

Extremely Fast Catalyst Temperature Pulsing: Design of a Prototype Reactor

Jasper Stolte* Ton Backx* Okko Bosgra*

* Eindhoven University of Technology, PO Box 513, 5600 MB
Eindhoven, the Netherlands (e-mail: j.stolte@tue.nl).

Abstract: This paper discusses a novel principle of advanced process control strategy: the extremely fast and local pulsing of temperature. This strategy leads to some interesting potential applications, but there are no devices implementing it available yet. One such device currently under construction by the authors is introduced in this paper. It operates by converting electrical energy into heat by forcing a very high current through a very thin resistive element, which also acts as the catalyst for heterogeneous reactions. A design procedure for the key parameters is developed and a simulation of heat distribution in the design under construction is presented. The simulation shows that it should be possible to get local temperature peaks of 500 K which exist for only about 20 μ s.

Keywords: Process Control, Pulses, Heterogeneous Catalysis, Temperature Forcing, Periodic Control, Non-Steady State.

1. INTRODUCTION

For various reasons, chemical reaction engineers prefer to operate reactions in steady state. In modeling and design of chemical processes, reactors are almost always assumed to be ideally mixed. Control of such processes boils down to maintaining constant reaction conditions as best as possible. However, chemical reaction systems can be seen as systems of highly nonlinear partial differential equations, which are typically full of transient dynamics. If we know that these dynamics can be present, is it not possible to find cases where the dynamics can be exploited?

Attempting to exploit the dynamics demonstrated by chemical processes is not new. Horn and Lin (1967) already introduces periodic reactor operation, and it is shown there that there are reaction complexes for which periodic operation is fundamentally better than any steady state operation. This idea was picked up by researchers all over the world, and in the following decades there have been numerous studies showing there exist reaction complexes for which non steady state operation gives fundamental advantages, see Bailey (1973); Matsubara et al. (1973); Silveston et al. (1995); Silveston and Hudgins (2004) for excellent reviews of this research field.

Although there are plenty examples of academic (often theoretic) research, there are few known examples of practical applications in industry. One promising direction of research which has already shown significant improvements in a number of studies is microwave assisted chemistry, sometimes called microwave enhanced chemistry Wan et al. (1990); Wan (1993); Will et al. (2004). When some parts of a reactor subjected to microwave irradiation are more susceptible than others, they will heat up more and create gradients in temperature. Wan (1993) specifically considers heating the catalyst particles directly. Microwave assisted catalysis is not very accessible

to most scientists, as powerful microwave equipment is expensive, it is difficult to model due to inhomogeneities, and measurements are difficult also. Still, microwave heating has shown to allow modes of operation that are impossible using steady state operation.

Silveston and Hudgins (2004) state that the field of temperature forcing is relatively underdeveloped compared to the periodic feed forcing, even though the reaction complexes show more strong non-linear behavior as a function of temperature. The reason given is that due to the large time constants and energy flows involved it is difficult to apply temperature forcing to large amounts of matter. That paper also indicates that the advance of micro-reactors may change allow for better heat transfer paving the way for new studies in the forced temperature direction.

The authors of this paper have started a project on dynamic operation of heterogeneous catalysis. A first theoretical result showed that very fast and local pulsing of temperature may in some cases fundamentally improve attainable results, see Stolte et al. (2008). Also, Wan et al. (1990) state that the fastest and most intense pulses of microwave energy shows the most interesting results for the important methane coupling reaction complex. Work has started on a setup that will create very fast and intense temperature pulses, of several hundred degrees Kelvin in tens of microseconds. To our knowledge this is orders of magnitudes faster than any setups reported in literature have realized.

This paper considers the considerations in designing a setup for heterogeneous catalysis capable of such temperature pulses, delivered directly at the catalyst. Section 2 describes the general reactor setup, as well as a design procedure to decide upon the critical design parameters. Section 3 considers a simulation of the heat distribution

within the reactor, which suggests that heating and cooling within such short timescales is possible. Section 4 discusses a few potential pitfalls that may be encountered when designing such a reactor.

