Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 110 (2005) 164–170

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Design and fabrication of a structured catalytic reactor at micrometer scale: Example of methylcyclohexane dehydrogenation

Marilyne Roumanie [a], Valérie Meille [b,*], Christophe Pijolat [a], Guy Tournier [a], Claude de Bellefon [b], Patrick Pouteau [c], Cyril Delattre [c]

[a] *Ecole des Mines de Saint Etienne, centre SPIN, Dpt MICC, LPMG-UMR CNRS 5148, 158 Cours Fauriel, 42023 Saint Etienne, France*
[b] *Laboratoire de Génie des Procédés Catalytiques, CNRS, CPE, 43 bd 11 novembre 1918, BP 2077, 69616 Villeurbanne Cedex, France*
[c] *Laboratoire d'électronique, de technologies et d'instrumentation LETI-CEA, 17 rue Martyrs, 38054 Grenoble Cedex 9, France*

Abstract

A silicon micro-structured reactor has been designed for gas–solid heterogeneous catalysis, in particular for the dehydrogenation of methylcyclohexane. Two types of catalyst deposition on silicon have been evaluated: the first consists of a washcoat deposition of a γ-alumina layer followed by Pt impregnation, the second is a cathodic Pt film sputtering. The Pt/Al_2O_3 catalyst reveals a higher activity for this reaction and was selected for further investigation. Since the micro-structured reactor is composed of pillars of typical dimension 5×100 μm, a special washcoat method has been developed leading to the controlled deposition of a homogeneous γ-alumina layer of thickness <1 μm. Because the dehydrogenation reaction is endothermic (204 kJ mol^{-1}) and conducted at ca. 380 °C, heaters have been integrated using screen-printing methods. FEMLAB simulations have helped to integrate the hot reaction zone and a low temperature section for connectors (<200 °C) in a 10×30 mm chip.

Keywords: Microreactor; Catalysis; Micro heater; Washcoat; Dehydrogenation

1. Introduction

Biomedical analysis was the first area where microdevices have found large applications, in particular with the development of DNA chips. These microdevices, often called ''lab-on-a-chip'' have attracted the interest of chemists, mainly for analysis purposes with micro-total-analysis systems (μ-TAS) but also for applications in both homogeneous and heterogeneous catalysis [1–4]. This stems from their potential to conduct mass or heat transfer-demanding reactions under safe conditions while maintaining and/or increasing selectivity and productivity. The small volumes involved and high heat transfer capabilities allow safe handling of hazardous reactions or chemicals to be achieved [1]. Furthermore, linkage with ongoing works on microfluidic for integration of micro-valves, pumps, sensors, mixers and separators will lead to complete process integration in micro-devices.

For research in catalytic processes, these developments call for new challenges such as multiphase contacting in micro-structured components, high pressure and high temperature conditions and the presence of solid catalysts, just to name a few. The development of micro-system for hydrogen generation in fuel-cell application for embarked energy sources is calling for such challenges. Thus, among the many reactions that generate hydrogen, the dehydrogenation of hydrocarbons is often cited [5,6]. This reaction is endothermic and requires high temperatures (>300 °C) to shift the thermodynamic equilibrium and reach high conversions. The use of a catalyst allows higher selectivity and avoids a too high reaction temperature that would lead to side products. The dehydrogenation of cycloalkanes is activated by Pt containing heterogeneous catalysts. Many methods have been reported for the deposition of active Pt material in micro-structured devices. Platinum can

---

* Corresponding author. Tel.: +33 4 72 43 17 55; fax: +33 4 72 43 16 73.
E-mail address: vme@lgpc.cpe.fr (V. Meille).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.09.013

be deposited using chemical vapor deposition CVD, physical vapor deposition PVD [7], impregnation of molecular material onto a porous washcoat, prepared by anodic oxidation or sol–gel techniques, or introduced as a powder [8]. According to literature records, the heater can be either integrated to the micro-component as Pt resistances deposited on the Si-device through cathodic sputtering [9] or by screen printing [10], or designed as an electrically heated metallic block supporting the micro-component.

