

## 4

# Catalyst Development, Screening and Optimization

*André C. van Veen, Yirk Schuurman, and Claude Mirodatos*

### 4.1

#### Introduction

Catalytic technologies play a key role in the strategic domain of fuel processing for hydrogen production for fuel cells (FCs). Fuel processors consist of a number of units, namely a fuel tank, a start-up burner, a vaporizer for liquid fuels, a reformer and one or two water-gas shift units (HTS and LTS). Targeting less than 10–30 ppm of CO before feeding a conventional low-temperature proton-exchange membrane fuel cell (PEMFC), a selective (or preferential) CO oxidation reactor or a Pd-based dense membrane for hydrogen purification is added at the current state of the art. Finally, a catalytic after-burner is integrated for energy recovery by burning the unconverted hydrogen exiting the FC (about 20%). The latter unit might be integrated within the start-up burner and is typically also capable of completing the energy balance by auxiliary fuel combustion. For each catalytic unit, catalyst design and formulation have to meet the process requirements: nature of the fuel, temperature, pressure, stability, dispense with or ease of regeneration, etc. All these catalyst engineering parameters are strongly intertwined with the thermal and mechanical engineering of the selected reactors, the latter depending directly on the targeted application (domestic, on-board, electrical power to be reached, etc.).

#### 4.1.1

##### Impact of Fuel Nature

For the reforming stage, a first essential feature to consider for any rational catalyst development is the nature of the fuel to be reformed and the degree of versatility of the hydrogen generator. Possible fuels are widespread, ranging from natural gas (C<sub>1</sub> to C<sub>3</sub> alkanes) to gasoline, kerosene and diesels, from methanol to ethanol and DME and from fossil to renewable fuels (e.g. upgraded bio-oils) [1]. Second, the proper reforming mode has to be selected among steam reforming (SR), partial oxidation (POX) and oxidative steam reforming (OSR), aiming at an autothermal

(ATR) process. The type and number of affordable downstream units also determine the reformer characteristics. For example, if the fuel is methanol, then a high-temperature water-gas shift reactor is not required, given that CO levels in the reformat do not significantly exceed 1%. High-temperature FCs (new generation of HT PEMFC, MOFC or MCFC) are more tolerant towards CO and the number of clean-up units in the reformer can be reduced.

Table 4.1 gives a brief overview of the operating temperatures and typical catalyst formulations used in the different fuel processor units. It also lists approximate values of the heat of reaction. The heat of reaction depends on the feed and, in the case of hydrocarbons, the absolute value of the reaction enthalpy will increase with increasing carbon number. A more detailed account concerning the catalyst formulation for the different steps can be found in [2] and in the references therein.

From Table 4.1, different observations can be made:

1. The different fuel processing steps are carried out at different temperatures and range from strongly endothermic to strongly exothermic. Hence proper heat management is indispensable for efficient hydrogen production.
2. The majority of the catalysts are alumina-supported (precious) metal catalysts. In fact, most of these materials have been developed for fuel processor applications. Fuel processor catalysts need to be robust in order to resist deterioration due to start/stop conditions; they need to be resistant preferably to air and liquid water exposure and they need to be able to be used in the form of a washcoat for high efficiency. For these reasons, often precious metals are preferred over the other less expensive transition metals.

Within the perspective of developing new generations of integrated and intensified fuel processors, miniaturized and integrated systems, known under the generic term

**Table 4.1** Overview of the different fuel reformer steps and their typical operating temperature, catalyst and approximate heat of reaction.

Process	Reactant	Operating temperature (°C)	Catalyst	Approximate heat of reaction (kJ mol <sup>-1</sup> )
Steam reforming	Methanol	200–300	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> , Pd/ZnO	50
	Ethanol	600–800	Ni/MgO/Al <sub>2</sub> O <sub>3</sub> , Ru, Rh/Al <sub>2</sub> O <sub>3</sub>	254
	Hydrocarbons	700–900	Ni/Al <sub>2</sub> O <sub>3</sub> , Ru, Rh/Al <sub>2</sub> O <sub>3</sub>	>200
Partial oxidation	Hydrocarbons	700–900	Pt, Rh/Al <sub>2</sub> O <sub>3</sub>	<–36
	HT-WGS	CO, H <sub>2</sub> O	350–450	FeCr, Pt/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>
LT-WGS	CO, H <sub>2</sub> O	200–300	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> , Pt/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	–42
Selective oxidation	CO, O <sub>2</sub> , H <sub>2</sub>	80–250	Au, Ru, Pt, Cu/Al <sub>2</sub> O <sub>3</sub>	–285
Methanation	CO, H <sub>2</sub>	200–300	Ni/Al <sub>2</sub> O <sub>3</sub>	–206
Combustion	Hydrocarbons,	700–950	Pt, Pd/Al <sub>2</sub> O <sub>3</sub>	–242
	H <sub>2</sub> , O <sub>2</sub>			

microreactors or microstructured reactors (MSRs) (see earlier chapters), have been developed. The catalyst development required for these specific microsystems has to meet further requirements imposed by the confined geometry of the microstructured substrates on which active phases coating has to take place. Thus, in order to maintain the already mentioned advantages of microdevices in terms of heat and mass transfer, the design of catalyst coatings has to be adapted to the geometry of the microchannels, which itself needs to fit to the kinetics of the considered reaction.

#### 4.1.2

##### **General Features of Coatings**

Washcoat technology was initially developed for the automobile catalytic converter, consisting of a ceramic monolith of many small parallel channels, in the mid-1970s. Monoliths have since then developed into a variety of different materials and configurations, essentially cordierite based [3].

Xu and Moulijn [4] described nine methods of active phase incorporation for monolithic catalysts: (A) impregnation, (B) adsorption and ion exchange, (C) precipitation or coprecipitation, (D) deposition precipitation, (E) sol-gel method, (F) slurry-dip coating, (G) *in situ* crystallization, (H) addition of catalytic species to the mixture of extrusion and (I) others, such as chemical vapor deposition and spray-coating. Washcoating techniques depend strongly on the substrate used and techniques used for cordierite monoliths cannot be applied directly to metallic microstructures. Parameters such as the porosity and the thermal expansion factor are different between ceramics and metals. Even in the case of metallic monoliths, synthesis methods do not translate to microstructured reactors as metallic monoliths are exclusively made of FeCr alloy that is oxidized at high temperatures to give a thin layer of  $\text{Al}_2\text{O}_3$ , which serves as an adherent layer for the washcoat.

