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Fast preparation and testing methods using a microstructured modular reactor for parallel gas phase catalyst screening

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Abstract

Heterogeneous gas phase catalyst screening with catalysts applied on titer-plates is presented. It will be shown that titer-plates can as well be used for the sample preparation outside the reactor *and* for the catalyst testing in the reactor. For the catalyst preparation, the known wash-coating-impregnation procedure is applied. An alumina coated precursor is introduced into a manifold which utilizes the flow features of the separated wells for the impregnation of the precursor with solutions of the salts of a collection of transition metals. The impregnation liquid is flowing through the wells thus impregnating the surface of the porous γ-alumina layers within the microchannels. Less porous coatings are realized by the simultaneous gradient sputtering process developed on the basis of the standard sputtering process.

Some details about the reactor development and characterization as well as problems which arose are reported. For the description of the reactor performance, a number of coated titer-plates were tested and these results are presented. After this so-called primary screening, a second evaluation phase normally follows. In this second phase, the kinetic properties of a single catalyst shall be studied. For this purpose, a model which describes the fluidic behavior of the reacting gas in microchannels was developed. Applying the model will give further insights into the underlying reaction kinetic of a single selected catalyst in the so-called secondary screening phase.

Keywords: Titer-plate; Sputtering; Wash-coating; Catalyst screening; Kinetic

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1. Introduction

Various reactors are recommended for fast parallel catalyst screening. Some authors recommend the use of pellets. Senkan et al. [1] developed a parallel reactor with 80 parallel channels which are equipped with impregnated γ-alumina pellets. The gas samples were delivered by a sample robot to a mass spectrometer. A 15-fold glass tube parallel reactor was introduced by Rodemerck and coworkers [2] close to conventional catalyst testing equipment. The same authors also reported a 64-fold ceramic block reactor and a ceramic monolithic reactor for the screening of up to 250 catalysts in parallel [3]. The individual catalysts were coated onto the ceramic walls of the monolith and the gas samples sent to a mass spectrometer by a sample

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robot. The group of Schüth and coworkers developed a number of reactors close to conventional testing methods with different degrees of sample integration. For multiphase reactions a 25-fold stirrer vessel reactor was developed [4] and for heterogeneous gas phase reactions a 16-fold fixed bed reactor was presented [5] which was later followed by a 49-fold parallel reactor [6]. High pressure applications have not been reported very often due to their high apparatus costs. A 14-fold stirrer autoclave was recently presented by Rampf and Herrmann [7] for liquid/gas reactions. Sample integrations close to pharmaceutical approaches were already examined 1997 [8]. A chip-like microsystem was integrated into a laboratory automaton which was equipped with a miniaturized micro-titer plate. Microstructures were introduced later by the group of Zech and Hönicke [9] for gas phase reactions. The principle of microprocess engineering is not widely used in combinatorial catalysis. One draw back is certainly the increasing distance to industrial applications with decreasing dimensions. On the other hand small structures exhibit laminar flow and the latter is without any doubt fully transparent to analytical and not only numerical macroscopic descriptions. This offers the chance to describe thoroughly the fluidic, diffusive and reactive phenomena in catalysis for the finding of true kinetics with, e.g. sputtered catalysts. That fast screening must not necessarily mean parallel screening is convincingly demonstrated by the group of Bellefon et al. [10]. They combined a micromachined mixer tube reactor with a pulsed injection of the respective catalysts for liquid/liquid and gas/liquid phase reactions. The throughput testing frequency was said to exceed 500 per day. Such a dynamic sequential method is a possible mode of operation for studying dynamic behavior also in heterogeneous gas phase catalysis, a method which will be regarded in the outlook.

In the literature, a number of measuring methods were reported which were considered as appropriate for the fast online screening of catalysts. IR-thermography measurements have been reported by the group of Maier and coworkers [11] who applied this method to heterogeneous catalysis and Reetz et al. who examined homogeneous catalysis in enantioselective reactions [12]. Maier also combined a laboratory sample robot with a heated catalyst library for spectrometric analysis [13].

Not only the screening of catalysts was reported. In the area of synthesis of new materials, the group of Weinberg et al. shall be mentioned which used sputter technologies to synthesize and screen new materials with luminescent features [14]. The same procedure is applied to produce transition metal catalysts [15]. The samples were heated locally by a CO_2-laser and the product gas was sent to a mass spectrometer for analysis. The same author also presented an overview article covering the state of screening 1999 [16]. In situ measurements offer the advantage to get information about the catalysts behavior (and possible surface changes) during the reaction. Such in situ-NMR-measurements were, e.g. reported by Haw et al. [17].

Screening was originally developed in the pharmaceutical industry to examine samples positioned on so-called titer-plates with up to several thousand species nowadays. Due to thermal cross-talk, this huge number can not be expected in the field of heterogeneous catalyst screening. Nevertheless an increase of efficiency and flexibility is desired. To some extent this difference is due to slow preparation methods for the samples. Some preparation methods in the literature [3,18,19] already apply sample robots to reduce the preparation time. In this work, new approaches for the preparation of samples on titer-plates are presented. The build up of a library of catalysts with a very dense format for later reference is facilitated by the standardized format of these plates. The standard format of the titer plate is the 48-well format with a respective number of individual catalysts. Plates with other configurations and a different number of wells are possible.

The preparation method should follow essentially the same procedure used in the pharmaceutical screening. This affords also the development of a technology to coat the catalysts in laboratory sample robots. The center part of the parallel screening reactor is the titer-plate which carries up to 48 single microstructured wells. Each of these wells consists of a number of parallel microchannels and carries an individual catalyst. The catalyst is immobilized as a layer on the walls of the channels. Highly porous or less porous layers were investigated. For preparing highly porous layers, the known wash-coating-impregnation process [20–22] was applied and adapted in such a way that the most time consuming impregnation step can be automated. Less porous layers were manufactured by applying a modified sputtering process in such a way that individual catalyst mixtures on one titer-plate are produced in an one-step procedure.