In the micro world, one very pragmatic problem is the connection, both fluidic and electric, to the “macro” environment. The tubing, connections and instrumentation, e.g. temperature and pressure sensors, have to be adapted to the small volumes, the very small flow rates and the temperatures used. Whereas solutions, such as e.g. welding, screwing or gluing, have been developed for metal and ceramic made micro-devices [1], it remains a problem for more brittle silicon based components. For silicon micro-devices, two solutions have been evoked in the literature: interfaced metallic connections between the Si micro-component that lower the temperature [11] and integrated Si tubes [12].

This report describes our ongoing work on the dehydrogenation of methylcyclohexane in a silicon micro-structured component. Heat management and connection to the macro-environment are particularly addressed because problems had to be solved due to both a high working temperature and an elevated endothermic heat of reaction. Two techniques for catalyst deposition are also evaluated, based on catalyst activity measurements.

2. Micro-component

The silicon chip used in the study has been developed at CEA-LETI for bio-medical applications (Fig. 1). It consists of a coiled micro-channel of 1500 μm width, 100 μm depth and 14 cm long made by Deep Reactive Ion Etching DRIE. The channel is packed with circular pillars of 5 μm in diameter and 100 μm high with a space of 5 μm between them (Fig. 1b). The pillars packing leads to a 10 fold increase of the wall surface thus a 13 fold increase of the specific wall area which amount 12 700 m^{-1}. That will result in an increase of catalyst surface as well as an improvement of mass and heat transfer capabilities. An evaporation section is integrated between the inlet of the micro-component and the reaction channel described above. It consists of a bent micro-channel of 100 μm width and 3.5 cm long. The micro-component is capped with a pyrex glass by anodic bonding.

Similar pillared structures are described by Jensen but the characteristic size of the pillars is 50 μm in diameter and 400 μm high with a space of 50 μm between them [13].

3. Reaction and catalysts

The catalytic dehydrogenation of methylcyclohexane to toluene was chosen as the test reaction (Eq. (1)).

$$C_7H_{14} \leftrightarrow C_7H_8 + 3H_2 \qquad (1)$$

This reaction is very endothermic (204 kJ/mol) and requires high temperatures (>350 °C), even at atmospheric pressure, to shift the thermodynamic equilibrium and reach high conversions. At temperature above 400 °C however, side reactions such as cracking lead to undesired products. Thus, one technical problem the microdevice must ensure is a gradientless temperature profile within the micro-reaction volume.

Two catalysts have been used: a Pt/Al_2O_3 solid very well reported to catalyze both hydrogenations and dehydrogenations albeit under different pressures and temperatures and a platinum film (Pt/film) made by cathodic sputtering. This latter film was deposited on a surface of so called “black silicon” obtained by dry etching of silicon using controlled process conditions that are reported in earlier studies [14]. A grassy surface is created with sharp and conical features with dimensions depending a lot on process conditions and reaching in this particular case 1 μm in height and 0.1 μm in width at mid-height (Fig. 2).

In the Pt/Al_2O_3 catalyst, γ-alumina is used as a high surface porous solid to support well-dispersed nanosized crystallites of Pt. The alumina layer is prepared from a suspension of boehmite γ-AlOOH (Disperal, Sasol) of high BET surface (190 m^2/g), which after calcination, gives γ-Al_2O_3 [15].

In order to test the anchoring of the alumina layer on the silicon components, either micro-structured or flat silicon, the surfaces were used as such, i.e. silicon, or pretreated. After washcoating with the suspension, the silicon components were dried (100 °C) and calcinated (600 °C) in an oven during 4 h, which leads to the γ-Al_2O_3 washcoat. ESCA analysis reveals an oxygen 1s shift at 531 eV comparable to that of a thermally treated boehmite powder, which confirms the nature of the washcoating layer after calcination. Platinum impregnation was done by dipping the samples for 3 h in a 1 g/L toluene solution of platinum acetylacetonate (from Strem Chemicals), drying at 100 °C, calcinating at 400 °C under air for 4 h and reducing under hydrogen at 400 °C for 2–4 h. A similar procedure was used for platinum or palladium deposition on an alumina layer