#### 4.1.3

##### **On-board Systems Integration and Requirements**

Another key aspect to be considered for catalyst development in micro fuel processors is the integration of all the individual units listed above, aiming at minimizing the energy losses and therefore increasing both the overall efficiency and the system compactness. Thus, in order to balance the heat produced and the heat required by various units incorporated, the corresponding elements may be coupled as heat exchanger reactors. Examples of relevant activities are the EU-funded project MiRTH-e [5, 6], the German projects NECAR3 and NECAR5 supported by Daimler-Chrysler [7], the French project MISTRAL [8] funded by Renault and the PACO network for on-board microprocessors designed for methanol and gasoline reforming. It can easily be rationalized that not only the design of the stacked microstructured elements, but also their assembly (e.g. brazing, laser welding and/or diffusion bonding) will directly govern the heat transfer efficiency. Thus, the thickness of the catalyst coatings and the efficiency of the selected formulations have to be properly adjusted, based on numerical simulation, know-how and a number of trial-and-error experiments.

As already mentioned, the choice of fuels, and hence the selection of catalysts, also involves several parameters. Despite the fact that the NECAR activities demonstrated methanol reformer technology for the propulsion of an entire car, the toxicity of methanol motivated the reorientation of reforming activities to the more challenging conversion of conventional hydrocarbons, with additional challenges such as high-temperature stability and coking resistance for adapted catalysts.

For on-board (a few kilowatts as exemplified above) or domestic applications (a few hundred watts for camping units or a few watts for powering portable computers or cellular phones), the adherence and stability of the catalyst coatings are obvious prerequisites for successful and long-lasting operation. Indeed, any catalyst disintegration or dusting within one of those integrated units might cause irreversible damage. Similarly, the resistance to corrosion of the substrate has to be considered carefully when designing the microdevice and specific alloys and/or surface treatments have to be applied before solder/braze deposition (by electroplating or chemical coating) and catalyst coating. For that critical domain, no detailed information is available in the open literature, unless a few patents to appear soon.

For on-board fuel reformers, the respective catalyst layers must withstand extremely severe conditions: the system must be fully operational within about a minute, i.e. reaching its operating temperature (700–800 °C) after a cold start, and must respond rapidly to varying loads. In fact, significant load transients occur frequently as a result of changes in power demands (for a car, acceleration, ramps, highway cruising, etc.), not to mention the impact of mechanical shocks that the catalyst undergoes continuously in on-board systems.

#### 4.1.4

##### **Laboratory-scale Requirements**

When investigating microstructured fuel processors on the laboratory scale, other requirements have to be considered, such as the possibility of screening several types of microstructured substrates and catalyst formulas and characteristics (coating methods, activation procedures, etc.). In the screening phase, the design of the microstructured stacks should permit the easy replacement of a catalyst layer by another one with a different composition or modification of its thickness or reloading assembled microstructures with fresh catalyst after long-term aging. The ultimate strategy for accelerating this screening/optimization process might also require high-throughput (HT) tools and methodologies. Such versatile options have already been applied successfully in various industrial or EU projects such as Demis [9–11], MINIREF [12, 13] and TOPCOMBI [14], where basically the microplatelets are not soldered but simply stacked within a stainless-steel housing and maintained by mechanical pressure, with even the possibility of coating several formulations on a single platelet, such as for the HT microdevice developed by the Institute for Microtechnology (IMM) [15].

From these statements considering state-of-the art and on-going laboratory- to pilot-scale developments, several key questions can be formulated, which will be addressed throughout this chapter:

- Which requirements have to be considered in terms of catalyst engineering (formulation, shaping, coating configuration and stability, etc.) and which implications have to be foreseen when downscaling from macro- (conventional) to microprocessing? For example, as mentioned above, the adherence of a coating is a new variable for catalyst engineering in micro fuel processors, as compared with conventional reactors. In this poorly documented area, the very large number of parameters to be considered such as the nature and composition of the metallic substrate, the profile of the microchannels, the way of stacking together microstructured platelets (with or without soldering or welding) is expected to have an extensive impact on catalyst engineering.
- Which preparation, characterization and screening methods exist today for evaluating catalyst performances (activity, selectivity and stability) in microdevices? For example, various procedures exist for depositing a catalyst layer on microstructured substrates: wet chemical methods, sol-gel techniques and chemical vapor deposition (CVD). However, few studies have report on the way to process, evaluate and compare these techniques. In turn, various key parameters of those techniques have to be screened for ranking the advantages and inconveniences of each technique.
- Which methods, theoretical and/or experimental, can be implemented for optimizing the performances of catalytic systems? In that context, it is desirable to establish kinetic criteria allowing one to define the optimal thickness of a catalyst layer, depending on whether a catalytic or diffusion-limited regime is controlling the process. It can be mentioned that, in the absence of limitations by physical phenomena, MSRs appear be well adapted for proper kinetic studies [16] in units at least theoretically scalable to industrial production capacities. As such, they offer the advantage of measuring the intrinsic kinetics in the same catalyst environment as the one to be used in a pilot-scale or even a full-scale process.

To address these questions, the next section concentrates on catalyst developments (requirements and implemented techniques for microstructures coating) and the following one on the use of kinetic and modeling approaches. Case studies from the literature and from our own work illustrate various items specific to micro fuel processors as mentioned above.

## 4.2

### **Catalyst Developments: Requirements and Implemented Techniques for Microstructure Coating**

#### 4.2.1

##### **Specificity of Characterization Tools for Coated Catalysts**

Characterization is as important for coated catalysts as for conventional systems. Indeed, all the tools developed for characterizing the precursors of coatings are also required for monitoring the numerous parameters that will control the final properties and structures of the catalysts coatings on microstructured platelets

(XRD, TEM, SEM, chemical analysis, XPS, slurry viscosity measurements, particle size distributions, BET, pore size distributions and magnetic measurements). Obviously, characterization could be carried out by detaching the catalyst from the substrate and then proceed using conventional approaches. However, a risk of modifying the sample characteristics, such as porosity, or introducing contaminations, such as residues from the substrate mechanically scraping the catalyst from the surface, make direct characterization of the coating attractive.

Due to the confined 3D structure of most catalytic coatings in microstructures, specific adaptation of conventional tools for catalyst characterization is required. For example, destructive SEM can be carried out on assembled microstacks, filled with epoxy resins and cut with diamond saws or lasers [17, 18]. XRD can be performed in a specific geometry, so-called shallow-angle XRD, to record diffraction patterns of thin films as long as flat model supports are used [19, 20]. The specific surface area of coated catalysts may be determined right on thin support sheets using the BET method with krypton as probe gas [17, 18]. Here the enhanced sensitivity related to the use of krypton allows the proper detection of relatively small absolute surface areas provided that adsorption cells with low dead volume are designed. Obviously, the direct measurement of the BET surfaces allows a proper comparison to the geometric surface of the substrate, and thus the surface enhancement factor (SEF). Using a chemisorption approach is equally possible, as demonstrated by  $N_2O$  reactive frontal chromatography using Cu/ZnO/ $Al_2O_3$  catalysts coated in a microstructured methanol steam reformer [18].

