptops or mobile phones. Here systems of microreactors are used to convert liquid or gaseous fuels like methanol or methane to hydrogen that is fed to fuel cells. The challenge is to develop microchemical systems in which all reaction steps are optimally integrated, in combination with appropriate sensors and actuators for process monitoring and control.

iii) **Process Intensification:**
Finally, microreactors have the potential for safe, continuous but flexible production of (fine) chemicals and pharmaceuticals in novel process architectures which may open up new and efficient synthesis routes. This application fits into foresight scenarios that aim at process and equipment intensification, flexibility and ease of use in chemicals production, and at production of end-

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products closer to the customer. This so-called distributed or on-site production of small amounts of chemicals seems to be possible with compact microreactor units and mini-plants.

Of course, at present there are still many practical problems associated with the potential of microchemical systems as chemicals production devices, such as plugging and fouling of microchannels, cost and availability of microreactor modules, lack of reliable catalyst coating techniques, supply and removal of reactants and products, use of reliable sensors and actuators for process monitoring and control, and last but not least production capacity and scale-up. However, a tremendous effort is being made by many academic, governmental, and industrial research groups [3] to push the technology forward while at the same time successful commercial applications of micro and miniature devices have already been realized.

At Eindhoven University of Technology, research on microreaction technology was started in 1999, initially with the focus on heterogeneous catalytic, gas phase systems. Research is carried out on (i) the development of zeolite catalyst coatings in microchannels, (ii) the application of microreactors for fuel processing and small scale fuel cell grade hydrogen production, and (iii) the application of microreactors for process intensification, in particular to enhance heat transport to avoid hot spots and to obtain an even temperature distribution to control selectivity and to increase conversion and production rates. In this paper, a short overview of this work is given with a particular focus on the development of an integrated microreactor and micro heat-exchanger for a catalytic, highly exothermic reaction as an example of the possible role of microtechnology in process intensification.

2. Zeolite Catalyst Coating in Microchannels

An elegant way to prepare catalytically active microreactors is to apply a coating of zeolite crystals onto a metal microchannel structure. Over the past decades, zeolite catalysis has expanded into the areas of synthesis of toxic and fine chemicals. Microreactors could very well be used for on-the-spot manufacture of chemicals that are required in small quantities like fine chemicals. Although the added value of fine chemicals is usually high, the market demand is relatively small compared to petrochemicals. Nowadays, this industry segment is growing at a rate which is higher than the industry average, but the production processes used are still mainly stoichiometric instead of catalytic. In some of them, the amount of waste produced exceeds that of the product by orders of magnitude. Obviously, replacing stoichiometric processes by catalytic ones will have a tremendous impact on the reduction of by-products. Several reactions are already performed *via* zeolite-based catalysts that involve the synthesis of fine chemicals. Zeolite crystals can be organized within a microchannels framework with a high spatial precision on the micrometer scale. Owing to the difficulty of synthesizing large zeolite monocrystals, various literature studies focus on the preparation of zeolitic thin films by depositing (*exsitu*) or *insitu* growth of crystals. However, obtaining a uniform thickness of the coating requires a careful control of the synthesis mixture characteristics (type and concentration of starting materials, amount of water, *etc.*), and of the procedures of coating and thermal treatment. When well-known zeolite synthesis techniques are used to obtain a zeolitic coating adherent to a substrate, there is a tendency for crystallization in the liquid synthesis medium. Then, due to the gravity, crystals formed will settle on the surface of a substrate rather than adhering to it.

In co-operation with Delft University of Technology, we have investigated the hydrothermal formation of ZSM-5 zeolitic coatings on AISI 316 stainless steel plates with a microchannel structure at different synthesis mixture compositions [4] (Fig. 1). The procedures of coating and thermal treatment have also been optimized. Obtaining a uniform thickness of the coating within 0.5 mm wide microchannels requires a careful control of various synthesis variables. In general, the synthesis is most sensitive to the H_2O/Si ratio as well as to the orientation of the plates with respect to the gravity vector. Ratios of $H_2O/Si = 130$ and Si/template = 13 were found to be optimal for the formation of a zeolitic film with a thickness of one crystal at a temperature of 130 °C and a synthesis time of about 35 h. Under such conditions, ZSM-5 crystals were formed with a typical size of $1.5 \times 1.5 \times 1.0\ \mu m^3$ and a very narrow (within $0.2\ \mu m$) crystal size distribution. The prepared samples proved to be active in the selective catalytic reduction (SCR) of NO with ammonia. The activity tests have been carried out in a so-called plate-type microreactor [4]. The microreactor shows neither internal nor external mass transfer limitations and a larger SCR reaction rate is observed in comparison with pelletized Ce-ZSM-5 catalysts under similar conditions.

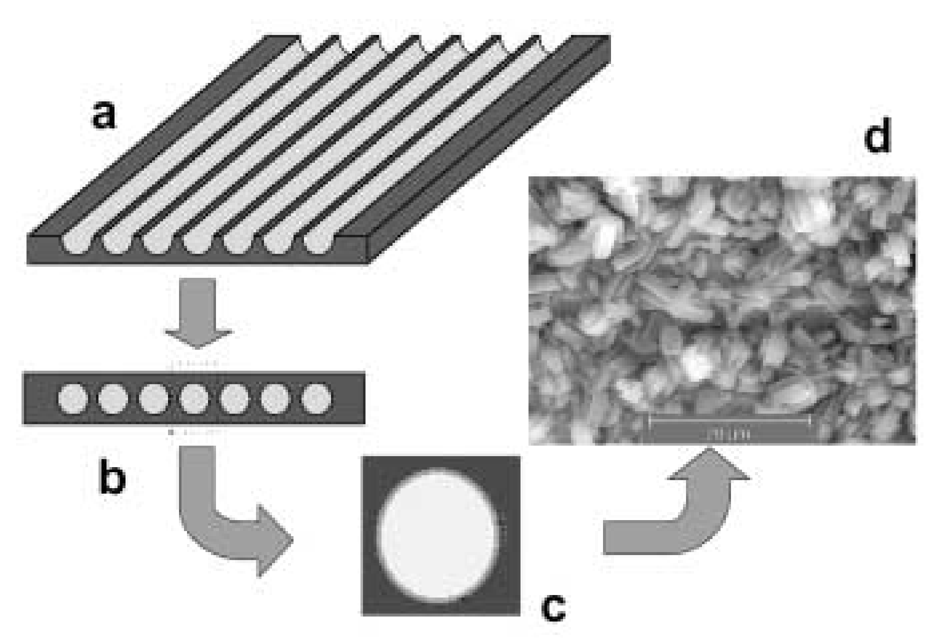

Fig. 1. Schematic representation of AISI 316 stainless steel plates with microchannel structure. (a) Isometric view of one plate with semicircular microchannels. (b) Front view of two plates sealed together. (c) Single microchannel with zeolitic coating. (d) Scanning electron micrograph of zeolitic coating.