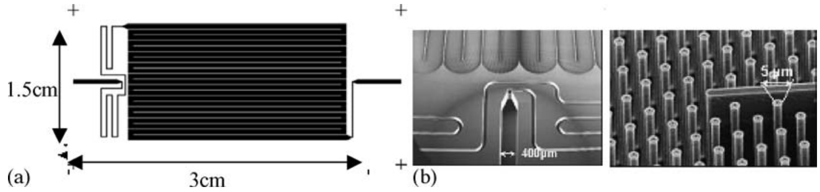

Fig. 1. Schematic presentation of the micro-component (a) and top view photograph of the pre-heating and reaction channels and detail of the pillared structure (b).

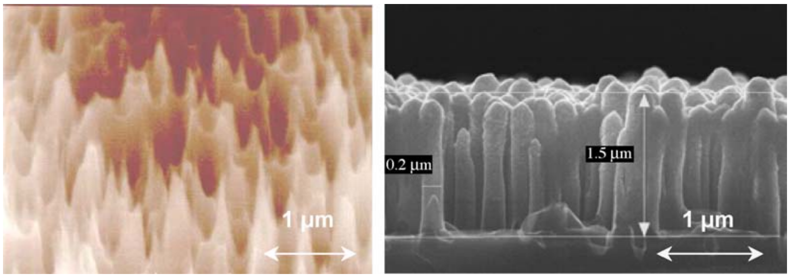

Fig. 2. SEM pictures of black silicon, before (left picture) and after Pt deposition (right picture).

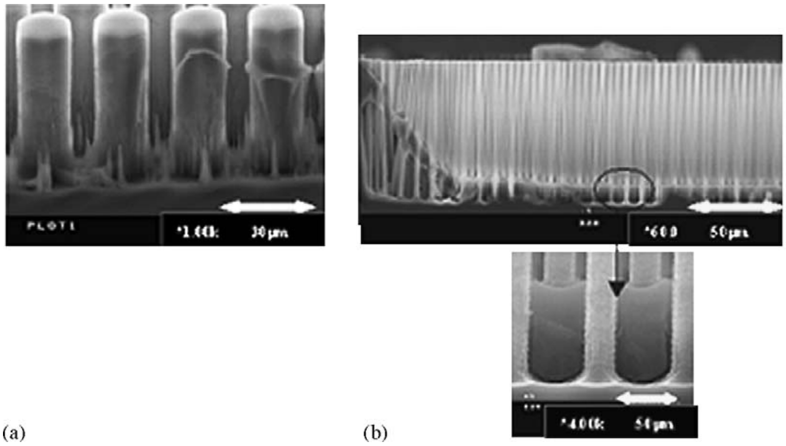

Fig. 3. SEM photographs of the γ-alumina layer after deposition in the micro-structured components: (a) with pretreatment and (b) without pretreatment.

for gas–liquid–solid hydrogenation in a micro-structured gas–liquid mesh reactor [16].

Silicon components can be either a simple Si-plate for deposition and catalyst testing (see below), or a micro-structured device (open or closed with a cap).

The alumina layer deposition is similar for the Si-plate and the open Si-micro-structured component. These microelements are dipped in an aqueous suspension of Disperal and treated as described above. SEM images reveal the importance of the presence of the surface treatment before alumina deposition (Fig. 3). Whereas blocks of alumina are obtained by decantation of the colloidal suspension in the bottom of the channel in the case of the untreated Si-component, isotropic and homogeneous alumina layer deposition over all the component is reached due to the pretreatment.

Alumina layer deposition in closed micro-structured devices requires a slightly different procedure. First, polyimide coated glass capillaries (Polymicro) of 350 μm outer diameter are placed in the inlet and outlet channels (350 μm) of the micro-component and sealed by means of epoxy glue. After a chemical pretreatment and washing with water, the boehmite suspension is introduced using a syringe pump. The component is then placed on a heating plate while gently blowing air through the capillaries and the structure. The airflow prevents aggregation of the alumina, which would result in clogging of the structure. The general procedure indicated above is then applied to obtain the Pt/Al_2O_3 catalytic layer.