#### 4.2.2

##### **Coating Stability and Adhesion: State of the Art**

One of the prerequisites to operate successfully a rather expensive microstructured device is durability in performance. In addition to the challenge concerning the catalyst phase itself, which is addressed in Section 4.3, the mechanical integrity of the catalytic coating needs to be preserved.

As already mentioned, the mechanical integrity of a coating is essentially determined by the adhesion of the catalytic layer to the channel surface of the microstructured device. Any detachment of the coated catalyst will cause a loss of performance as (i) the heat transfer between detached catalyst slabs and the reactor is severely decreased and (ii) the hydrodynamics of the reactor might suffer when loose catalyst particles cause flow obstruction in certain channels, thus not being efficiently used any longer. Any endothermic process such as hydrogen production by reforming of hydrocarbons or alcohols is susceptible to suffering greatly from either the consequence of coating failures, namely inefficient heat transfer, or irregular flow distribution among channels.

##### **4.2.2.1 State of the Art in Durable Coating Techniques from a Catalyst Designer's Viewpoint**

One should first note that adhering layers in catalytic reactors impose different characteristics to those for conventional protective coatings [21]. For example, a

catalytic coating always aims at maximizing the surface enhancement factor [SEF, calculated as the ratio of the surface area ( $S_{\text{BET}}$ ) of the coated platelet to the geometric area of the platelet] to expose for a given channel volume a maximum of the catalytic surface. On the other hand, the resulting need for high porosity of the layer is typically to the detriment of its adhesion. Therefore, it is easily understandable that other optimization criteria apply to catalytic coatings than those for protective layers in ceramics or paintings. Moreover, the functional character of a coated catalyst also imposes a strong coupling of mechanical and chemical aspects, therefore tightly interfacing material science considerations to catalytic constraints for a successful development of coatings in MSRs.

Note finally that, as mentioned in the Introduction, the corrosion of the substrate may also damage irreversibly a microstructured device under the severe conditions of fuel processing reactions. For example, under water vapor pressure, many detrimental effects can occur, such as surface migration of Ni in stainless-steel alloys, surface oxidation of metals (Fe to  $\text{Fe}_2\text{O}_3$ ), surface enrichment with trace elements able to alloy/react with the coated catalyst (Sn, Pb,  $\text{Cl}^-$  ions) and poison it or surface substrate restructuring.

To overcome these medium- to long term substrate degradation issues, the surface of the structured material has to be properly prepared and protected during the phase of assembly and catalyst coating. This feature is so important that, as mentioned before, almost no relevant and detailed long-term studies have been reported yet on the corrosion effects on stainless-steel microstructured platelets.

From our own experience, series of various steels (for low and high temperature) were tested under reaction conditions (for example, for methane and methanol steam reforming and partial oxidation to formaldehyde) either as raw materials or after protective layer coating, including the soldering/brazing materials used for assembly. The inertness of each material and coating layer were thus established, with XRD measurements performed in parallel to detect any major change in substrate structures [22].

We will not consider here the large domain of silicon-based microdevices (including silicon nitrides and carbides), which would hardly be considered for fuel processing at the industrial level due to the cost of the substrate material. A general literature review and detailed information on silicon technology-based microreactor design can be found elsewhere [23].

#### 4.2.3

#### Characterization of Coating Adhesion

As a first critical point approaching the development of a coating procedure, one needs to address the characterization of adhesion in a 3D structured system. At present, an internationally recognized, standardized procedure for testing the adhesion of coatings in microchannels is lacking. The very primitive adhesive tape technique could give some tendencies for varying parameters in a washcoating approach applied to flat surfaces. However, the behavior of the coating in channels typically differs due to the change in geometry, and it can be predicted that

the absolute adhesion strength is altered according to the channel environment. Alternatively, a drop test might be employed to yield information on samples carrying a real channel structure. Such an approach has recently been reported in detail [21]. Other workers made use of a more precise and reproducible technique, monitoring the weight loss as a function of time during which ultrasound impulses created a mechanical stress [24, 25].

#### 4.2.4

#### Deposition Techniques

Information concerning coating procedures for microstructured devices is sparse. Most studies available in the open literature present essentially performance data for the reactor without detailing extensive information on the preparation of the catalyst coating or its characteristics. Several publications have discussed briefly the coatings on metallic microchannel platelets, but covered not much more than the preparation methods [26–31]. In the more general context of structured elements, a recent review has collected coating strategies for addressing a multitude of relevant objects, including monoliths where information is more widespread [32].

Deposition techniques most often mentioned include washcoating [24, 27, 33–37], sol–gel approaches [30, 38, 39], chemical vapor deposition (CVD) [26], electrochemical deposition [40] and the Langmuir–Blodgett (LB) method [41].

##### 4.2.4.1 Washcoating

The most common means of depositing a catalyst within microchannels is to make use of the washcoating technique. In the context of washcoating, it seems reasonable to distinguish two subcategories.

**Sequential Washcoating** An inactive support layer, most frequently a  $\gamma$ -alumina, is coated and the active phase is added most frequently by impregnation. The obvious advantage of such a procedure is the possibility of using inexpensive material being less sensitive towards heating (sintering or phase transformation) and chemical (impact of combustible binders or their decomposition products) influences during the coating, layer-stabilizing calcinations and possibly even the reactor assembly. Then, after introducing the catalyst precursor in the second step, the activation could proceed in the assembled system under milder conditions. In turn, the essential drawback of this procedure is that the loading of the active material has to be kept low so as not to harm the layer properties established during the initial deposition. In fact, large quantities of active compounds in an existing layer would massively decrease its porosity, thus leading to a decline in general of the catalyst activity. Accordingly, essentially supported (noble) metal catalysts with relatively low loadings are prepared in this way. Furthermore, the mastering of catalyst activation is crucial and this holds even more if that step proceeds in a preassembled device. Inadequate activation steps, possibly resulting from the difficulties in controlling such a procedure in a supported layer, might result in a lack of specific activity, making the microdevice inefficient.



**One-step Washcoating** This procedure is applied for washcoating preformulated catalysts, such as heavily doped formulations requiring several distinct steps to add successively all components or bulk catalyst prepared by precipitation, with well-adapted and very specific procedures to yield the active material. It takes advantage of established, well-controlled procedures building the catalyst with fine control of all parameters and the wider range of catalysts usable. Furthermore, it is easily possible to check the quality of the catalyst prior to coating it on to the costly structured elements. On the other hand, several drawbacks can be identified: (i) catalyst and coating procedure need to be compatible so that there is no, or practically no, negative impact on the catalyst performance during the deposition, and (ii) risks exist such as leaching of active compounds in suspension, negative action of solvents or additives in suspensions, degradation during the layer stabilization by heat treatments after coating and during assembly of the device, extensive exposure of the catalyst to air and negative impacts of the milling required to achieve a suitable grain size distribution of the catalyst powder.