2. Coating catalysts

2.1. Wet-chemical procedure (wash-coating/flow impregnation)

The preparation of the catalysts applying a wet-chemical method was executed in a two-step procedure. First, a porous γ-alumina layer applying the wash-coating method is deposited in the microstructured channels of the titer-plate. Therefore, aqueous suspensions, consisting of γ-alumina, binder (PVA) and other additives are applied. After drying, the wash-coats are calcined at 600 °C. Scanning electromicroscopical studies showed the porous surface of these wash-coats (Fig. 1).

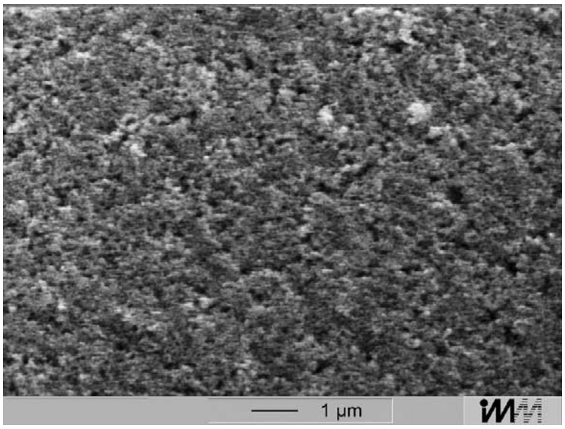

Fig. 1. SEM micrograph of a porous γ-alumina washcoat.

In a second step, the γ-alumina precursors were impregnated with the salt of transition metals using an automated high-throughput method. For this step aqueous solutions of metal salts (e.g. H_2PtCl_6, $RhCl_3$, $Ni(NO_3)_2$) were used. The procedure and further details are summarized in Table 1. A titer-plate coated with γ-alumina is shown in Fig. 2.

The whole set-up consists of several plates which are used for the feed of the impregnation liquid, the sealing of the wells and the removal of the excess liquid (Fig. 3). The contact time for the impregnation is adjustable by closing the exit channel for a defined time. The flow manifold was designed to fit into a typical laboratory sample robot and is operated in a semi-continuous mode. When the titer-plate is inserted into the manifold, the cover is closed. The exits of the wells are connected via capillary tubes and syringes and a rubber vacuum hose to the water jet suction pump. The flow is adjustable by a manual valve. The cover of the manifold has feeding funnels which are filled with the individual impregnation liquids. In order to fill the wells with the liquids, the valve is slightly open for less than a second and then closed again for the duration of the impregnation. Excess impregnation liquid is removed by opening the valve again.

The time for the preparation of the 48 single mixtures can thus be reduced from several days to about 24 h from which 20 h can be fully automated. Thus, the time for the sample preparation is in the same range as the estimated time for the forthcoming sample testing and analysis with the parallel reactor (Table 1).

Table 1
Procedure of semi-automated sample preparation on a titer plate

Process steps	Pretreatment of titer plate	Wash-coating	Calcination	Flow impregnation	Calcination
Expended time (h)	0.5	3	10	Variable[a]	10
Temperature (K)	298	298	873	298	Variable[b]
Amount of substance (ml)	–	48 × 0.5	–	48 × 0.5	–

Remark: Only the time for the penetration of the liquid into the pores is considered. The time for the preparation of the impregnants is not included because this can be done by a laboratory sample robot.

[a] Depends on the desired amount of catalyst in the alumina layer. One hour is often sufficient.

[b] Depends on the catalytic reaction. In order to hold the layer stable during the reaction, the calcination temperature should be higher than the reaction temperature.

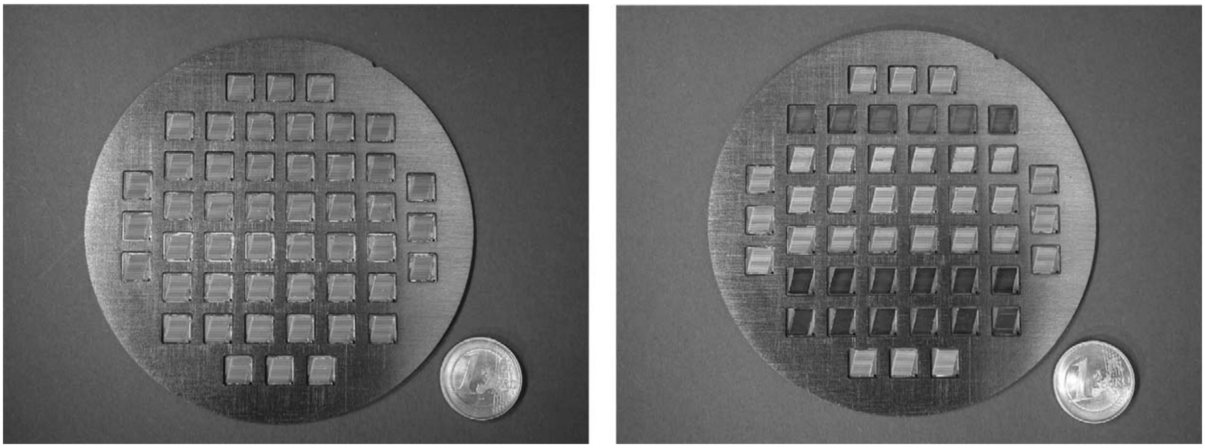

Fig. 2. A 48-fold titer plate coated with γ-alumina after calcination (left) and after impregnation (right).

2.2. Simultaneous gradient sputtering process

If catalysts for a fast reaction have to be screened, the gas components will mainly react at the surface of the catalyst and the porosity of the catalyst is not important (Fig. 4). For this purpose, a conventional thin film technology, the sputter process, was modified to allow the manufacturing of layers with thickness