SEM analysis demonstrates the presence of the alumina layer on the pillared structure (Fig. 4). While the quality of the alumina layer is not as good as that obtained with the open components (Fig. 3a), it is encouraging in view of the simplicity of the method used.

Further work is required to improve the quality of the alumina layer deposition in closed components but also to integrate all fabrication steps for catalyst/alumina layer in the fabrication process at the full wafer scale and in clean rooms.

4. Catalytic tests

A rig has been built to compare the catalytic properties of the deposited Pt/Al_2O_3 layer and the sputtered Pt film (Fig. 5). For that purpose, no micro-structured components were used. The catalysts were prepared on silicon wafers (500 μm thick) and

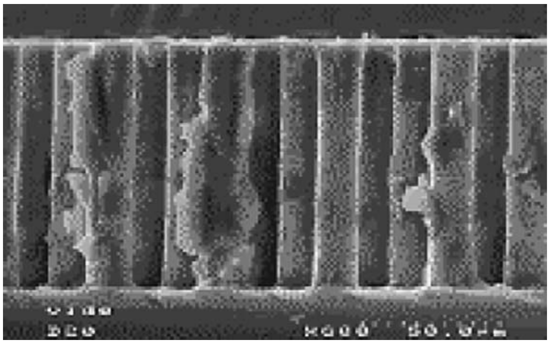

Fig. 4. SEM photographs of the pillared structure covered by a γ-alumina layer after deposition in a closed micro-structured component.

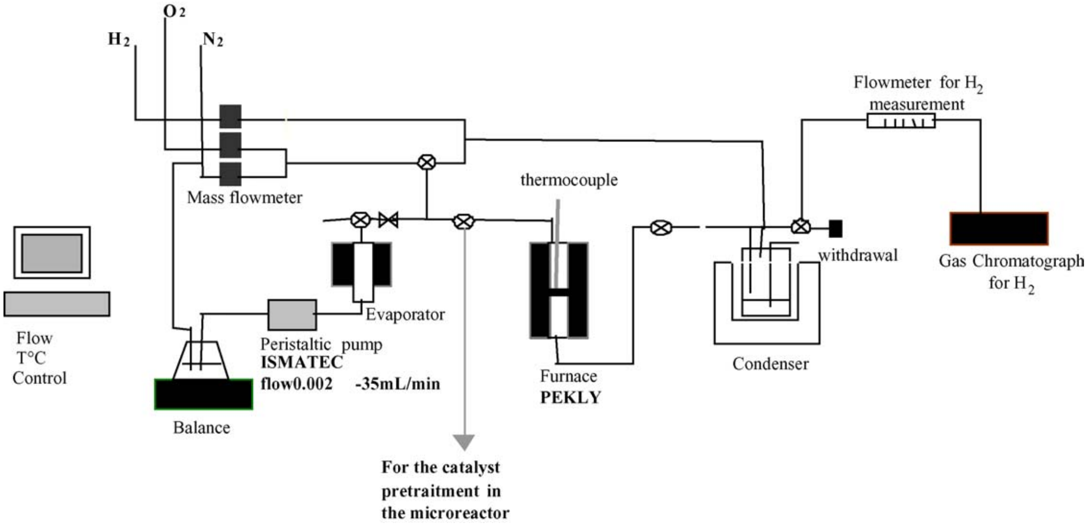

Fig. 5. Schematic drawing of the rig.

cut into small pieces (1 mm × 1 mm) to fit the dimensions of the catalytic fixed bed reactor in the rig.