Attempts have been made to overcome some of the obstacles, for example by flowing coating suspensions through a preassembled device, but typically other problems may arise from the lack of control over where the catalyst is deposited or simply the fact that there is no easy way to inspect the resulting layer without destroying the microdevice.

**Case Studies** In the case of hydrogen production by methanol steam reforming or hydrogen purification by the water-gas shift (WGS) reaction, a commercially available  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst is frequently used for washcoating microdevices. Using non-metallic substrates, a method has been developed to control the thickness from 1 to 25  $\mu\text{m}$  employing a liquid film coating and controlled gelation of a boehmite slurry [42]. Obviously, a calcination step was required and apart of the effect of the Cu:Zn ratio and the impact of metal loading, the influence of the calcination temperature has been investigated to optimize the catalyst layer. Other workers [43, 44] performed similar studies replacing zinc with cerium. Furthermore, Germani *et al.* [45] performed a systematic study on the nature of binders used for coating a  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst into microchannels and their influence on catalytic activity for the WGS reaction. They concluded that binders play a major role in (i) slurry viscosity by their chemical structure but also through their molecular weight, (ii) coating adhesion and (iii) catalytic activity by redispersion of the active phase because of metal complex formation.

Although hardly used for fuel processors, washcoatings with zeolite-based material deserve to be mentioned for their specificity. Hiemer *et al.* [46] opted for a washcoating procedure leading to iron-exchanged ZSM-5 coatings in which alumina was added to the ZSM-5 material in order to allow the formation of a stable and adherent layer. As an alternative approach, Rebrov *et al.* [47] outlined in a review article a procedure to prepare ZSM-5 catalysts for selective catalytic reduction of NO with ammonia by controlled growth of layers. The coating thickness was adjusted by varying the reaction temperature, the synthesis time, the  $\text{H}_2\text{O}:\text{Si}$  and  $\text{Si}:\text{template}$  ratios and the orientation of the platelet with respect to the gravity vector.

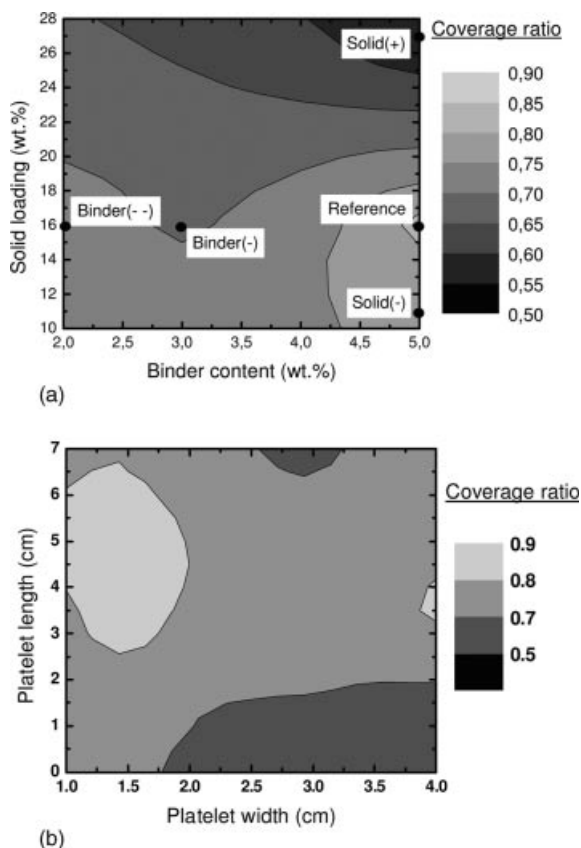
Subsequently, a ZSM-5 zeolite coating was prepared with a zeolitic layer thickness of a single crystal, particularly suitable for the considered catalytic reaction.

**Compatibility of the Structured Substrates, Washcoating Procedure and Catalytic Activation with the Requirements for a Catalyst** Obviously, it is necessary to limit contamination of the catalytic formulations possibly impacting on the performance. Zapf *et al.* [48] reported on a study concerning the preparation of porous alumina washcoats in the microchannels, focusing on the pretreatment of the microstructures, properties and adhesion of the washcoats. Anodic oxidation and thermal treatment of the microstructures significantly reduced the undesirable chlorine content, which was assumed to have deleterious effects on the catalyst activity. From the same study, an impregnated  $\text{Cr}_2\text{O}_3$  within alumina washcoat was shown to be homogeneously distributed in vertical (depth of the coating) and horizontal (at the coating's surface) directions. In turn, the content of CuO decreased with the washcoat depth and islands of accumulated material were observed on the coating surface. The activity of the CuO/ $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  system was investigated for methanol steam reforming.

Concerning the case where a readily prepared catalyst is applied to a structured substrate (one-step deposition), it is important that chemicals added for the coating do not harm the catalyst. Germani *et al.* [45] illustrated the possible negative impact of organic binders and acetic acid on the activity of a CuO/ $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst for the WGS reaction in an MSR. It was concluded that dissolution–complexation–redosition processes especially caused by the acetic acid decreased the catalytic performance substantially.

**Flexibility of the Coating Procedure** Another essential parameter to be considered for promoting a method of catalyst coating is its ability to be adapted to a given system. Often, promising techniques suffer simply from the fact that a procedure is only feasible for certain conditions or from a restricted range of layer thickness. Moreover, the control of the layer thickness and the homogeneity of the thickness, both across the channel structure and also at a given spot for the bottom of the channel and the sides along the fins, are essential for high-performing devices in hydrogen generation from fuel processing.

Generally for a washcoating procedure, it is observed that the overall layer thickness is influenced by the solid loading of the suspension, as is rationalized by the fact that the channel structure becomes filled with the suspension and the catalyst quantity contained in that volume will form the layer. On the other hand, the viscosity of the suspension seems to impact on the cross-sectional shape of the coating, yielding a more U- or V-type coverage of the channel perimeter, thus indicating for a given position in the channel a homogeneous or irregular layer thickness, respectively [45]. As a higher viscosity favors local regularity, the suspension viscosity should be high. On the other hand, viscosity is limited by the fact that the homogeneous spreading of the suspension throughout the channels should not be affected. Furthermore, one can rationalize that the particle size of suspended catalyst grains should be small and homogeneous to prevent irregularities by sedimentation effects during the time span between suspension spreading and



**Figure 4.1** (a) Coverage ratio as a function of binder content and solid loading. (b) Coverage ratio over the platelet using the reference slurry as a function of the position of the coated channels over a microstructured platelet.