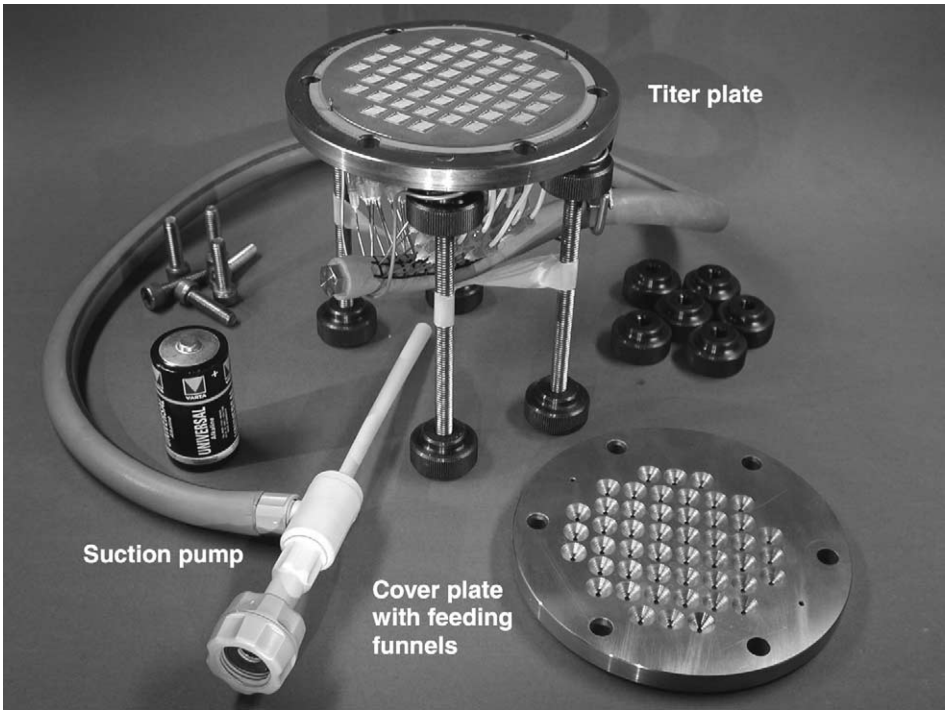

Fig. 3. Flow manifold for wet-chemical online coating.

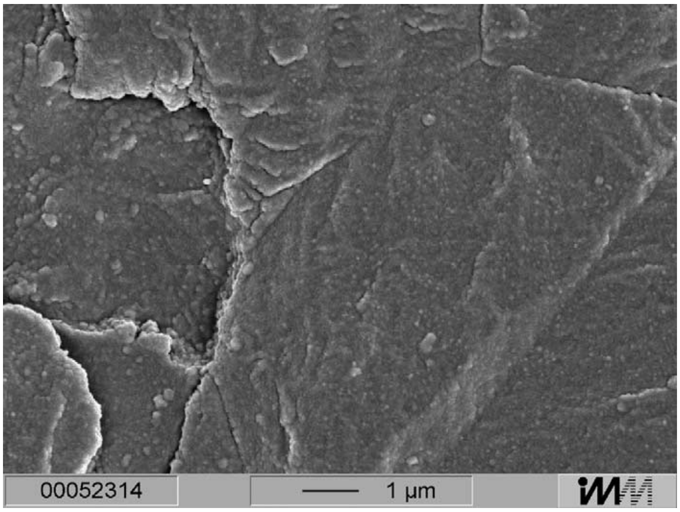

Fig. 4. SEM image of a sputtered catalyst.

gradients. These thickness gradients are combined in such a way that catalysts with individual compositions consisting of up to three components are manufactured.

Existing thin film technologies for catalyst coating could not be applied. Instead, a new method—the simultaneous-gradient-sputtering-process (SGSP)—was developed. During this process, the layer thickness of three catalyst components on a titer-plate is simultaneously varied in such a way that 48 single catalyst mixtures are obtained in a one-step process. Thus, the amount of each catalyst component in the mixture can either be decreased or increased, resulting in a homogeneous multi-component layer.

The catalysts to be deposited are inserted into the sputter plant as the so-called targets. The shuttle carries the titer-plate and revolves below the metal targets (Fig. 5). In every rotation up to three sublayers are deposited. For a binary system, the sublayer thickness is 10 nm in every revolution. The thickness gradients are realized by aperture orifices which shape the particle beam. Every orifice has an individual geometry. The rotation frequency of the revolving shuttle influences the homogeneity of the layer. A faster rotational speed will result in thinner sublayers and thus in an increased layer homogeneity. The rotational speed is restricted by mechanical properties of the turning table (Table 2).

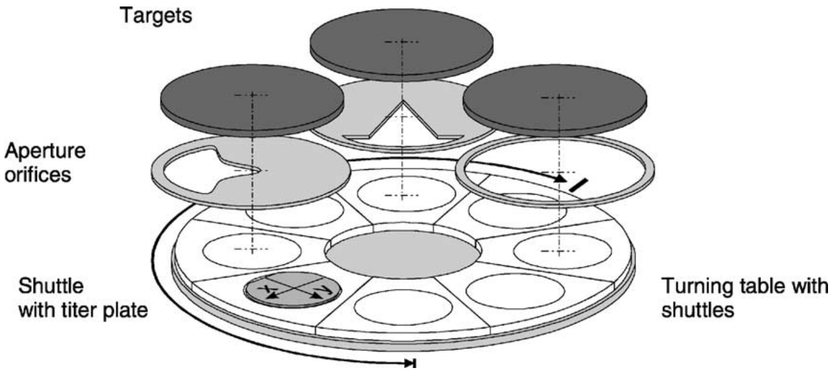

Fig. 5. Principle of the simultaneous-gradient-sputtering-process with three targets.

Table 2
Typical process parameters of the SGS-process

Process properties	
Pressure (mbar)	5×10^{-3}
Gas	Argon
Power (W)	1000
Targets ($Ø_{max}$, mm)	200
Rotational speed (rpm)	10
Deposit rate (nm/min)	2
Substrates ($Ø_{max}$, mm)	125

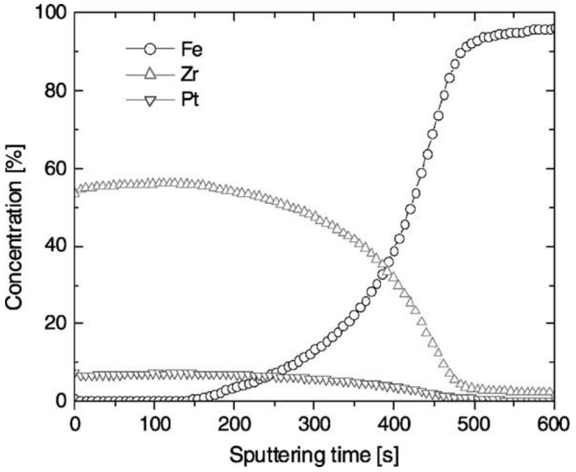

Fig. 7. SNMS analysis of a binary catalyst.