The gas supply of the rig includes hydrogen and oxygen to regenerate the catalyst and an evaporator unit to produce gaseous methylcyclohexane. All the tubing and connection between the evaporator and the reactor are heated to avoid methylcyclohexane condensation. The catalytic fixed bed reactor is composed of a quartz tube of 0.8 cm i.d. and 24.5 cm long placed in a tubular oven. The catalytic silicon pieces (2 g) are placed in the tube on a sintered quartz frit, leading to a packed bed of 1.5 cm high. The outlet is equipped with a condenser to cool down the gas mixture and to trap the toluene and the unreacted methylcyclohexane. The liquid phase can be sampled and analyzed by gas chromatography. A mass flow controller and a gas chromatograph allow the accurate determination of the composition of the cooled gas phase, composed of hydrogen and trace amount (<0.1%) of methane. The temperature of the heater and the oven are controlled with a homemade utility developed with the LABVIEW® software.

Sample 1 contains the Pt/Al_2O_3 catalyst prepared as above. Sample 2 bears the Pt/film catalyst. The composition of the two catalysts/silicon samples has been analyzed by elemental analysis (ICP) (Table 1). The exposed platinum surface for each catalyst has been estimated assuming that the exposed surface is the geometric surface in case of Pt/film and that the dispersion of platinum is 50% in case of Pt/Al_2O_3 catalyst. The average yields and conversion numbers of the two catalysts have been compared at 370 °C, ambient pressure and 0.1 $cm^3\ min^{-1}$ methylcyclohexane liquid feed flow rate (Table 1).

According to the stoichiometry of the reaction (Eq. (1)), the molar yields of hydrogen and toluene should be equal. The observed difference is attributed to some leaks in the outlet gas line that are untraceable considering the very low flow rates used. It is very clear that the Pt/film catalyst is performing worse. Since the amount of Pt is only half that of catalyst 1, it can be concluded that the dispersion of Pt is much better in the latter catalyst than in catalyst 2. It is well known than Pt/Al_2O_3 catalysts prepared by the impregnation/calcination/reduction method used in this work provides nano-sized Pt crystallites (1–3 nm). The Pt film catalyst likely presents larger particles. The Pt sputtering method is thus not advisable for the preparation of Pt-based catalysts in micro-structured reactors, at least for hydrogenation/dehydrogenation reactions. The same conclusion was reached in a previous report albeit using a palladium catalyst for the gas–liquid–solid hydrogenation of nitrobenzene [17].

A slight decrease of the conversion number with time on stream has been noticed for catalyst 1 (Fig. 5). Such behavior is likely to happen with catalyst 2 because the active component is also platinum, but it was not investigated since the activity is very low. Such deactivation of catalysts is a well-known phenomenon. The characteristic time for the deactivation process is several hours and the catalyst can be regenerated in the fixed bed reactor by oxidation with oxygen followed by a reduction step under hydrogen. After such regeneration, the activity is restored and conversion and yields comparable to those of a fresh catalyst are obtained (Fig. 6). For the Pt/film catalyst, attempts to increase the yields, e.g. by increasing the residence time, mostly result in an increase of the side reaction thus a decrease of the hydrogen and toluene selectivities. This result clearly demonstrates the importance of the homogeneous

Table 1
Composition and catalytic properties of the catalysts

	Catalyst	
	1	2
Description	Pt/Al_2O_3	Pt/film
Support	Treated SiO_2	Si black
Weight Pt (ppm)	916	435
Weight % Al	0.64	0.0024
Exposed Pt surface (cm^2)	3000	500
C_7H_{14} conversion[a] (%)	88.5	<2
H_2 yield[a] (%)	66.5	n.d.
C_7H_8 outlet[a] (mol %)	88.3	n.d.

[a] Yields and outlet mole fraction after ca. 1.5 h on stream.

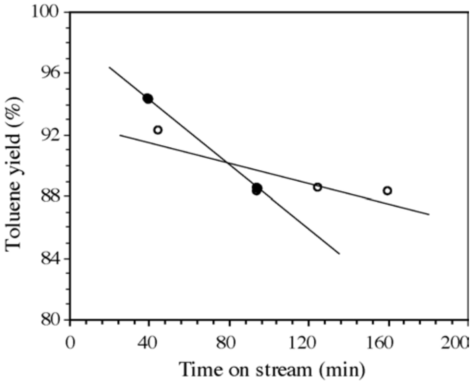

Fig. 6. Yield vs. time on stream diagram showing the decrease of the activity for catalyst 1: fresh (○) and regenerated (●).

uncatalyzed gas phase cracking reactions and has an impact on the micro-component design.