2. REACTOR CONCEPT

The goal of this setup is to create a reactor which is capable of operating heterogeneous catalysis reactions where the catalyst is turned into an actuator which creates very fast and large pulses in temperature. Pulse shaped temperature profiles indicate that very fast heating as well as very fast cooling are required. A very schematic 2D-view of the reactor under construction is given in figure 1.

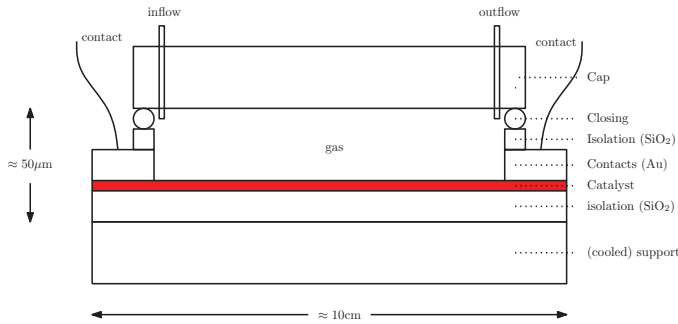


Fig. 1. Schematic view of the prototype reactor concept (not to scale). A channel is created where gas can flow through, with a floor consisting of a thin catalyst layer which is heated.

The concept is based upon a micro-flow-channel reactor, but it has a 'floor' consisting of a thin layer of catalyst through which an electrical current can be driven. Contacts are mounted at the sides to connect a source of electrical energy. For this general heterogeneous catalysis setup the catalyst is chosen to be platinum, which has excellent conductive properties. The reactor heating is supplied by the electrical source, but the cooling cannot be done actively. The heat simply has to flow to cooler areas to cool down the catalyst layer. The bulk of the energy in the catalytic layer will be conducted through the SiO₂ layer to the cooled support which consists of pure silicon. To get a nice pulse like temperature profile it is desired to have the time constant for cooling approximately equal to the time constant for heating. If it is too small, the energy will flow away already while the pulse is still being applied, and if it is too large it will simply take a long time to cool down. The thickness of especially the catalyst layer and the SiO₂ layer supporting it are critical degrees of freedom to shape the time constant for cooling.

Reasons to choose for this design are:

- Energy is by definition directly added to the catalyst
- Fast creation of electrical currents is a well developed field
- Platinum resistance depends on temperature almost linearly. By measuring voltage over and current through the catalyst layer an indication for its temperature can be found.
- By electrochemical deposition very thin layers of other catalyst can be deposited on the platinum, giving flexibility in using different catalysts.

- There are no fundamental reasons preventing this design from being scaled up for application in industry.

2.1 Basics of Electrical Heating

This subsection will summarize the basics of electrical heating as needed for this application. When voltage and current are used to heat a layer of resistive material and no heat is lost to the environment, all electrical energy is directly converted into temperature and the following relation holds:

$$\frac{dT}{dt} = \frac{P}{\rho c_p V} \quad (1)$$

where T is temperature [K], P is electrical power [W], ρ is material density [kg/m³], c_p is specific heat [J/kg K] and V is volume [m³]. Since the layer is rectangular in shape it can be described by a certain length l [m], height h [m] and width w [m], which together make up the layer volume as given in (2). Also there are the basic electrical relations for power and resistance given in (3) and (4):

$$V = lhw \quad (2)$$

$$P = \frac{U^2}{R} \quad (3)$$

$$R = \frac{l}{\sigma wh} \quad (4)$$

where R is the electrical resistance [Ω] and σ is the electrical conductivity [S/m]. Combining all the equations above, the following relation is found for the temperature gradient due to electrical heating:

$$\frac{dT}{dt} = \frac{\sigma U^2}{\rho c_p l^2} \quad (5)$$

The relation as stated in (5) is used in the simulation of section 3. It can be seen from (5) that the heating is dependent on some material parameters, and on the applied voltage squared per unit length squared. This means that if a higher temperature gradient is desired for a given setup the voltage should be increased, or the length should be decreased.

The limiting factor is the electrical current. The voltage in the formulas above can only exist if the corresponding current runs through the material. The electrical current I [A] for a voltage applied to a layer of material is given by Ohms law:

$$I = \frac{U}{R} \quad (6)$$

From this relation it is evident that by increasing the voltage, the current increases also. Furthermore making the length smaller decreases the resistance according to (4) and therefore will also increase the current. Although there is no fundamental limit to the current, there is a practical limit in how quickly a large current can be created and switched.