For the single component zirconium the gradient of the layer thickness was measured on a silicon monocrystalline wafer. The resulting thickness gradient is shown in Fig. 6 as a function of the wafer diameter and can well be approximated by a linear fit.

For binary catalysts two of these profiles have been combined, with the second profile being mirrored to the first one. Platinum was chosen for the second component. By adjusting the target powers (150–2500 W), individual gradients can be defined.

The homogeneity of this binary layer composition was examined using the secondary neutral particles mass spectrometry (SNMS) at the IFOS. This procedure removes the layer stepwise and gives the amount of the components depending on the sputtering time. One second of sputtering time here corresponds to a layer removal of approximately 1 nm. Thus, the sputtering time is also a measure of the layer thickness. The maximum layer thickness was 500 nm.

Layers consisting of two components are realized by employing two targets. This is demonstrated in Fig. 7 with the components zirconium and platinum

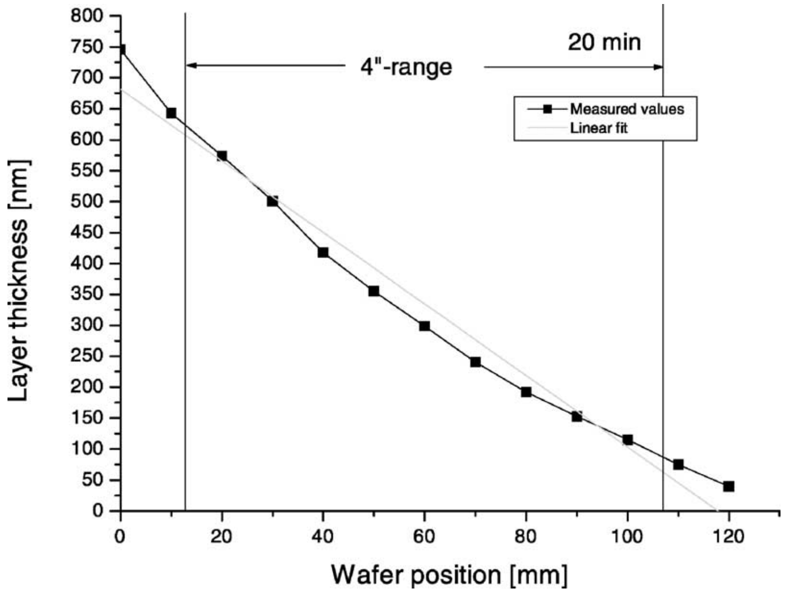

Fig. 6. Distribution of the layer thickness for a single component (zirconium).

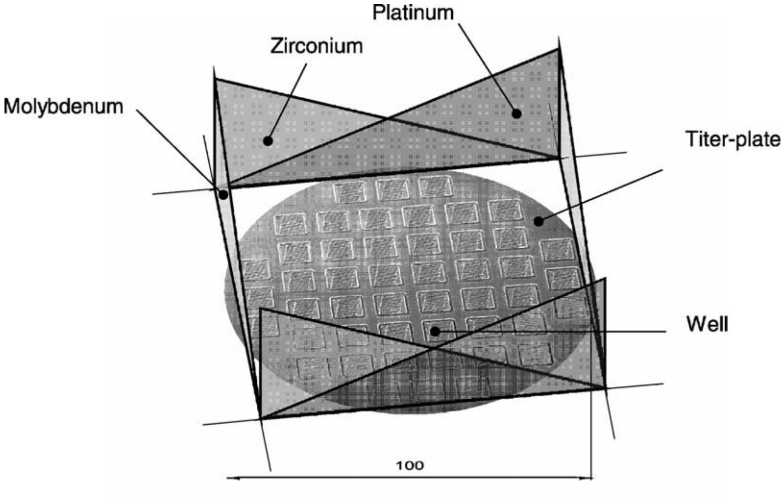

Fig. 8. Expected qualitative ternary layer composition represented by the three wedge-shaped profiles.

on a stainless steel substrate. Zirconium and platinum are evenly distributed within the layer. The surface roughness of the steel substrate is responsible for the steady incline of the iron concentration curve.

To increase the number of catalysts, the binary catalyst system zirconium/platinum was extended to a ternary system by adding a third component such as molybdenum. The expected quality of such a composition is given in Fig. 8. First results of such a ternary layer are presented in Fig. 9 (left). The layer was deposited on a silicon monocrystalline wafer and the layer composition again examined with SNMS.

By oscillating the titer-plate, a third gradient can be sputtered by moving the substrate half way underneath the target. The effective speed of this oscillating table is lower than the rotating speed of the table as in the case of only two targets. This leads to a deposition of less homogeneous films. Nevertheless, the average composition in the layer is constant and widely stable. This is not the case at the catalyst surface. The composition here is not well defined and a method to stabilize it was searched. Because the vertical depth of the sputtered sublayers was only 2 Å, to reach a homogenization by solid-state diffusion seemed to be possible. A number of sputtered ternary catalysts was sintered at a temperature of 850 °C under vacuum conditions for 4 h. The result is given in Fig. 9 (right) as the concentration of the components depending on the layer depth. The unit of the layer depth is again given in seconds and 1 s corresponds to approximately 1–2 nm. This is a result of the consecutive removal of the layer by the SNMS process which uses the sample as a target and removes the layer by (de-)sputtering with a rate of 1–2 nm/s. Comparing the untreated catalysts on the left side with the sintered catalysts on the right side, proves that heat induced molecular diffusion reduces the inhomogeneity visible as oscillating concentration distributions. During the sintering process the plates were lying on a heated plate on the uncoated side of the wafer. Thus, the coated upper surface of the samples was not as well heated as the internal sublayers. This is the reason why the composition of the internal sublayers are already balanced while the sublayers close to the surface are still inhomogeneous (Fig. 9, right).