5. Heater

A heating system has been integrated on the backside of the silicon substrate. For such micro-heater, the best material used is generally platinum. This metallic film can be deposited either by thin film or by thick film process. In taking into account the large area to heat, in our case, and the possible degradation of the thin film resistance [18], the thick film solution has been chosen. The thick platinum resistance is deposited by conventional screen-printing technology using a commercial platinum ink (ESL 5545) (Fig. 7).

For the electrical connection of the resistance, a square in gold ink (Dupont 5744) is deposited with the same process. The connection is done with a 0.33 mm diameter gold wire. This wire is stuck to the square with gold ink. Each deposit is dried at 100 °C during 10 min. After the connection of the gold wire, all the system is annealed at 600 °C during 1 h. The connection is then consolidated with a glass prepared like screen-printed ink: 1 g of powder, 0.4 g of binder, 2 drops of solvent. The substrate is dried and annealed at a temperature above the glass transition one (T_g) during 1 h. To protect the resistance and to stick a K thermocouple, a dielectric layer (Heraus IP91175) is deposited by screen printing on the platinum resistance, dried at 100 °C and annealed at 600 °C.

The temperature homogeneity over the Si-component is checked by thermo-IR mapping with a thermal IR camera. The silicon substrate is placed at 10 cm from the camera. Since, in the range 0–500 °C, silicon is transparent to IR, we need to deposit a material on the silicon substrate to observe the temperature distribution.

For our first experiments, we tried to use a thin platinum film, which has an emissivity of 0.3. But for these experiments, the results (Fig. 8a) are not satisfying due to the too thin platinum layer, which leads to an inhomogeneous layer. In taking into account these previous results, we have done some specific microreactors capped with pyrex glass to IR observations (Fig. 8b). This cartography shows a homogeneous temperature distribution on the pyrex in the zone where the heater is deposited.

6. Connection

The connection used in this study to supply the gas to the microsystem stems from the biology microfluidic application. It comprises a glass capillary covered with polyimide and epoxy glue. The capillary is inserted on the microreactor slices and stuck with the epoxy glue. This connection has been chosen because it is well-known connection. But the problem with this connection is the temperature limitation due to the epoxy glue $T_{max} = 150$ °C, whereas we want to work at 400 °C. Thus, to

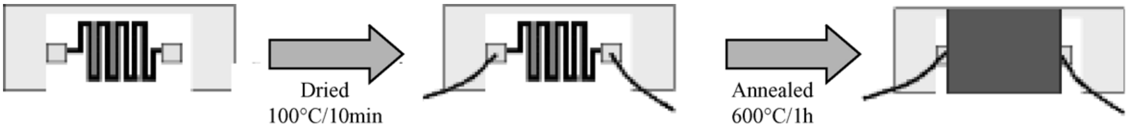

Fig. 7. Schematic representation of the screen-printing process.

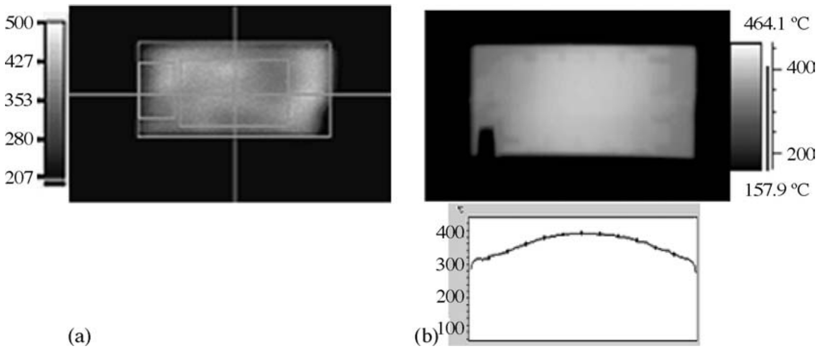

Fig. 8. Temperature distribution: (a) silicon plate thickness = 500 μm, platinum emissivity = 0.3 and (b) micro reactor capped with pyrex thickness = 1 mm, pyrex emissivity 1 (black body).