3. Micro Fuel Processing

3.1. *Silicon-based Microreactor for CPO Kinetic Studies*

This work focuses on the development and application of a silicon-based microreactor to study the intrinsic kinetics of the catalytic partial oxidation (CPO) of methane to hydrogen and carbon monoxide. CPO is considered an efficient way to

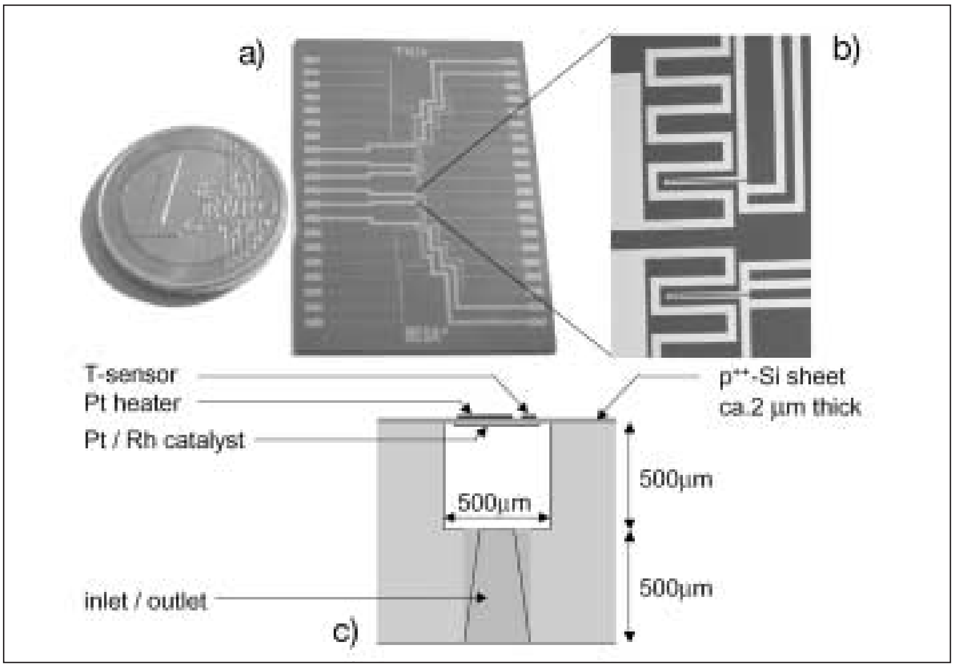

Fig. 2. (a) Prototype of a silicon-based microreactor (30 × 45 mm) fabricated from two silicon wafers. This prototype is used to quantify the heat and mass transfer in the 500 µm diameter, 30 mm long microchannel. A second prototype with a rhodium catalytic layer will be used to study the kinetics of the catalytic partial oxidation of methane to synthesis gas. The grey lines are platinum wires. Near the long edges of the reactor device, the lines end in pads for connections to a printed circuit board. In the middle of the reactor device, these platinum wires form five heating sections and twelve temperature sensors on top of a silicon sheet that covers the reaction channel. (b) Enlargement of part of the heater and temperature sensor structures. The thick meandering lines (50 µm wide) are platinum heater elements and the tiny loops (10 µm wide) are two platinum temperature sensors. (c) Schematic representation of a cross-section of the microreactor device. The reactant gas inlet and the product gas outlet are situated at the bottom in a second silicon wafer.

synthesize hydrogen from gaseous or liquid fuels, as needed in fuel cells for electricity production, after water-gas shift and selective CO oxidation or purification by means of membranes to remove the carbon monoxide. The CPO reaction requires contact times in the order of milliseconds, and therefore a microreactor is very suitable to study the kinetics as the reacting species typically have a residence time of this order of magnitude. The microreactor used (Fig. 2) is made from silicon wafers at the MESA$^+$ Research Institute (University of Twente, Enschede, the Netherlands) using lithographic techniques [5]. It is positioned in an aluminum housing with the appropriate electrical connections for the temperature sensors and heating wires. The reactor has a square reaction channel with a diameter of 500 µm and a length of 3 cm. The top wall of the channel is formed by a thin silicon sheet with a thickness of 1.9 µm. This thin top layer will allow a good thermal contact between the rhodium catalyst beneath it and the five platinum heating wires and twelve platinum temperature sensors on top of it.

The first prototype device, as shown in Fig. 2, does not contain the catalytic layer yet as it is first being used for a study of the heat transport characteristics and the temperature distribution. The heat produced by the heating elements on top of the covering silicon sheet mimics the asymmetric heat production in the microchannel by the exothermic CPO reaction. Computational fluid dynamic simulations are performed to determine the heat and mass transport characteristics under laminar as well as plug flow conditions. These simulations are experimentally validated by comparing the simulated and measured temperature difference between the top wall and the side walls at different levels of the power supplied to each of the five heaters (Fig. 3). From the simulations, empirical Nusselt and Sherwood correlations are derived that are a function of the Graetz number which is dependent on the axial reactor coordinate [5]. It is found that the flow profile is being developed along a considerable part of the microchannel. For both laminar flow and plug flow conditions, a heat flux reversal is observed on the side and bottom walls of the microchannel when the temperature of these walls is higher than the gas inlet temperature. When the inlet gas temperature is equal to the temperature of the side and bottom walls, the asymptotic value of the Nusselt number is the highest. In case of using the microreactor for a kinetic study, this condition is preferred as a high Nusselt number results in a high heat transfer coefficient, reducing the influence of heat transfer limitation on the reaction kinetics. The Nusselt and Sherwood correlations are used to readily quantify the heat and mass transport in this microreactor to support the kinetic CPO study.

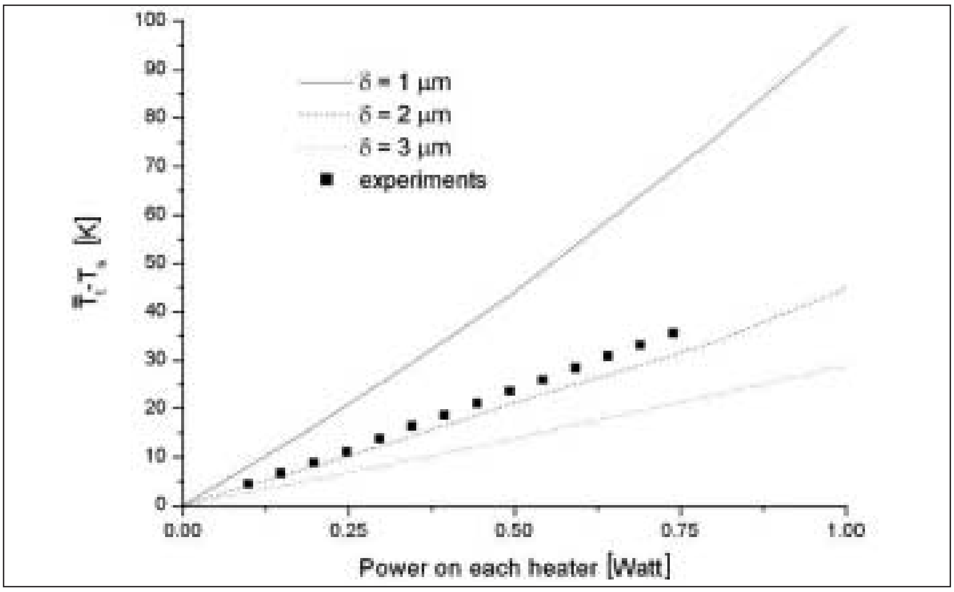

Fig. 3. Difference between the temperature T_t of the top wall of the microchannel as measured with the platinum temperature sensors and the measured temperature T_s of the side walls as a function of the electric power supplied to each of the five heater sections on top of the microchannel (see Fig. 2). The data points are experimental data, the lines are obtained from computational fluid dynamic simulations with the FLUENT® code for different top wall thickness δ.