Up to 48 ternary catalyst mixtures are prepared simultaneously in less than 1 h. Thus, the sputtering procedure is much faster than the wet-chemical route. This advantage is bought at the price of a low layer porosity. Thus, sputtered catalysts are new artificial catalysts and not directly comparable to catalysts prepared by wet-chemical procedures. These catalysts offer the advantage of being fast manufactured and characterized compared to alumina-based catalysts. They also might be used for obtaining so-called true kinetics because there is no influence of diffusion.

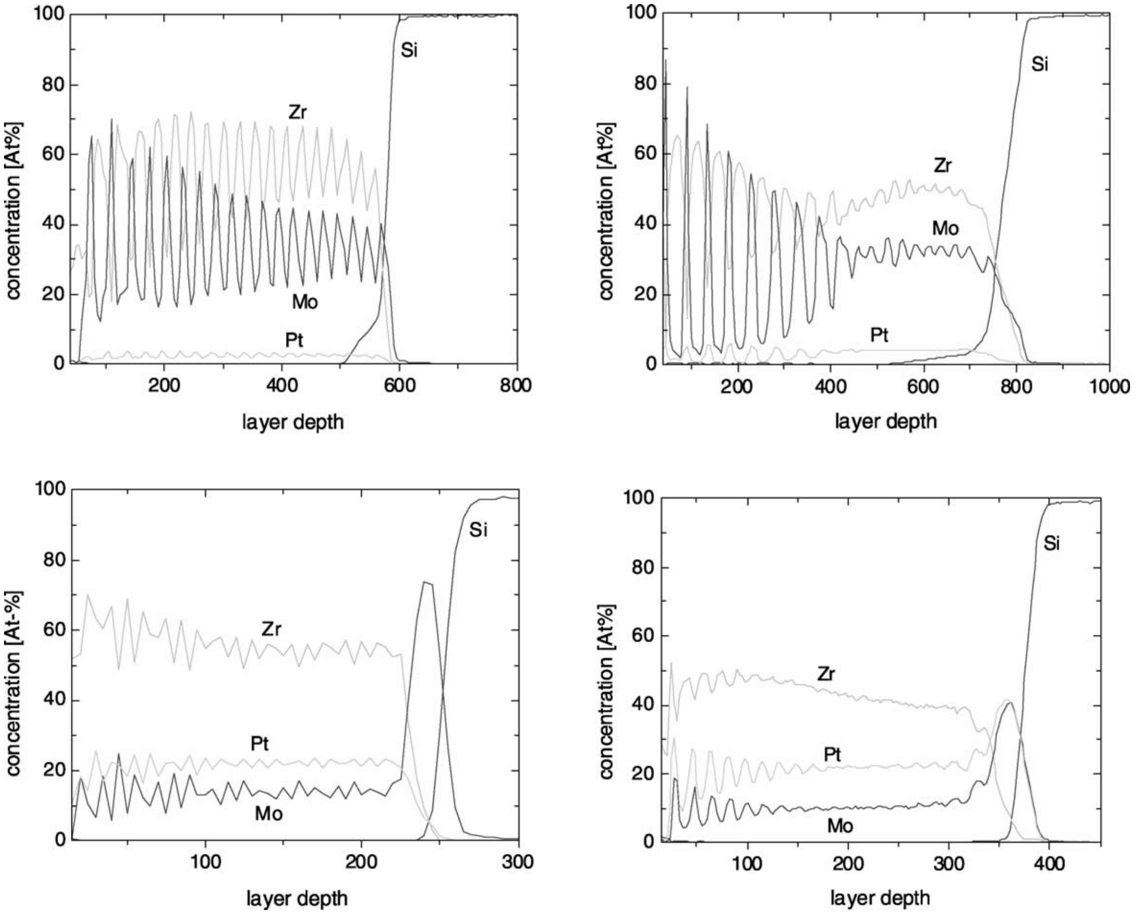

Fig. 9. Layer composition of two ternary catalyst mixtures examined with SNMS before tempering (left) and after tempering at 850 °C for 4 h (right).

3. Reactor development

The parallel reactor for the screening of the titer-plates consists of several modules. Each of them is responsible for just a single operation. The gas flow, for example is preheated and evenly distributed within the distribution module and delivered to the wells on the titer-plate which is clamped between the distribution module and the insulation module and is itself also a separate reaction module. The insulation module separates the heated section of the parallel reactor from the unheated section and is further cooled by the heat exchanger module on top of it. The last module just above the heat exchanger module is the multiport valve which delivers the product gas to the gas-chromatograph (Fig. 10).

The complexity of the reactor produced a number of problems, first of all leakage and cross-talk problems. Thermal and fluidic cross-talk was expected in the section of the titer-plate but had not been observed. The thermal cross-talk was in advance already checked by simulations of the thermal influence between wells with a different conversion and could be excluded for the small gas flow range applied here. Instead problems were encountered when the product gas flow had already left the wells and entered the multiport valve. At this position the individual gas flow of every well had to be diverted to the circumference of the

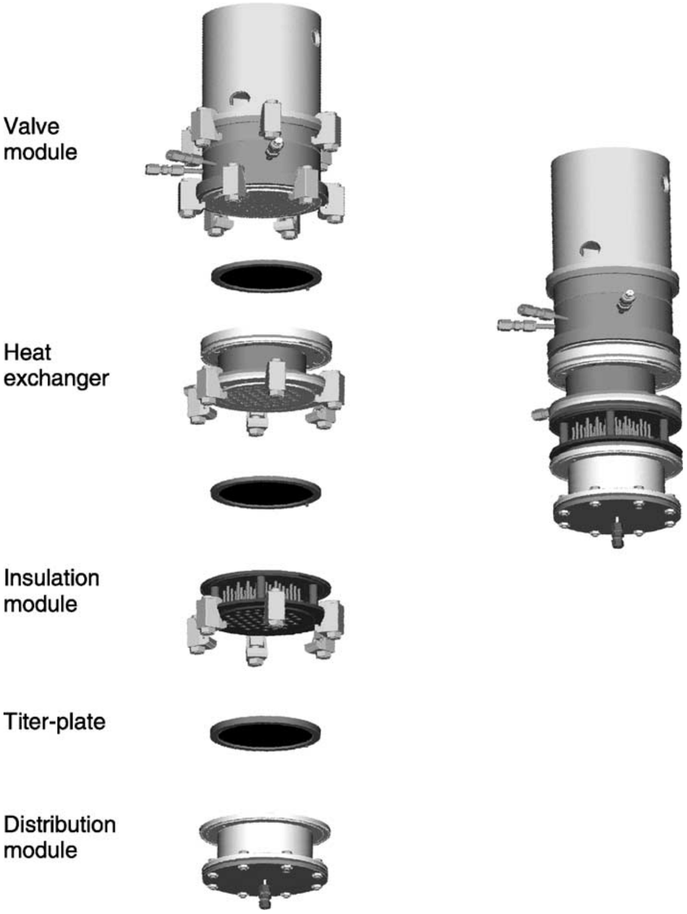

Fig. 10. Modular concept of the 48-fold parallel screening reactor [23].