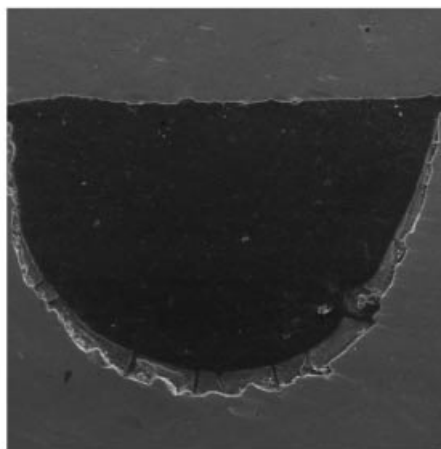
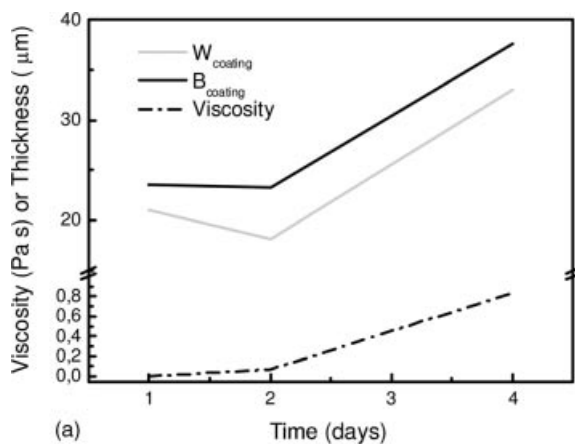
complete drying. The latter constraint should be especially addressed, as studies in our laboratory indicated that this also impacts greatly on the adhesion of the coating.

Figure 4.1a illustrates a complex relationship that was established between two washcoating parameters, the content of binder and of alumina/boehmite (referred to as “solid”) added to the slurry and the observed coverage ratio of the microstructured platelet after calcination at 800 °C and the formation of a  $\gamma$ -alumina layer. Figure 4.1b indicates that heterogeneity in surface coverage may also depend on the position of the channels over a given microstructured platelet [37].

Figure 4.2 illustrates the relationship between viscosity, wall and bottom thickness of the washcoated layer and time of aging of the slurry before coating.

#### 4.2.4.2 Sol–Gel and CVD Methods

When coating methods such as dip or spin coating of sol–gel systems are employed, parameters other than viscosity or solid loading may also govern the layer thickness



(b)

**Figure 4.2** (a) Relationship between viscosity, wall and bottom thickness of the washcoated layer and time of aging of the slurry before coating. (b) SEM image of a channel section showing differences in wall and bottom coating thickness.

and homogeneity of the deposited layers. Detailed information on influencing parameters for the case of coating channel-structured substrates are scarce. However, some general observations on sol-gel coating should be extendable to this special case:

1. In the case of dip coating, the regularity of the extraction velocity of the substrate for the sol impacts directly on the homogeneity. Given the risk of local accumulation of the sol in the channel structure when the direction of extraction does not coincide with the channel axis, reasonable results should be expected for linear channel configurations whereas less uniformity should be expected with other geometries (e.g. spiral or fractal, adapted to the targeted reaction). Although spin

coating of flat substrates typically yields very homogeneous results, a study in our laboratory revealed that this is far from certain for structured substrates with channels [17]. This observation was explained by the fact that the structure hinders free flowing of the sol on the substrate, preventing the simple establishment of a homogeneous sol film under the influence of the centrifugal force during spinning, resulting in local accumulation in the channels.

2. Obviously, as in the case of washcoating, the solid content of the sol impacts directly on the film thickness, but viscosity might also play a direct role for both dip and spin coating.
3. In the case of CVD coating, the homogeneity of temperature across the channel structure will determine the regularity of the film thickness, given that optimized operating parameters for the CVD process ensure that the flow of the CVD precursor through the reactor is laminar and the deposition rate is controlled by the chemical deposition reaction. In ideal cases, the film thickness should be directly proportional to the deposition time. It should also be stressed that CVD coating presents the potential advantage of permitting reloading/revamping of assembled microstructures with active components, after long-term aging operation resulting in active phase losses.

#### 4.2.5

#### Other Requirements for Coating Optimization

Finally, it needs to be stressed that especially the area of fuel processing for hydrogen production targets the rapid introduction of product to the market with severe constraints on the production costs. This obviously explains why any coating procedure needs to have reasonable potential for *automation and time savings*. First developments reported for coating automation might lead to more economic coating at larger scales [49]. In this context, it should also be stressed that the control of coating selectivity (i.e. the way of depositing the active phase precisely where it is required) is a savings issue to be considered, (i) to avoid wasting often costly catalytic material and (ii) to avoid surface cleaning steps if a catalyst is not just applied to the channels. The latter cleaning steps might even have a negative impact on the catalyst if not just a mechanical action, such as stripping off or scraping off excess material, needs to be applied, such as chemical attack of the excess or cleaning using specific solvents. Thus, from an industrial point of view, the most promising process route might involve the following strategy provided that suitable catalyst performances are achieved: first, coating more or less selectively an inexpensive catalyst support such as  $\gamma$ -alumina, then cleaning the structure, adding and activating the active phase of the well-located support.

In the case where bulk catalyst needs to be coated, the chemical compatibility of the suspension solvent and additives with the catalyst phase and the larger consumption imposing relatively low catalyst prices are issues. Fortunately, it is generally the case that catalyst formulations making use of expensive precursors such as noble metals contain only low relative loadings on an inexpensive support to improve dispersion. Therefore, it

seems possible to follow the first proposed route whereas bulk catalysts requiring processing according to the second route are generally much less expensive material. Nevertheless, recycling strategies for the eliminated catalyst excess seem to be desirable.

### 4.3

#### Catalyst Screening in MSRs and Optimization from Reaction Modeling

The distinct advantages of MSRs for fuel processors have already been discussed in previous chapters. An additional advantage is the possibility of screening catalysts in MSRs in the laboratory. First, the device is close to that used for commercial application. More integrated units consisting of mixers and heat exchangers, all on the microscale, can be readily tested (see Introduction). The hold-up of reactants and products is smaller, giving improved safety. In some cases, especially MSRs based on silicon technology, sensors can be built [23]. However, drawback is that often a more elaborate catalyst development is needed, as thin layers inside microchannels have to be synthesized. Post-mortem catalyst characterization will be more difficult for closed stacks. *In situ* characterization is still an important area to be developed.

To illustrate this specific capability of MSRs, this section focuses on the performance testing of catalysts for fuel reforming reactions. There exist a number of reviews on the use of MSRs for catalytic reactions [6, 11, 50]. The emphasis here will be on the catalyst–MSR couple. The testing of integrated fuel processors consisting of reforming and clean-up units such as the examples quoted in the Introduction [5, 6, 8] are beyond the scope of this section as (i) very few process data have been published yet and (ii) this topic is treated in other chapters of this book. A separate section is devoted to the use of laboratory-scale MSRs for kinetic measurements, as this requires certain precautions.