3.2. *Micro Reactor Technology for Hydrogen and Electricity – MiRTH-e.*

The European Union funded project MiRTH-e focuses on the design, micro-fabrication, and testing of a miniaturized, integrated fuel processor for the conversion of methanol to clean, fuel-cell grade hydrogen for low-power (20–100 W_e) electricity generation. This work is done in a co-operation of six project partners, *i.e*. Shell Global Solutions International, Institut für Mikotechnik Mainz (IMM), $MESA^+$ Research Institute, Netherlands Energy Research Foundation (ECN), Laboratoire des Sciences du Génie Chimique (CNRS), and Eindhoven University of Technology (TU/e) [6]. The low-power micro fuel processor should provide hydrogen for use in low-temperature proton exchange membrane (PEM) fuel cells. The integrated unit will provide a portable power source and is an alternative for battery packs or hydrogen storage in metal hydrides. Possible applications will be in laptop computers, portable TVs, camping site equipment, and lawn mowers. As indicated in Fig. 4a, the fuel processor will consist of a vaporizer and three catalytic microreactors. In the methanol reformer reactor, the endothermic methanol steam reforming reaction and the reverse water-gas shift reaction take place over a copper/zinc oxide/alumina catalyst. To avoid poisoning of the fuel cell's anode catalyst, it is necessary to bring down the carbon monoxide concentration to below 10 ppm. For this purpose, a second microreactor is needed where carbon monoxide is selectively oxidized with air, using a supported noble metal catalyst. In the fuel cell, most hydrogen will be converted into heat and electricity. The leftover hydrogen from the fuel cell will be catalytically combusted in the afterburner microreactor, using a platinum/alumina catalyst, to provide the necessary energy for the reforming reaction. A pinch analysis was carried out of the complete system to derive an efficient energy integration scheme of the micro fuel processor. The process is divided into three separate combined microreactors/heat-exchangers (Fig. 4b), which all operate at different temperatures, based on an overall process efficiency of 35% (methanol to electricity) at an electrical power output of 100 W. At present the combined CO selective oxidation microreactor & heat-exchanger has been designed at TU/e and has been microfabricated at IMM and is currently being tested.

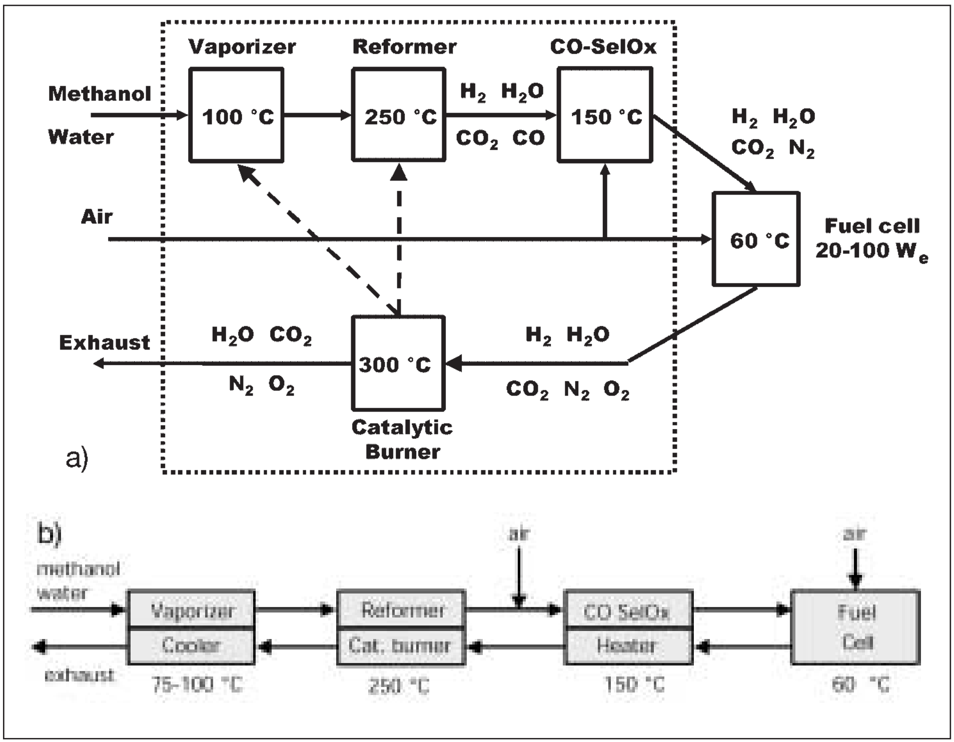

Fig. 4. (a) Basic process scheme of the MiRTH-e micro fuel processor, indicated by the dotted box, in combination with a PEM fuel cell. The heat generated in the catalytic burner of the leftover hydrogen from the fuel cell is used to evaporate and reform the methanol–water mixture. By direct feeding of methanol to the burner reactor, start-up of the device is foreseen (not shown). (b) Energy integration scheme of the MiRTH-e micro fuel processor, including the PEM fuel cell. The process is divided into three separate combined and integrated microreactors and micro heat-exchangers, which all operate at different temperatures.

4. Process Intensification by Applying Microtechnology

Recent work has demonstrated the clear advantages of applying microtechnology in the optimization of a highly exothermic reaction at conditions that were initially inaccessible [7–9]. In this overview paper we will address the different issues related to the variety of problems which have been solved to obtain the maximum yield of nitrous oxide in the platinum-catalyzed ammonia oxidation in a microstructured reactor. Nitrous oxide (N_2O) is considered as a soft electrophilic oxidant which can be used in a number of catalytic partial oxidation processes, among them one-step selective oxidation of methane to methanol and benzene to phenol. Furthermore, the choice of ammonia oxidation as a test reaction is suggested by the fact that the reaction is strongly exothermic. Therefore, the heat distribution between the catalytic surface and the gas phase along these microchannels is important to obtain the highest possible selectivity to one of the reaction products (N_2, N_2O, NO), as this is strongly dependent on the reactor temperature. The selectivity toward nitrous oxide has a sharp maximum at about 325 °C. Therefore, under steady state conditions the highest possible N_2O yield can only be obtained in the reactor operating at isothermal conditions. The choice of platinum as a catalyst is based on the highest turnover frequencies, and therefore the highest reaction rates observed in the kinetic region. In spite of the fact that some metal oxide catalysts are more attractive from the N_2O selectivity standpoint, the specific catalytic activity of oxide catalysts appears to be at least two orders of magnitude lower than that of the platinum group metals, decreasing considerably the total throughput of the microreactor. Finally, the ammonia oxidation on a Pt catalyst is structure sensitive, as the selectivity is also strongly dependent on the Pt dispersion.