rotary multiport valve. In this region an etched stainless steel plate diverts the individual product gas flow from the chequered arrangement on the titer-plate to the ring shaped arrangement inside of the valve. The cross-talk was mainly due to the bending of the plates when the hydraulic press was closed in order to seal the reactor. The bent plates allowed a cross-talk in the developing gap between the plates. A similar problem was encountered within the distribution module. The upper plate of the housing was slightly bent downwards and the individual gas streams leaving the exit channels out of the module were interconnected in the developing gap between the module and the titer-plate. This did not lead to cross-talk because the reaction only happens in the titer-plate after the gas passed that gap. Nevertheless, uneven heating was expected and an additional counter bearing inside of the distribution module was added to support the upper plate.

In a first attempt to distribute the gas flow evenly, stainless steel wire mesh sieves with very small pore diameters up to 10 μm were used as a kind of pressure resistor which supports the gas distribution. The first tested titer-plates had all been proven not to be active. When these plates were examined right after the test with EDX, a closed layer of iron oxide inside of the wells was detected. The reason for the inactivity of the catalysts thus became obvious. The small wire diameters of the sieves exhibit a huge metal surface. This metal surface was oxidized during the heating of the distribution module up to 600 °C and particles were emitted. The iron oxide particles then

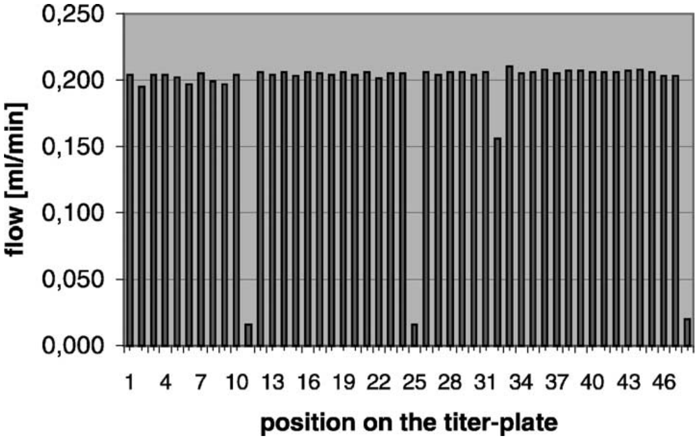

Fig. 11. Velocity distribution of the single channels of the parallel reactor measured with a mass flow sensor at the reactor exit. (Three positions have been closed in order to check the fluidic cross-talk. Position 32 was partially blocked. Sensor offset was 0.016 ml/min.)

were coated onto the titer-plate upstream. In order to prevent further unwanted coating, the metal sieves were exchanged against a fixed bed consisting of inert glass beads with a diameter ranging from 177 to 250 μm. The velocity distribution with these particles was as even as with the sieves and is shown in Fig. 11.

The reactor set-up in the laboratory is shown in Fig. 12.

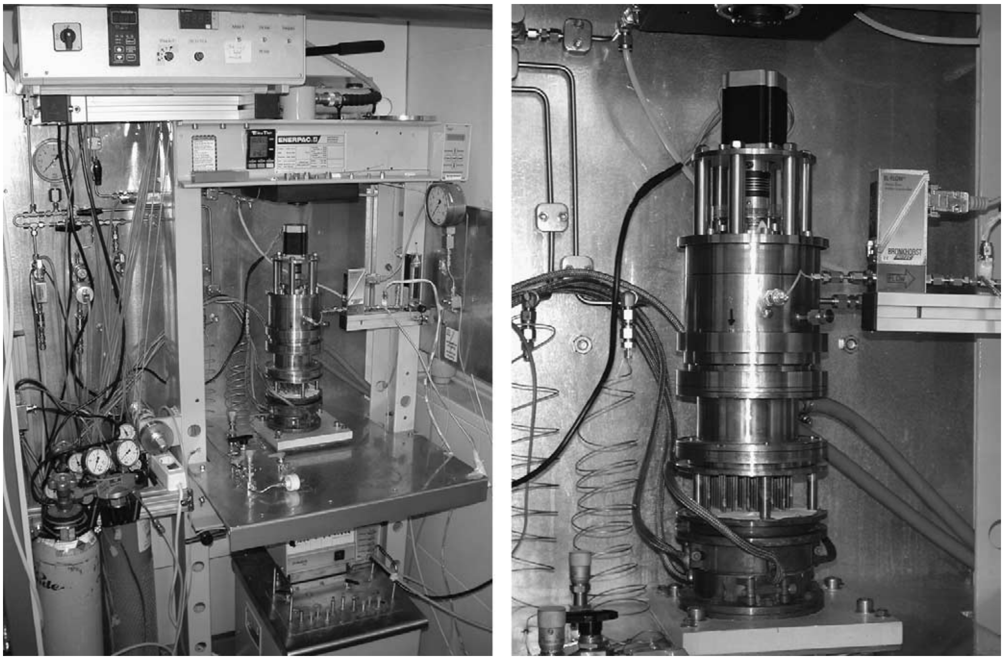

Fig. 12. Reactor set-up in the laboratory. Left: the hydraulic table press which seals the reactor; right: the reactor with heating bends; on top: the stepping motor and in front: the online-connection to the GC.

4. Experimental and discussion

After coating the titer-plates were inserted into the reactor to test the activity of the catalysts. The reaction conditions were held constant in all of the following experiments. The reactor was heated up to 475 °C and held under a pressure of 0.2 bar(g). The heat exchanger was operated at 50 °C, the throughput for a single well was adjusted to 1 ml/min which gives a total space velocity of 9000 h^{-1}. The residence time in the wells was 0.4 s.