#### 4.3.1

##### Catalyst Performance Testing in MSRs

Different configurations are used for the screening of catalyst activity in MSRs. As stressed before, the easiest way to incorporate a catalyst is by filling the microchannels directly with catalyst powder. This allows the use of optimized powder catalysts while still taking the benefit of good heat transfer by coupling it to a microstructured heat exchanger [51].

In most cases, the catalyst is deposited inside the microchannels by using one of the many methods discussed in detail in the previous section. Compared with the packed-bed reactor, MSR heat- and mass-transfer phenomena are improved and the pressure drop is substantially reduced.

There are some other configurations of structured beds with microscale dimensions such as the use of parallel fibers [52], gauzes [53] and foams [29].

##### 4.3.1.1 Examples of Reforming in MSRs

Among several studies reporting catalyst development in MSRs for the steam reforming of methanol over well-known catalysts such as Cu/ZnO and Pd/ZnO [16, 54–56],

one proposes the coupling of this endothermic reaction with the exothermic total oxidation of methanol in a two-pass reactor [57]. A commercial copper-based catalyst was used for the steam reforming, whereas for the total oxidation a cobalt oxide catalyst was developed. Both catalysts are used in the form of thin layers on the wall of the microchannels. Complete conversion of methanol above 250 °C was observed in the oxidation reaction. For the steam reforming, the hydrogen and CO<sub>2</sub> selectivity is higher than 96% for methanol conversion up to 90%. In addition to the steady state, the dynamic behavior of the coupled system was studied. It was shown that the transient behavior is mainly determined by the thermal inertia of the system.

Rh/Al<sub>2</sub>O<sub>3</sub>/FeCr alloy microchannel monoliths were compared with Rh/alumina foams for the production of hydrogen from propane. Temperature profiles obtained along the central axis were valuable in understanding the different behaviors of the reactor systems [58].

Gd-doped CeO<sub>2</sub> with 0.5 wt% Pt formulas were tested both using pellets and in an MSR for the autothermal reforming of isooctane. The use of an MSR led to a five-fold increase in the hydrogen production per unit weight of catalyst [59].

#### 4.3.1.2 Examples of CO Clean-up in MSRs

The preferential oxidation of CO was studied in a silicon MSR consisting of two inlets, a premixer, a catalytic zone and an outlet cooling zone [60]. A Pt/alumina catalyst layer of 2–5 μm was obtained by successive sol–gel procedures. Using appropriate criteria, it was estimated that no heat- and mass-transfer limitations occurred below 220 °C, thus giving access to the intrinsic reaction kinetics. The authors pointed out the advantage of their MSR compared with packed-bed reactors that they were able to avoid any hot spots in the reactor, thus preventing the reverse WGS reaction from taking place.

Preferential oxidation (PROX) catalysts were prepared by washcoating of alumina suspensions with PVA and acetic acid [61]. The stainless-steel reactor contained heat exchangers at the inlet and outlet and the stacks were sealed with graphite seals. Temperature was measured with a thermocouple at the reactor outlet. Noble metal-based catalysts supported on alumina were tested. The influence of the temperature, space velocity and O<sub>2</sub>/CO ratio and the effect of water were studied. The CO content could be reduced from ca 1% to 10 ppm. The authors recommended a dual-stage PROX reactor in order to minimize the hydrogen loss.

The advantage of thin catalyst layers has been demonstrated for the WGS reaction over a Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst [16]. The conversion of CO was measured at various temperatures over both a powder sample with an average particle size of 250 μm and over the same catalyst prepared by a sol–gel method in stainless-steel microchannels. The equivalent particle diameter of the catalyst layer inside the microchannel was 37 μm. The initial rates obtained at low temperatures over the powder sample compare well with those obtained over the microstructured platelets. However, the data between powder and platelets deviate substantially at higher temperatures. The conversion over the powder samples is lower than that over platelets, indicating that there might be diffusion limitation inside the powder grains. A simulation that took into account the diffusion of matter inside the

powder grains and the reaction rates measured in the MSR confirmed this. This kinetic study was extended and a detailed mechanism for the WGS reaction over a Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was derived [62].

Selective methanation of CO has been investigated over washcoated supported metal catalysts in a microchannel reactor with simulated reformat feeding [44]. An Ni/CaO/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited the highest methanation activity with CO conversion higher than 93% and a relatively low conversion of CO<sub>2</sub> into methane among investigated catalysts at 300 °C. CO methanation occurred exclusively below 250 °C. The catalysts inside the microstructures were prepared by washcoating of alumina suspensions with PVA and acetic acid.

Görke *et al.* [63] performed CO methanation over Ru/SiO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts with co-feeding of oxygen. If CO in the presence CO<sub>2</sub> has to be converted by methanation, a sufficient amount of O<sub>2</sub> has to be added and temperature has to be controlled precisely. The authors state that this is easily feasible using microstructured reaction technology. Catalysts were synthesized by a two-step procedure: washcoatings in the microstructured channels of oxides of silica and alumina were prepared by a sol-gel method. After calcination at 500 °C, these oxide layers were impregnated with a solution of RuCl<sub>3</sub>.

By using integrated heat exchangers, researchers at PNNL [64] were able to control the temperature of a microstructured WGS reactor and impose a near optimal temperature profile, thus reducing the size of the unit by a factor of two.

Görke *et al.* [65] prepared different microstructured catalysts (Au/CeO<sub>2</sub>, Ru/ZrO<sub>2</sub>, Ru/ZrO<sub>2</sub> Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, CuO/CeO<sub>2</sub>) on both FeCr alloy and stainless-steel platelets for the WGS and Selox reactions. The good temperature control of the MSR proved to be essential for good performance of the Selox reaction.

The examples of catalyst screening cited above mainly demonstrate the concept of MSRs for fuel reforming processes. In addition, MSRs show some additional experimental benefits such as rapid response times for transient experiments and the coupling of endo- and exothermic reactions. Note, however, that as already stressed, if all studies claim excellent adherence and catalyst activity, key information is usually missing, such as a comparison of different catalyst synthesis methods, catalyst characterization or measurement of the temperature inside the reaction channels.

#### 4.3.2

##### Microstructured Reactors as Kinetic Devices

###### 4.3.2.1 Criteria for Proper Reactor Operation

As stated above, dimensions in MSRs are often representative of the final application as these devices are generally not scaled-up but numbered-up. Thus catalyst screening in microstructured devices allows for proper catalyst performance evaluation under realistic conditions. In this case, these studies will be sufficient as they give all the necessary information to estimate the performances of full-scale units. If, however, the MSR needs to be optimized in terms of channel geometry or washcoat design (porosity, thickness), then kinetic studies will be necessary. Another reason for using MSR to study kinetics is that these devices might allow one to study



the intrinsic kinetics by eliminating transport resistances that exist in fixed-bed reactors. This is not a completely new concept as structured catalytic reactors are often used for kinetic studies where thin layers are necessary to overcome internal diffusion limitations [66, 67].