Thus, the desired product yield essentially depends on the catalyst selectivity and on the microreactor operating conditions. Although all the related important aspects of the process design will be addressed, greater emphasis will be placed on the microstructured reactor design work. Due to a complex interrelation of all aspects of the problem, it seems reasonable to consider them successively. So, we shall consider: (1) main peculiarities of ammonia oxidation on platinum catalysts, (2) kinetics of ammonia oxidation, (3) factors determining process efficiency, (4) principles for designing the isothermal micro catalytic system based on mathematical modeling of ammonia oxidation.

4.1. *Main Peculiarities of Ammonia Oxidation on Platinum Catalysts*

A selective catalyst is supposed to perform a dual function: activate oxygen by generating oxygen species of proper reactivity, and activate the starting material to direct the oxidation in the desired way. Optimization of these two functions is a difficult problem, since one cannot tune them independently by varying the state of an active component in the catalysts. Often gaining in one aspect, we are losing in the other.

The platinum cluster size plays an important role in the activity of supported platinum catalysts and also it could have an influence on the product distribution to a great extent. Oxidation of ammonia on a single site is based on an Eley-Rideal mechanism. Even isolated dual sites cannot offer an optimum configuration [7], since the NH_3 oxidation requires surface sites for the adsorption of two ammonia molecules and two oxygen atoms. The formation of Pt clusters is responsible for the better performance of catalysts with the high Pt loadings in the ammonia oxidation. From the surface mechanism it can be concluded that a cluster of at least five atoms is needed to form the most favorable configuration of species in a surface complex. We observed a pronounced increase of turnover frequencies from 20 to 40 s^{-1} at 300 °C, when a catalyst containing isolated Pt atoms was substituted by the catalyst which consisted of small Pt clusters of 2.3 nm in size [7]. It was also reported that the stoichiometry of oxygen chemisorption increases by a factor 2.7 with increasing platinum crystallite size [10][11]. A variation of the turnover frequency for catalysts with platinum contents varying from 0.05 wt.% in a supported catalyst to 100% in a Pt monolith showed that there was a certain limit to the effect. Actually, the turnover frequency changed only slightly with increasing Pt loading from 1.3 to 3.5 wt.% [7], whereas a further increase of the Pt loading above 3.5 wt.% did not cause any changes in the turnover frequency.

The increase of supported platinum particle size led also to considerable changes in selectivity in the ammonia oxidation over a Pt/Al_2O_3 catalyst [7][8][12]. Large crystallites of 15.5 nm, for which over 98% of the surface atoms are plane atoms [13], exhibited low selectivity to nitrogen formation. Selectivity to nitrogen increased with decreasing platinum loading [7][8]. Based on aforementioned issues, one can conclude that an appropriate choice of the catalyst configuration is very important.

4.2. *Kinetic Study of Ammonia Oxidation in an Aluminum-based Microreactor*

So far, there has been no attempt recorded in the literature to incorporate the detailed surface chemistry of the ammonia oxidation in a reactor model. Most of the studies have been done on platinum catalysts and several reaction mechanisms have been suggested (see [8] and references herein). In all cases, the surface chemistry was approximated by a number of global steps whose rates were described by empirical rate models. However, accurate elementary step descriptions are particularly advantageous, because they provide insight into the most effective ways to improve system performance. They also provide a much better framework for extrapolation. Finally, they identify those particular sets of initial conditions in which to focus experimental efforts.

Depending on the temperature employed, the ammonia oxidation reaction passes through the following phases: (i) at low temperatures the reaction is controlled by the intrinsic surface kinetics; (ii) in the intermediate temperature region the reaction rate becomes mass transfer controlled and thus catalytic activity comparison is not valid in this region; (iii) at higher temperatures there is a significant contribution from gas phase homogeneous reactions to the overall reaction rate. However, in a microreactor, due to a very high surface-area-to-volume ratio, it is possible to eliminate gas phase reactions. Furthermore, due to the very small diameter of the reaction microchannels, the transition to the mass transfer controlled region happens at higher temperatures in comparison to ordinary reactors, making it possible to study the reaction kinetics at elevated temperatures whilst still in the kinetic mode.

If the goal is to provide the best description of a particular system where there are substantial data available, one might start assembling a reaction mechanism using the most reliable information for the individual reactions and then systematically optimizing it by adjusting rate coefficients, preferably within the error limits, to better describe the experimental database. This approach has been employed in [8] for the development of the ammonia oxidation mechanism on a Pt catalyst. Current understanding of the ammonia oxidation reaction for surface temperatures below 500 °C is that ammonia and oxygen, after adsorption on a surface, form several active adspecies which react to form N_2, N_2O, and NO. In this mechanism nitrogen-containing adspecies are assumed to occupy single 'on-top' adsorption sites, and all other species occupy adsorption sites equivalent to that of oxygen 'hollow sites' [14]. The kinetic parameters of the elementary reaction steps were determined by regression on integral data from 103 NH_3 oxidation runs over the microreactor, with NH_3 conversion, and N_2 and N_2O selectivities as the experimental responses. In general, the model predictions showed a very good agreement both with published literature data and our experimental results for ammonia partial pressures above 0.03 atm (Fig. 5).