For the binary compositions the components zirconium and platinum were sputtered onto a microstructured stainless steel substrate. Zirconium was used as the inactive component which serves as a kind of dilutor for the known good activity of platinum. According to the chosen orifices the two components were deposited in a number of mixed compositions. Six of these compositions—evenly distributed on a titer-plate along the platinum gradient—were tested of their activity to the catalytic combustion of methane. An understoichiometric mixture of methane and oxygen (2:1) was diluted with 70% nitrogen, preheated and distributed within the distribution module and continuously delivered to the single wells. For the combustion of methane, a number of parallel and consecutive reactions are known to happen [24]. Only two of them are given here and during the tests mostly carbon dioxide was obtained according to the following formula:

$$CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$$

$$CH_4 + \tfrac{1}{2}O_2 \Leftrightarrow CO + 2H_2.$$

The methane conversion of each of these compositions is given in Fig. 13. The layer content of the respective component is indicated by the triangles.

The degree of the methane conversion follows directly the content of platinum in the mixture which proves that the catalysts are active and selective for the methane oxidation.

Catalysts prepared by the wash-coating method were first used in order to check the reproduction of the measured values. For this reason six elementary metal salts (platinum, zirconium, molybdenum, nickel, silver, rhodium) were solved and impregnated onto a titer-plate. The catalysts were prereduced inside the reactor with 5% hydrogen in 95% nitrogen at 250 °C. The results were recorded first before the prereduction and then after the prereduction (Fig. 14). The repeated measurements indicated a good reproduction in both cases. The conversion of methane with the rhodium catalyst is better after the prereduction. The diagram on the right side also proves that the methane conversion after 18 h runtime is still stable.

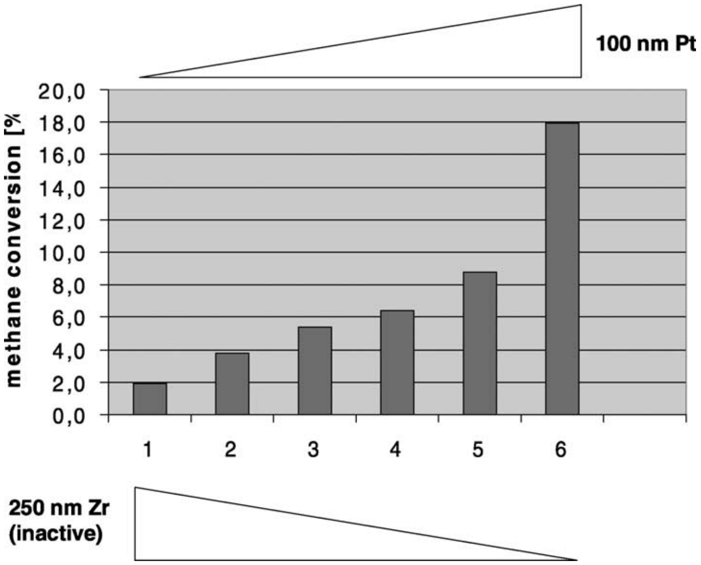

Fig. 13. Conversion rates of sputtered binary catalyst mixtures.

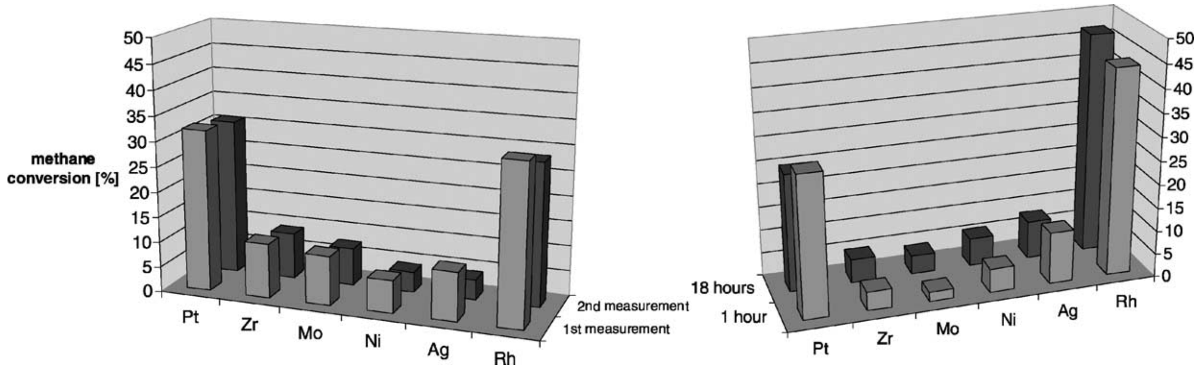

Fig. 14. Repeated measurements of not prereduced (left) and prereduced catalysts (right) for six transition metal catalysts.

In order to check, if fluidic or thermal cross-talk exists, the same six metal catalysts were coated in six rows on one titer-plate. Active catalysts have been neighboured to less active catalysts (Fig. 15).

The result was that the two active rows (platinum and rhodium) did not influence the neighboured less active rows (zirconium and silver). Thus, cross-talk was not observed.

In the next test elementary, binary and ternary mixtures of the same metal catalysts were examined. Every mixture was deposited on four different wells to check the reproduction (Fig. 16).

Except for some of the ternary mixtures, the results were well reproduced and were consistent with the known well activity of rhodium (row 1) and the mixture of rhodium and platinum (row 5) which had the highest activity.

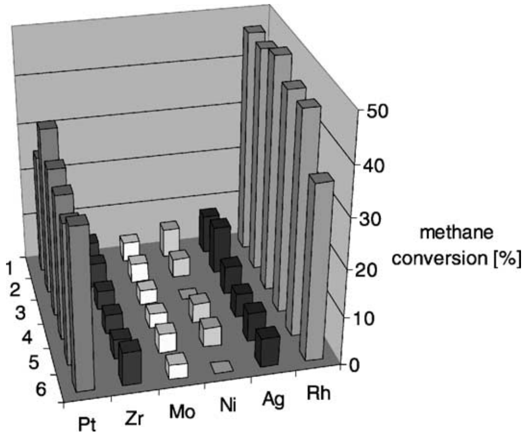

Fig. 15. Six metallic catalysts each deposited on six different wells onto a titer-plate (the conversion is correlated to the correct geometric position of the wells).