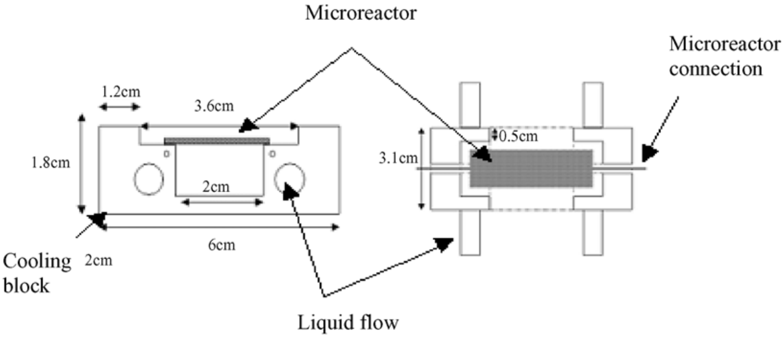

Fig. 9. Drawings of the cooling copper block: left, side view; right, top view.

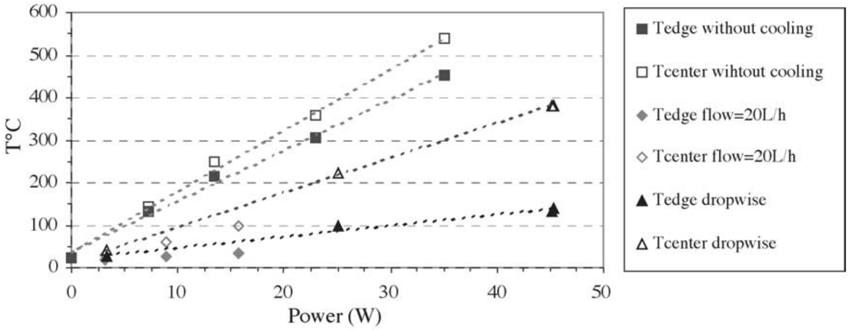

Fig. 10. Temperature vs. power of a microheater on the silicon plate placed on the cooling block.

study our endothermic reaction and to use the low temperature connection, we need to find a system to have 150 °C on the edge of the micro reactor whereas the reaction zone is at 400 °C.

To have an autonomous system and to have the temperature configuration previously described, a first idea was to make some slits in the micro reactor. Simulations with FEMLAB software showed the maximum temperature difference between the reaction zone and the micro reactor edge is only 20 °C. A second idea was to put in contact a structured piece with the micro reactor. These pieces, used as a heat sink, ensure to decrease, according to the simulations results, the temperature on the edge until 150 °C and to have the reaction zone at 400 °C. But these structured pieces are very delicate to design according to the micro reactor dimension.

Ouyang and Besser used a block on which the microreactor is placed [19]. This block, developed by these authors, is used both to supply the microreactor in gas and to cool its entrance/exit while heating the reaction zone. On the same idea, we have designed a copper piece to answer the temperatures requirements of the micro reactor itself and of our endothermic reaction (Fig. 9). This piece allows to cool the micro reactor entrance/exit with a reaction zone maintained at 400 °C with the platinum resistance. To decrease the temperature on the micro reactor edge, recycled water circulates through the metallic piece.

Fig. 10 shows the power heater versus the temperature according to the different water flows in the cooling block. We have verified that without water flow in the copper piece, the temperature of the micro reactor edge is close to the reaction zone one. According to the water flow, it is more or less difficult to obtain the desired temperatures. With a high flow of 20 l/h, it is impossible to heat the reaction zone at 400 °C because of thermal flows due to the metallic piece. The water flow has to be adapted. By consequence, it is necessary to have an accuracy control of the water flow to dissipate correctly the heat. As it can be observed in Fig. 10, with the low flow (dropwise), the temperature is correct, i.e. 400 °C on the reaction zone and 150 °C on the edge of the micro system. This current process allows us to perform our experiments with the micro reactor and the low temperature connection. But with the high power supplied to the system to have this temperature distribution and in taking into account that glass capillaries are brittle and the glue temperature limitation, it is necessary to develop high temperature connections. We are currently working on a solution using metallic tube directly welded to the silicon reactor with ceramic glues.