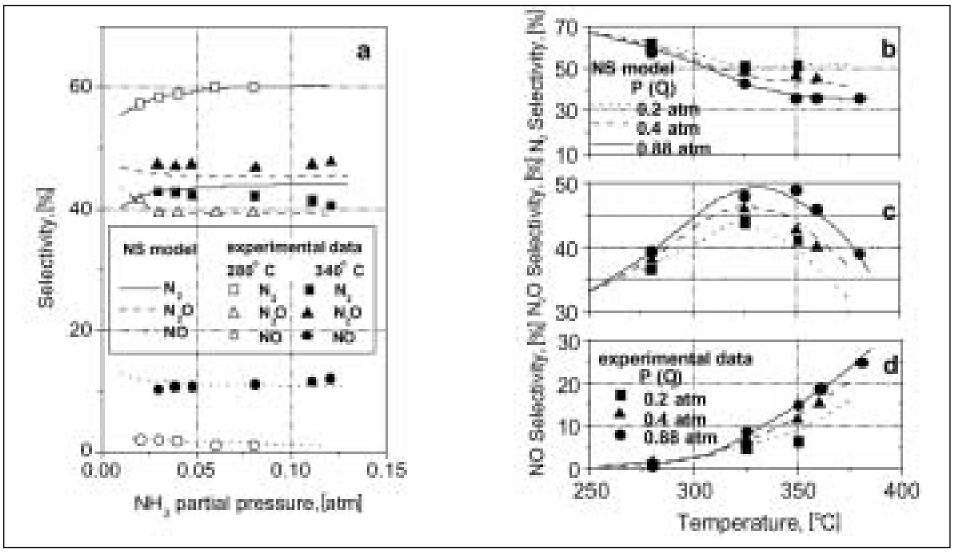

Fig. 5. Experimental data *versus* simulation results obtained with the complete Navier-Stokes (NS) reactor model including the reaction kinetics. (a) Selectivity to all end products as a function of the ammonia partial pressure. O_2 = 0.88 atm. Inlet gas mixture temperature: 25 °C. Flow velocity: 3500 cm^3/min (STP). (b-d) Selectivity to nitrogen (b), nitrous oxide (c), and nitric oxide (d) as a function of the average catalytic wall temperature for three different oxygen partial pressures. NH_3 = 0.066 atm. The other conditions are the same.

4.3. *Factors Determining Microreactor Performance*

The catalyst system used in microstructured reactors usually consists of an active component and a support/substrate. A number of materials, such as alumina, molecular sieves, solid superacids, monoliths, silica fibers, metal-oxides was reported as supports for Pt-based oxidation catalysts. The support has to provide a high dispersion of an active component. At the same time, a high thermal conductivity of the support material is important to obtain a high heat removal rate from the reaction zone. There are no support materials that can satisfy both of these requirements completely. Therefore, the best way to solve this problem is to deposit a thin coating with a high surface area on the wall of the reactor channels that are machined in a highly heat conductive material. This coating can already be catalytically active or can be used as a support for a catalyst precursor.

In our study we compared the performance of three microstructured reactors made of aluminum, nickel, and platinum. All reactors were inserted in a specially designed reactor housing shown in Fig. 6. The microreactor MR-1 consists of a stack of twenty removable aluminum plates, each with a length of 0.7 cm, a width of 0.434 cm, and a thickness of 0.03 cm, which are placed in the nickel housing at equal distances of 280 µm from each other. A 25 µm alumina layer on both sides of each plate was produced by anodic oxidation followed by platinum impregnation. The detailed view of this type of microreactor was shown elsewhere [7]. The 100% platinum microreactor (MR-2) contains 49 microchannels of 500 µm in diameter and a length of 0.9 cm produced by conventional machining in a metallic Pt cylinder with a diameter of 1 cm. The Pt reactor was positioned in the nickel housing. Each row contains seven microchannels positioned at equal distance of 500 µm from each other. The distance between the rows was also 500 µm. The aluminum-based microreactor (MR-3) is assembled from fourteen individual aluminum plates of 0.9×0.9 cm^2, and a thickness of 0.05 cm. Each plate contains seven semi-cylindrical microchannels of 280 µm width and 140 µm depth, 0.9 cm long, arranged at equal distances of 280 µm. A 25 µm alumina layer was produced in each microchannel by anodic oxidation followed by platinum impregnation. The details of the preparation procedure are given elsewhere [8]. The assembled aluminum reactor was inserted in the nickel housing.

The thermal profiles along the microchannels of the different microreactors were estimated using CFD calculations with the FLUENT® code and the kinetic mechanism of the Pt-catalyzed ammonia oxidation [7][8]. Fig. 7 demonstrates the differences between the microreactor and furnace temperatures (T_2–T_1, see Fig. 6) at the same power load of the furnace. The smallest thermal resistance is clearly associated with the microreactor MR-3. Because of the excellent intrinsic heat conductivity of aluminum (240 Wm^{-1}K^{-1}), the only significant heat transfer resistance in this case is located at the interface between the external microreactor wall and the nickel housing. For the Pt-based MR-2, due to the relatively low thermal conductivity of platinum (72 Wm^{-1}K^{-1}) compared to that of aluminum, the heat generated inside the reaction channels cannot be transferred fast enough to the cooler. As a result, at the full conversion of 6 vol.% NH_3, a hot spot of about 25 °C inside this microreactor can arise [7], which gives poor selectivity control. Although the geometry of the MR-2 is suitable to provide a high heat transfer rate, the thermal conductivity of the reactor material creates considerable heat transfer resistance. As for the MR-1, the only significant heat transfer resistance in this case is due to the relatively small contact area between the catalyst plates and the nickel housing (heat conductivity of approx. 80 Wm^{-1}K^{-1}). The result of this poor heat transfer was observed in the experiments with high ammonia concentrations. Several plates positioned in the middle of the MR-1 were melted when 12 vol.% NH_3 in the gas inlet mixture was used. In contrast to this case, in the MR-3, the radial temperature gradient (difference between furnace and microreactor temperatures) did not exceed 5 °C in all experiments. This allowed extension of the investigation to high NH_3 inlet concentrations and feed flow rates, both conditions being associated with large thermal loads. The MR-3 operated au-