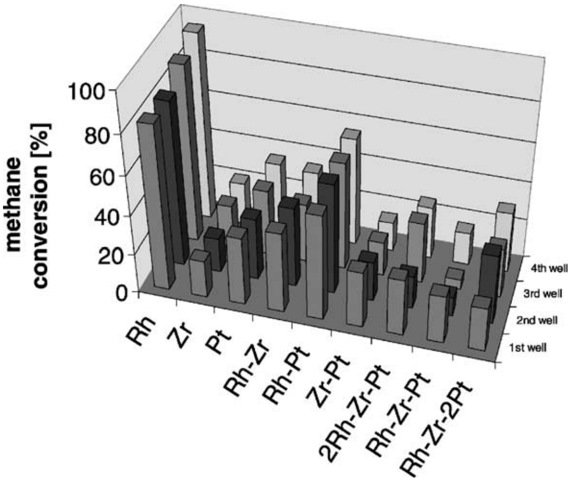

Fig. 16. Elementary (rows 1–3), binary (rows 4–6) and ternary (rows 7–9) catalysts, respectively, deposited on four different wells.

5. Outlook

Screening in stationary mode will only give information about the activity of a single catalyst or a catalyst mixture. When a proper catalyst for a certain reaction is found the next important information to know is the underlying kinetic reaction. To reach at this information, a number of methods and reactors are recommended in the recent literature [24–30]. Most of them apply transient reactor operations for finding detailed kinetic information. Microreactors are particularly suited for such an operation, since their low internal reaction volumes enables a fast response to process parameter changes, e.g. concentration or temperature changes. This feature was already applied by some authors to increase the product yield in microreactors [31–33]. To accommodate such measurements with the existing reactor, the reactor set is equipped with a second rotary valve which replaces the gas distribution module. Bellefon et al. [10] reported a dynamic sequential method to screen liquid/liquid and liquid/gas phase catalytic reactions by the injection of samples followed by barrier liquid. While he applied the pulsed input to establish spatially separated samples, this method might as well be applied to study dynamic behavior in gas phase reactions. Typical process parameters which can be changed are the pressure, the temperature or the gas mixture composition. Fast mixture or pressure pulses will be realized by the injection of reaction gas into the system by a micro-dispense valve. The transition into the next stationary mode will be recorded by a mass flow sensor. Necessary for the fast evaluation of such response signals is a diffusion/dispersion model which must also consider the heterogeneous wall reaction. A simplified dispersion model assuming a first-order reaction was recently presented [34,35], which enables the prediction of the concentration distribution in rectangular microchannels. Some of the results shall also be given in this context because they prepare the way to an extended type of secondary screening in which case screening could mean the evaluation of catalysts applying various reactor geometries and transient operations for the collection of kinetic information. Fig. 17 gives the concentration in a channel as a response to a pulse test function.

The pulse was released at the entrance at time $t = 0$. Measuring the response of such a test function gives information about the kinetic rate constant k according to the following formula:

$$c_A(x,t) = c_{A,0}(t)\exp\left[-kt - \frac{(x_1 - k_v t)^2}{4k_r t}\right].$$

The constants k_v and k_r are calculated numbers and functions of k, and x_1 is the axial coordinate.

The often used limitation of such a model to first-order reaction rates is not that restricting as it may seem. In fact many reactions might at least be considered being of “pseudo”-first order which means that they behave macroscopically like first-order reactions. This is the case for diluted fluids, for non-catalytic gas/solid reactions like the so-called shrinking core or shrinking particle model. Another example are electrochemical reactions [36]. For the above applied oxidation of methane to carbon dioxide on some metal oxide catalysts also a reaction order of one is assumed ([24], pp. 182 and 193). However, in combinatorial catalysis it may be sufficient to have quickly

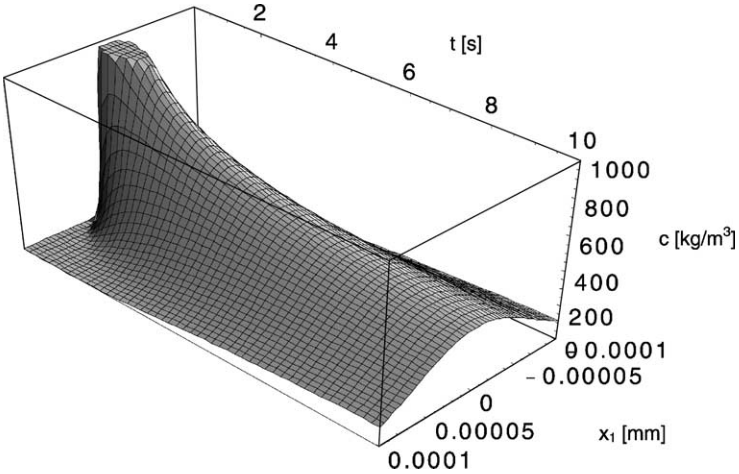

Fig. 17. Concentration distribution in a rectangular microchannel calculated for a Dirac impulse test function.

a first rough idea about the underlying kinetic. Without having any hints about the kinetic, engineering a reactor is touched with a huge uncertainty. This is obvious if one considers the wide variation of reaction rates. Pre-exponential factors of reaction rate constants derived by the transition state theory vary widely from approximately $10–10^{16}\,s^{-1}$ [24]. This first information might then be used to develop a pilot plant for the up-scaling and for further more detailed kinetic examinations.

6. Conclusions

Methods of thin film technology were used to deposit selective catalysts. Homogeneous sputtered layers were obtained for binary catalysts, while ternary catalysts are still not homogeneous enough for screening purposes. It was shown that solid-state diffusion can be applied to mix inhomogeneous layer compositions. Catalysts positioned on titer-plates produced by the wash-coating-impregnation method were screened in a novel parallel reactor and proved to give selective methane conversion rates. A different configuration of the parallel reactor is already manufactured to enable future transient measurements for kinetic studies.

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