7. Conclusion

This report describes our ongoing work on the development of silicon micro-structured components for high temperature catalytic reactions. Many issues has been tackled and solved. The dehydrogenation of methylcyclohexane into toluene and hydrogen was the test reaction used to evaluate the best catalyst deposition technique. Based on catalyst activity measurements, it was found that the catalyst prepared by the conventional method leading to Pt/Al_2O_3 was better than that made from physical vapor deposition of a platinum film, PVD. However, the former catalyst requires deposition of an alumina layer that was achieved using colloidal alumina, both in open or capped silicon micro-structured component. The issue raised by the elevated endothermic heat of reaction was solved using integrated Pt resistances to maintain a constant and uniform temperature of 400 °C over the reaction zone. Moreover, a low temperature (80 °C) connection zone is ensured using a cooling copper block supporting the micro-structured component. Future works aim at using the capped silicon catalytic micro-structured component to perform the target reaction and to further develop the alumina layer deposition process on closed components.

References

[1] V. Hessel, S. Hardt, H. Löwe, Chemical Micro Process Engineering, Wiley-VCH, Weinheim, 2004.
[2] P.D.I. Fletcher, S.J. Haswell, E. Pombo-Villar, B.H. Warrington, P. Watts, S.Y.F. Wong, H. Zhang, Tetrahedron 58 (2002) 4735.
[3] A. Gavriilidis, P. Angeli, E. Cao, K.K. Yeong, Y.S.S. Wan, Trans. IChemE Part A: Chem. Eng. Res. Des. 80 (2002) 3.
[4] K. Jähnisch, V. Hessel, H. Löwe, M. Baerns, Angew. Chem. Int. Ed. 43 (2004) 406.
[5] R.S. Besser, X. Ouyang, H. Surangalikar, Chem. Eng. Sci. 58 (2003) 19.
[6] G. Maria, A. Marin, C. Wyss, S. Muller, E. Newson, Chem. Eng. Sci. 51 (1996) 2891.
[7] S. Zhao, R.S. Besser, IMRET, 2002.
[8] S.K. Ajmera, C. Delattre, M.A. Schmidt, K.F. Jensen, J. Catal. 209 (2002) 401.
[9] A.I.K. Lao, T.H.M. Lee, I-Ming Hsing, N.Y. Ip, Sens. Actuators 87 (2000) 11.
[10] B. Rivière, J.P. Viricelle, C. Pijolat, Sens. Actuators B 93 (2003) 531.
[11] H. Surangalikar, X. Ouyang, R.S. Besser, Chem. Eng. J. 93 (2003) 217.
[12] L.R. Arana, S.B. Schaevitz, A.J. Franz, K.F. Jensen, M.A. Schmidt, IEEE (2002) 232.
[13] K.F. Jensen, Chem. Eng. Sci. 56 (2001) 293–303.
[14] H. Jansen, M. de Boer, R. Legtenberg, M. Elwenspoek, J. Micromech. Microeng. 5 (1995) 115–120.
[15] V. Meille, S. Pallier, G.V. Santa Cruz B., M. Roumanie, J.P. Reymond, Appl. Catal. A 286 (2005) 232–238.
[16] R. Abdallah, V. Meille, J. Shaw, D. Wenn, C. de Bellefon, Chem. Commun. (2004) 372.
[17] K.K. Yeong, A. Gavriilidis, R. Zapf, V. Hessel, Catal. Today 81 (2003) 641.
[18] S.L. Firebaugh, K.F. Jensen, M. Schmidt, J. Microelectromech. Syst. 7 (1998) 128–135.
[19] X. Ouyang, R.S. Besser, Flexible microreactor system for chemical research at moderate temperature, in: SPIE Conference, San Francisco, 2003.