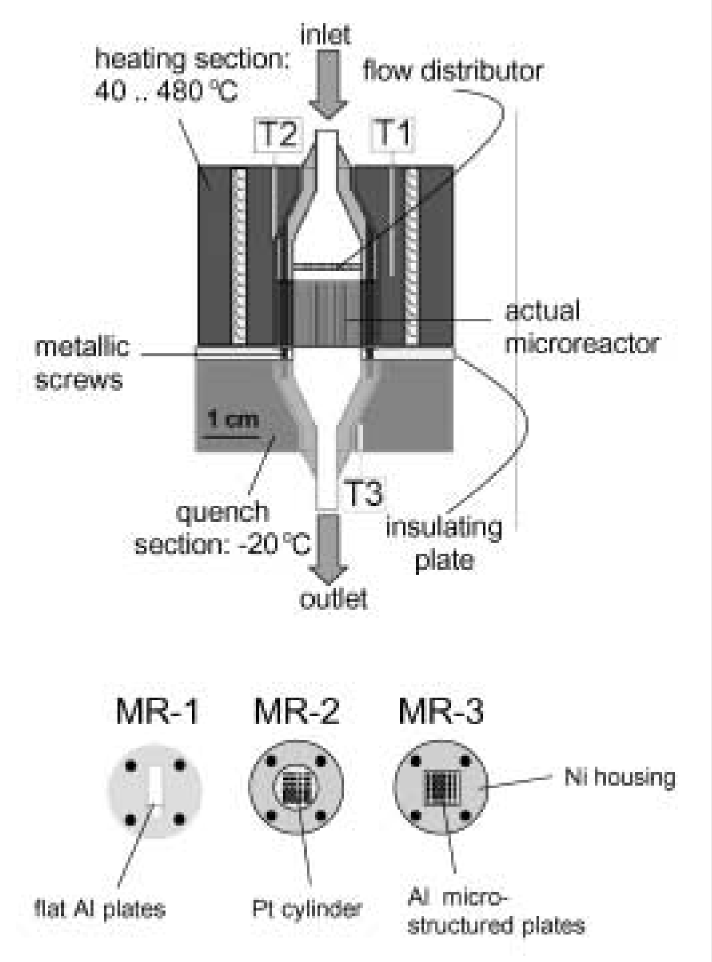

Fig. 6. Microreactor test module consisting of the actual microreactor (MR-1, MR-2, or MR-3), the furnace, and the cooler. The reactor has a nickel housing with standard tube connections and is heated by an electrical furnace. The furnace is made of copper and could provide power input up to 185 W. The temperature is measured both inside the furnace (T1) and at an outer surface of the reactor (T2). Another thermocouple is positioned on the outer surface of the cooler (T3). To isolate the cooler section from the microreactor, a 2-mm ceramic ring is positioned between the microreactor and the cooler. The temperature of the cooler is maintained at –20 °C by a circulating cooling agent in order to provide the fast removal of heat produced in the reactor zone *via* four stainless steel screws to the cooler.

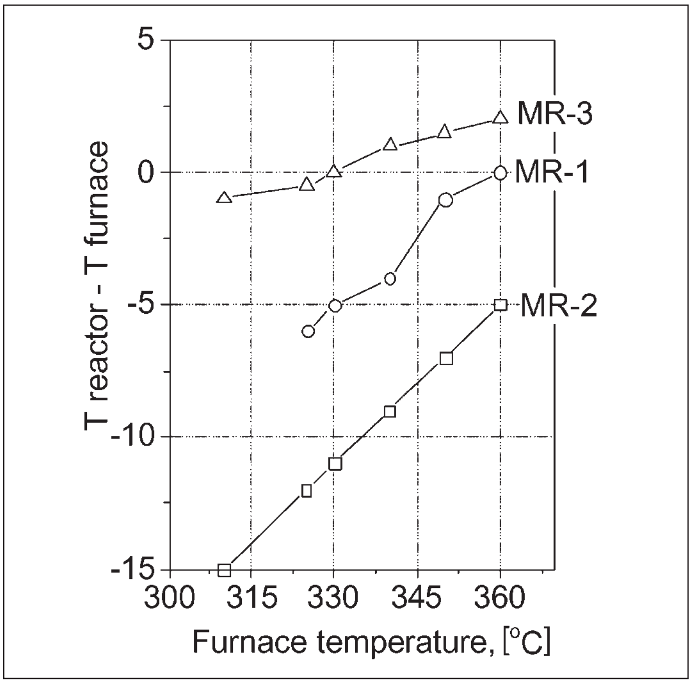

Fig. 7. The differences between the furnace and microreactor temperatures for the microstructured reactors MR-1, MR-2, and MR-3. The furnace load was kept at 90 W, the cooler was set at –20 °C. The inlet NH_3 concentration was changed to provide a desired microreactor temperature.

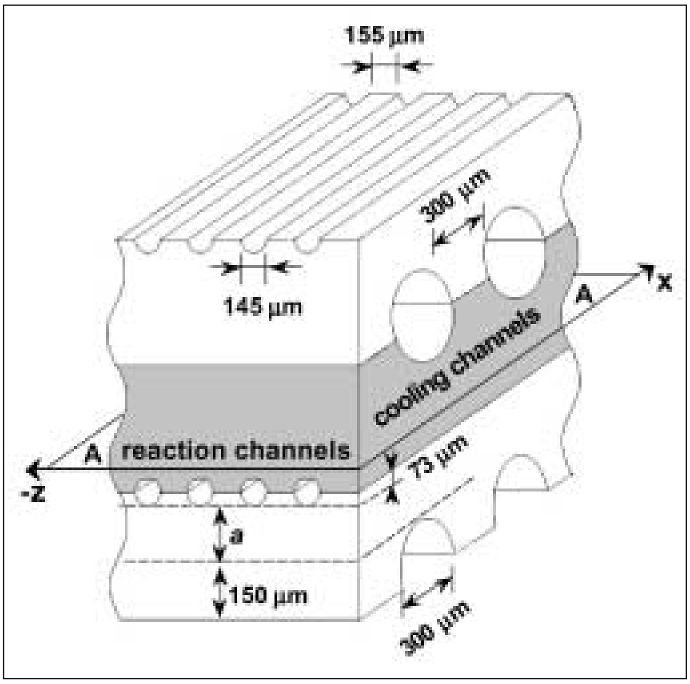

Fig. 8. Schematic view of the micro-reactor/heat-exchanger: by stacking two plates, a set of reaction channels is produced. By adding a third plate, a set of cooling channels is produced. A single periodic unit, which was the region of numerical simulation, is shown in gray. Plane A-A indicates the position at which the temperature distributions are shown in Fig. 9.

tothermally at 325 °C with 14 vol.% of NH_3 in oxygen as inlet mixture.

Summarizing, both the intrinsic heat conductivity of the reactor material and the geometry of the microreactor are crucial to provide near-isothermal conditions inside a microreactor. A microstructured reactor made with highly heat conductive metals has practically the same reaction conditions in all microchannels. This leads to an even reaction rate and considerable increase in selectivity to a desired product.

However, even in the MR-3, further increase in the inlet NH_3 concentration would also increase the reactor temperature while decreasing the N_2O selectivity. Therefore, to operate a microreactor with maximum selectivity at such conditions, a cross flow design was adopted to increase the surface that is available for heat-exchange. This design was realized in an integrated, cooled microreactor/heat-exchanger (MRHE). The feasibility of using an MRHE to carry out hydrogen oxidation in a cross flow arrangement has been experimentally demonstrated by Janicke *et al.* [15].

4.4. *Design of an Isothermal Catalytic Microreactor/ Heat-exchanger*

An axial temperature gradient of 15 °C is observed in the MR-3 at full conversion of 6 vol.% ammonia in oxygen mixture and it is caused by the varying reaction and heat production rates along the reaction channels [8]. The selectivity to nitrous oxide can be improved by decreasing the axial temperature gradient in the reaction channels. The idea is to apply a non-uniform flow distribution in the cooling channels with the maximum coolant flow close to the area of maximum heat production.

The influence of the coolant flow distribution on the temperature field was studied together with the effect of the aluminum layer thickness to find the optimal design for the MRHE. A schematic view of a part of the MRHE is shown in Fig. 8. Temperature profiles at the plane positioned at a distance of 75 µm from the centers of the reaction channels were calculated for four distances between the reaction and cooling channels at several different cross flow distributions of the coolant flow. Results of simulations for the uniform and the best non-uniform distribution are shown in Fig. 9.