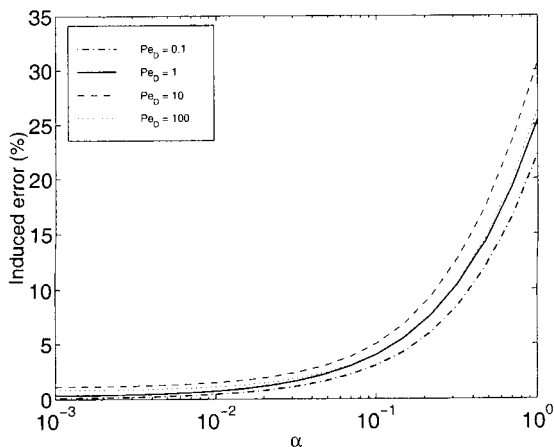
The reactions involved in fuel processing such as reforming of hydrocarbons and the PROX reaction are extremely fast and accompanied by strong heat effects and the measurement of the intrinsic kinetics in a fixed-bed reactor is not possible. Hence the use of microstructured devices that conduct the heat well might help to establish isothermal reaction conditions and the thin catalyst layers employed avoid internal concentration gradients. This section explores the possibilities of using the special features of microstructured devices for kinetic experiments. The use of the MSR as a kinetic device gives some distinct advantages, but a number of precautions have to be taken into account. These issues are discussed in the following.

By reducing the channel dimensions, the wall effects will become more and more important and beyond a certain point the hypotheses of the classical engineering continuum transport models will no longer be valid. In general, classical flow models can be used with appropriate slip boundary conditions in microstructured devices with characteristic dimensions larger than  $10\ \mu\text{m}$  [68].

Most MSRs used in fuel reformers have channel diameters on the order of  $100\text{--}1000\ \mu\text{m}$ . The flow through these microchannels is laminar. Laminar flow through circular ducts requires a two-dimensional flow model to describe the velocity and concentration field accurately in both the radial and axial directions. For kinetic studies involving parameter estimation, simplified models are preferred. Different one-dimensional approaches have been proposed. Commenge *et al.* [69] compared a two-dimensional convection–diffusion equation for transport and reaction in cylindrical channels with first-order reaction at the wall with a pseudo-homogeneous plug-flow model and a one-dimensional dispersion model. They solved the 2D problem numerically and compared the results with the two 1D solutions. In this way, they were able to examine the influence of radial mass transfer on the accuracy of heterogeneous kinetic measurements in microchannel reactors. The solutions of the 2D problem depend on the radial Peclet number and the heterogeneous Damköhler number. The error induced in the heterogeneous rate constant measurement by using the plug flow assumptions depends strongly on the value of the Damköhler number and only weakly on the Peclet number. Figure 4.3 shows the error induced in the rate constant as a function of the Damköhler number for different radial Peclet numbers. For Damköhler numbers smaller than 0.1, the error in the rate constant is less than 3%.

Walter *et al.* [70] discussed the different experimental test methods to verify the absence of external or internal diffusion limitations in coated microchannels. They proposed to vary different operating conditions or to modify the reactor geometry. Apart from changing the reaction temperature, the other proposed methods are either difficult to realize in MSRs or the effect on the transfer phenomena is small.

Berger and Kapteijn [71] have developed criteria involving only the observed conversion to justify neglecting radial concentration gradients and to be able to use the simple plug-flow model to describe the reactor performance.



**Figure 4.3** Variation of the error induced in the measured rate constant  $k_s$  under plug-flow assumptions as a function of the Damköhler number  $D$ , for various values of the radial Peclet number  $Pe_D$  and a microreactor channel length  $L = 10R$ . Reproduced from Commenge *et al.* [69].

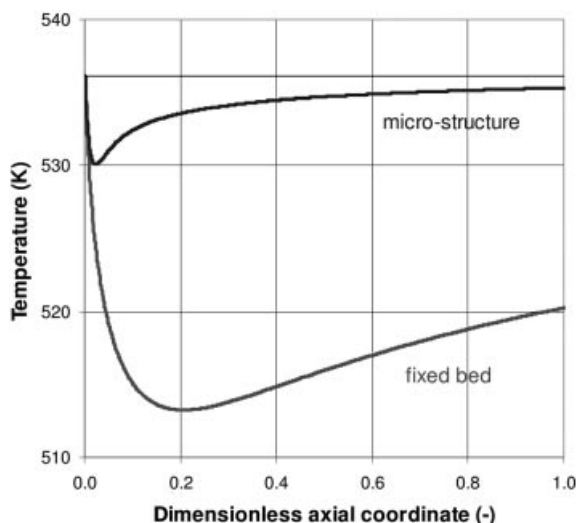
Rouge *et al.* [27] determined experimentally the dispersion in an MSR by introducing a gas pulse at the reactor inlet. Five plates containing 34 quadrangular channels of width  $300\ \mu\text{m}$ , depth  $240\ \mu\text{m}$  and length  $20\ \mu\text{m}$  were stacked together. A Bodenstein number of 70 was calculated from the outlet response, indicating that the reactor behaved almost as a plug-flow reactor. The catalyst coating did not influence the Bodenstein number but it changed if graphite seals were used instead of a glued stack.

Delsman *et al.* [72] studied the influence of variation of channel width and variation of the catalyst weight on the overall conversion. They showed that for a first-order reaction, both experimentally and theoretically, variations in the amount of catalysts per channel lead to lower conversions. In fact, this is analogous to a powder catalyst badly diluted with an inert powder in the case of fixed-bed reactors. This can be avoided by carefully selecting platelets with similar catalyst weights.

Note that the requirements for plug-flow conditions and the need for small deviations in the catalyst amount per platelet favor an MSR design that stacks the platelets in a serial fashion rather than in the commonly encountered parallel layout.

Although the thermal conductivity of stainless-steel MSRs is in general better than that of fixed-bed reactors, this is not a guarantee that the MSR will be isothermal under reaction conditions. In the case of methanol reforming over  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalysts at a wall temperature of  $260\ ^\circ\text{C}$ , the temperature profiles for both a fixed-bed reactor (i.d.  $4\ \text{mm}$ ) and a stainless-steel-based MSR (hydraulic channel i.d.  $0.3\ \text{mm}$ ) were calculated [18]. This endothermic reaction proceeds with a reaction enthalpy of  $+57\ \text{kJ mol}^{-1}$ . The results are presented in Figure 4.4.

For the MSR, the heat conduction in the axial direction is not taken into account, which would have flattened out the profile. The calculated temperature profile in the fixed-bed reactor corresponded well with the experimental data. In the MSR, the



**Figure 4.4** Comparison between calculated temperature profiles for methanol steam reforming in fixed-bed and microstructured reactors.