One can see that for the non-uniform coolant flow distribution there is an optimal distance between the reaction and cooling channels of about 470 µm at which the temperature differences in both axial and transverse dimensions are minimal. This can be explained by the fact that changing the distance between the reaction and cooling channels produces two effects which act in the opposite way. On the one hand, increasing the distance between two sets of microchannels increases the axial heat conduction through the metal framework, thereby decreasing the temperature gradient and the difference in conversion between the 1st and 20th reaction channel. On the other hand, an increased heat conduction in the direction of the reaction channels decreases the positive effect of a non-uniform flow distribution in the cooling channels, thereby increasing the axial temperature gradient along the reaction channels. Furthermore, increased heat losses to the environment create the temperature non-uniformity between the central and outside reaction channels.

A non-uniform flow distribution in the cooling channels considerably improves the temperature field in the MRHE. The required flow distribution was obtained by appropriate designs of the inlet/outlet reactor chambers which was found by CFD simulations with the FLUENT ® code. This procedure is described in [9] in detail.

In order to validate experimentally the behavior of the MRHE, this device was constructed in the TU/e university workshop according to the developed design. The complete flow chart of the experimental set-up is shown in Fig. 10. To provide an effective mixing and preheating of the reaction mixture to the desired temperature, a micromixer combined with the inlet cham-

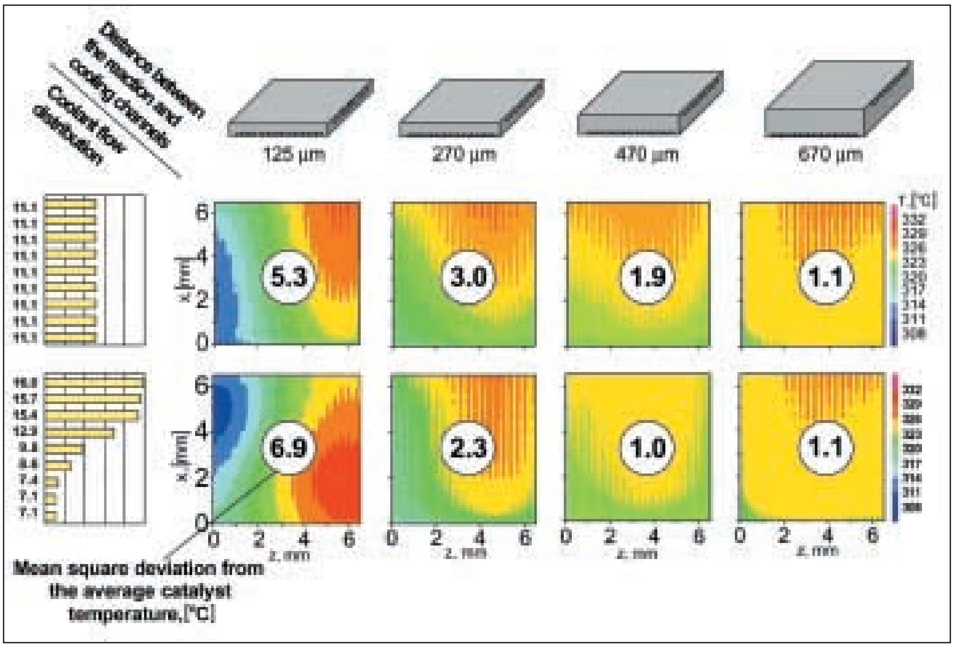

Fig. 9. Mean square deviations from the average catalyst temperature at a position of 75 µm from the center of the reaction channels as a function of distance between the reaction and cooling channels and coolant flow distributions. The reagents enter from the bottom, the coolant enters from the left. The distance between the reaction and cooling channels is shown at the top. Flow distributions in the cooling channels are shown at the left. The numbers on represent percentage of the total coolant flow. Reagent inlet gas flow velocity: 1.98 l/min, coolant flow velocity: 5.36 l/min (STP). Ammonia inlet concentration: 20 vol.%, oxygen inlet concentration: 80 vol.%. Ammonia conversion: 75%. The areas with the optimal temperature of 325 °C are shown in yellow.

ber was positioned upstream of the MRHE. The micromixer consists of two inlets for the reagents, a channel to mix the gases, and the outlet to the reagent chamber. The external heater was inserted in the nitrogen line to initiate the reaction. Fig. 11 shows the temperature at different positions in the MRHE as a function of time. After 12 min, the temperature reached the set-point and the heater was switched off. After adjustment of the flow velocities of ammonia, oxygen and nitrogen, the targeted steady state was reached. At these steady-state conditions, the temperature at the product outlet side (R2) was 2 °C higher than that at the coolant outlet side (R3). In turn, the temperature at the coolant outlet side (R3) was 2 °C higher than that at the coolant inlet side (R1). A total temperature non-uniformity of 4 °C was observed in the MRHE.

An additional number of experiments were carried out to compare the behavior of the MRHE and the best microreactor (MR-3). Fig. 12 clearly shows that the MRHE yields more N_2O than the MR-3 in the whole range of conditions studied. This is definitely due to the very flat temperature profile in the MRHE.

5. Concluding Remarks

The case discussed in section 4.4 of ammonia oxidation in the integrated microreactor/heat-exchanger (MRHE) demonstrates clearly that the choice of the basic reactor material plays a crucial role in managing the temperature profile of an MRHE. However, an aluminum microreactor has a maximum operating temperature at about 400 °C, while numerous catalytic applications require temperatures higher than this. In order to realize such applications, new techniques must be developed for producing microchannels in refractory metals or aluminide intermetallics, which is a real challenge. These materials have high melting points, a good corrosion resistance, and a relatively low thermal expansion coefficient. Some of them have also a rather high thermal conductivity, which is, however, still a factor of 2–4 less than that of aluminum. The corrosion resistance of most of these materials can be improved by electrochemical deposition of thin niobium or hafnium films [16].

An important incentive for applying catalytic microreactors (or minireactors) in industrial practice will be the fact that small reactor volumes are desired, or are even re-

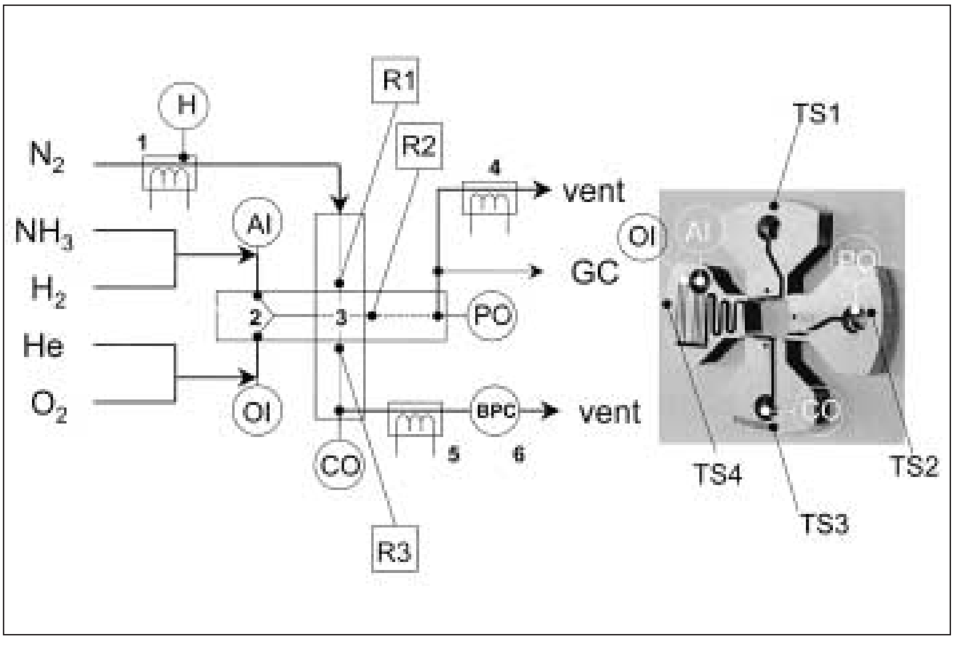

Fig. 10. Flow chart (on the left) and the detailed view of the optimized configuration of the MRHE inlet/outlet chambers for the reagents/products and the coolant (on the right). Definitions: 1– external heater; 2 – micromixer combined with the inlet reagent chamber, 3 – microreactor/heat-exchanger chamber (the MRHE not inserted, chamber size 6.5x6.5 mm), 4 – cold trap, 5 – second heat-exchanger (to protect the back pressure controller from the hot nitrogen flow), 6 – back pressure controller. Thermocouples: H – external heater, AI – ammonia inlet, OI – oxygen inlet, PO – product outlet, CO – coolant outlet, R1, R2, R3 – temperature inside reactor's chambers at the distance of 1 mm from the corresponding reactor walls. TS0, TS1, TS2, TS3 – temperature on the outer surface of the corresponding chambers of the microreactor/heat-exchanger. S0 – reagent inlet; S1, R1 – coolant inlet; S2, R2 – product outlet; S3, R3 – coolant outlet.

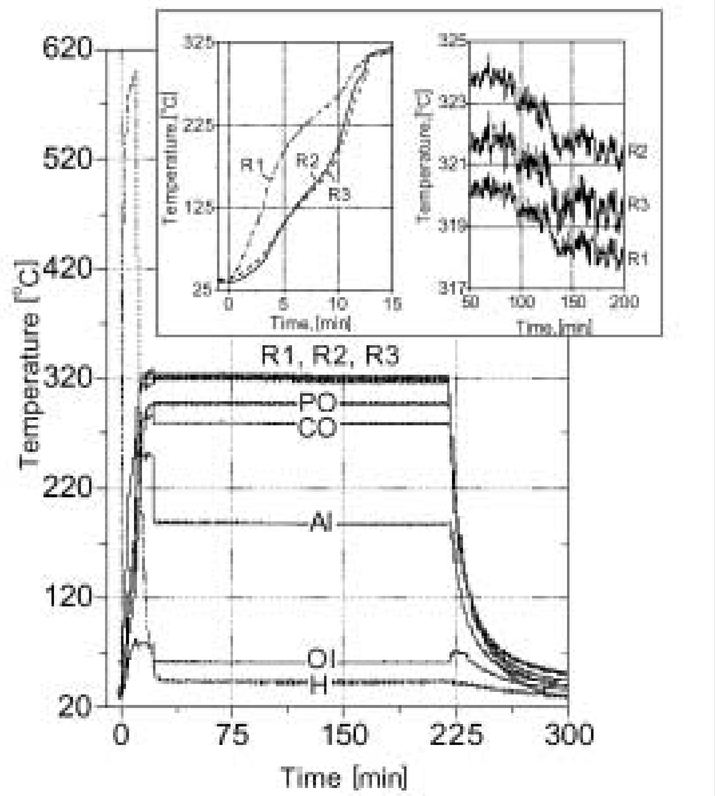

Fig. 11. Temperature responses for the microreactor/heat-exchanger. For definitions see Fig. 10. Reagent flow rate at steady state conditions: NH_3 0.30 l/min, oxygen 1.70 l/min, coolant 5.36 l/min. In the frame on the left side a detailed view of the start-up interval is shown. After 3 min, the hydrogen oxidation reaction ignited, as temperature R2 was higher than temperature R3 for the rest of the experiment. After the heater was switched off, temperature R3 was always higher than temperature R1. This is clearly shown in the frame on the right side. After the ammonia supply was switched off, the reaction was quenched immediately and it took 3 min to decrease the temperature below 200 °C.

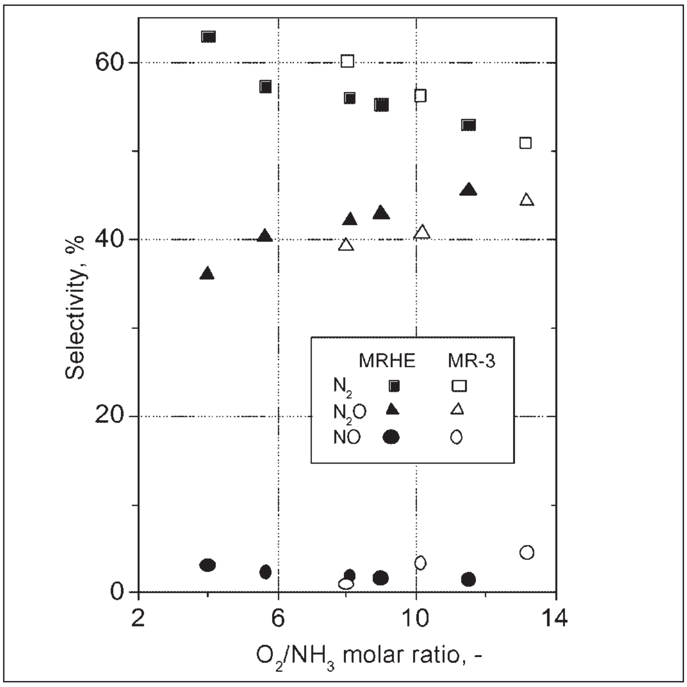

Fig. 12. Selectivity to nitrogen, nitrous oxide, and nitric oxide as a function of O_2/NH_3 ratio. Temperatures R1: 319 °C, R2: 323 °C, R3: 321 °C. Total flow rate in the reaction channels: 2.04 l/min. No diluent gas was used in all experiments.

quired, when very active catalysts are used. (At the same time, heat and mass transfer limitations are also eliminated as characteristic length scales are decreased.) This imposes another challenge on the microchemical engineering community, namely the development of, on the one hand, much more active catalysts and, on the other hand, the appropriate techniques to deposit the catalyst coatings in microstructured channel geometries or similar process architectures.

The future development and the industrial and commercial application of heterogeneous catalytic microreactors will largely depend on how successfully these challenges will be met. However, the effort is well worth it, as intriguing prospects for catalysis and process engineering are foreseen.

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