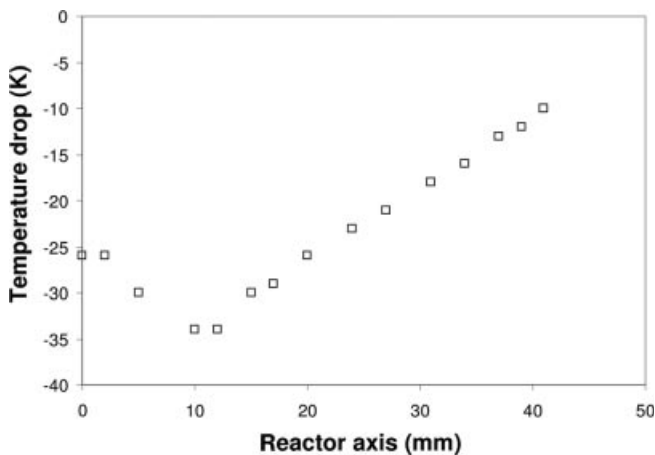
temperature profile has not been measured, as the insertion of a thermocouple inside the microchannels was not feasible. By diluting the fixed-bed catalyst 10-fold with SiC, a similar temperature profile to that in the MSR can be obtained, but at a considerably higher pressure drop. Although this example shows that for this moderately endothermic reaction quasi-isothermal conditions can be obtained, experimentally measured temperature profiles for the four times more endothermic methane steam reforming ( $\Delta H = +225 \text{ kJ mol}^{-1}$ ) in a stainless-steel MSR at  $800^\circ\text{C}$  showed a cold spot at the reactor entrance of 35 K, as shown in Figure 4.5 [73].

#### 4.3.2.2 Existing Links Between Kinetics and Catalyst Preparation in MSRs?

The use of kinetics to optimize the design of an MSR is an important perspective although rarely applied and/or described so far. In this context, several features deserve to be considered as modern microstructured devices approach an efficiency such that the catalyst in the reactor itself becomes performance limiting. Therefore, the specific catalyst activity should be maximized and, assuming already optimized formulations, one way to proceed is to target relatively thick and porous layers, which obviously requires an optimization process, as described below. Here, the current discussion on better using micro- or milli-structured devices fully applies.

There are three upper limits to the layer thickness in structured reactors:

1. The coating stability, essentially related to the preparation process, usually decreases with thickness and layer porosity.
2. The radial temperature gradient in the catalytic layer should be minimized for taking full benefit of the microstructured configuration. This gradient is obviously proportional to the specific activity and inversely proportional to the thermal



**Figure 4.5** Experimental temperature profile measured for the steam reforming of methane in a stainless-steel microstructured reactor at 800 °C

conductivity of the layered catalytic material. However, the specific activity scales typically with the specific surface area of a given material, and hence its porosity, which then unfortunately decreases the thermal conductivity. Obviously, here is a first optimization problem directly linking the kinetics and the preparation of catalyst coatings in a complex way. Note also that measuring the proper thermal conductivity of a catalyst layer in an MSR remains a challenge, since it is strongly dependent on the state of the interface between the layer and the substrate. However, advanced heat transfer modeling from cold model experimentation may at least partially substitute real *in situ* measurements.

3. Finally, the efficiency factor of the catalyst should be close to unity, implying that there should be no diffusion limitation in the catalyst layer. Here porosity generally enhances the diffusion, which brings the optimization process back to the previous features.

In summary it seems that the ideal catalyst layer design in a microstructured devices is achieved by solving quantitatively the opposite trends between (i) porosity, which means effective diffusion and high specific activity, and (ii) denseness, which means high thermal conductivity and layer stability. The resulting maximum should lead to an optimal reactor design in terms of heat transfer and productivity determined by intrinsic kinetics.

#### 4.4

#### Conclusions and Perspectives

From this survey of catalyst development for micro fuel processors, it can be seen that achieving targeted performances of MSRs requires investigating relationships

between (i) the tested preparation methods and (ii) the catalytic behavior of the microstructured platelets assembled as microreactors. Although still scarce, the most detailed studies reported to date demonstrate that the preparation and deposition methods influence tremendously key properties such as adhesion, uniformity, material characteristics (porosity, crystallographic structure, etc.) and intrinsic catalytic activity.

The microreactor performance can therefore be considered to be linked to all these parameters in a highly complex manner, depending both on the microplatelet design (and composition) and on the deposition technique. Consequently, from the published literature, no unique best-fitted method for depositing the desired catalytic layer on microstructures, meeting the targeted performances, can be unambiguously proposed. This relates to the differences in development for each deposition technique. However, some general trends for developing a performing micro fuel processor can be proposed for further optimization:

1. For the most common case of hydrocarbon reformers based on Ni catalysts, the presence of a promoter introduced by a method creating strong interactions with base material such as alumina ensures satisfactory stability under the test conditions while permitting full conversion of the probe hydrocarbon with a high yield in hydrogen production.
2. For the most frequently used washcoating technique, a catalyst powder with small-sized particles permits superior adhesion to be achieved. However, during the preparation steps, the presence of an interlayer, acting as an interface between the structured substrate and the catalytic layer, represents a prerequisite for acceptable mechanical stability of the catalyst.
3. Using the CVD technique offers the unique feature of a non-line-of-sight deposition, particularly well adapted to the confined and hardly accessible geometry of an assembled microreactor. In addition, a virtually unlimited catalyst loading with active metal is possible. Finally, the possibility of performing the CVD reaction quasi-*in situ*, directly in the closed microstructured reactor, might be well adapted to the development of industrial microsystems and maintenance (reloading of active phase for a deactivated unit).
4. Improved or new techniques for platelet assembly (low-temperature soldering and/or brazing rather than high-temperature diffusion bonding) should be carefully adapted to the specific properties of the catalyst coatings to avoid any contamination or poisoning effects, while ensuring their adherence and long-term stability.

A second major feature of the MSR in the domain of fuel processing is their ability to be used as kinetic devices for efficiently investigating the correct platelet design (channel dimensions) and catalyst coating parameters. As such, microreactors, if properly used, can serve as realistic tools for screening catalyst formulations, with the potential of being used as effective combinatorial devices. In addition, the robust kinetic models derived from these studies can be used (i) for optimizing the thickness and porosity of the catalytic layer for a given platelets design and configuration and (ii) for optimizing process operation in pilot-scale units.

To conclude, laboratory- and pilot-scale investigations of MSRs as fuel processors have demonstrated their industrial potential in those cases where fast reaction rates or strong heat effects become major obstacles to proper process design. However, effective industrial implementation is still under debate. Nevertheless, MSR investigation remains a fascinating domain for academia, able to bring new insights to innovating fields positioned at the interface of materials science, applied catalysis and engineering processing for integrated systems. As with most emerging technologies, this research is still in its infancy and should converge sooner or later towards the confidential R&D carried out within large industries and small & medium enterprises.

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