2.2 Resonant Circuit for Energy Transfer

To create short bursts of energy, a resonant circuit is used. The basic resonant circuit is shown in figure 2, where R represents the resistance of the catalyst layer. This layer is connected to two external components, a capacitor C and an inductance L . The capacitor is charged to a certain

voltage separately, and then connected to the other two components resulting in the circuit of figure 2. Due to the charge in the capacitor, current will flow and through the inductance and the resistance dissipating energy which is released as heat.

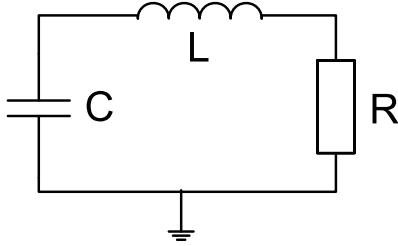


Fig. 2. Basic resonant circuit consisting of a capacitance, an inductance and a resistance. The resistance represents the catalytic layer.

From linear circuit theory, the circuit of figure 2 is governed by (7):

$$U_R = \frac{sRC}{s^2LC + sRC + 1} U_{C0} \quad (7)$$

where U_R is the voltage over the catalytic layer [V], U_{C0} is the initial voltage over the capacitor [V] and s is the Laplace operator. This equation shows second order dynamics in the numerator, which can be associated with a natural frequency ω_0 [rad/s] and a quality factor Q [-] as given in (8).

$$s^2/\omega_0^2 + s/\omega_0 Q + 1 = s^2LC + sRC + 1 \quad (8)$$

The natural frequency gives the frequency of the oscillation in the circuit, and the quality factor roughly indicates how many periods can be seen before the oscillation is gone and all the energy from the capacitor is dissipated in the resistance. From (8) the natural frequency and quality factor for a given circuit can be calculated:

$$\omega_0 = \frac{1}{\sqrt{LC}} \quad (9)$$

$$Q = \frac{1}{R} \sqrt{\frac{L}{C}} \quad (10)$$

In this application it is desired to release the energy stored in the capacitor as quickly as possible in the catalyst layer. A quality factor of 0.5 together with a high natural frequency is considered optimal.

2.3 Design Strategy

The question of how to choose values for R, L, C etcetera is an important one. This subsection proposes a strategy for consistent selection of most of the free parameters. The simulation introduced in section 3 is needed to verify the time constant for cooling and verifying validity of the thickness of the catalyst layer. The following design strategy is proposed:

- (1) Fix resistance R and its dimensions: The value for the resistance should be the dominant resistance in the circuit. Wires and connections can easily account for up to 1Ω , and the catalyst layer should have significantly more resistance. A value of 100Ω is chosen. For this laboratory setup it is desired that the

Table 1. Design Parameters Chosen

Description	Parameter	Value	Unit
Resistance	R	106	[Ω]
Catalyst length	l	50	[mm]
Catalyst width	w	0.5	[mm]
Catalyst height	h	100	[nm]
Temperature rise	ΔT	1000 (500)	[K]
Pulse energy	E	7.1	[mJ]
Quality factor	Q	0.5	[-]
Capacitance	C	14	[nF]
Inductance	L	40	[μ H]
Natural Frequency	ω_0	1.32	[Mrad/s]

amount of energy needed to create a significant heat pulse is not too large, so volume should be kept small. At the same time it is desired that the width and length of the layer are much larger than the height, such that the energy loss to the sides can be neglected. Also the sizes should be chosen such that the device can be created using integrated circuit techniques. The layer should be very thin, a value of 100 nm is chosen for the height h . To make the resistance approximately 100Ω , we choose w to be 0.5 mm and l to be 5 cm.

- (2) The next step is to determine the pulse amplitude. Since we want to significantly influence kinetics for a very short time, the temperature pulse should be large. A value of 1000 K is chosen. Since the dimensions are already specified, the amount of energy needed to make the platinum layer temperature rise by this amount can easily be calculated. For the selected dimensions, this energy is 7.1 mJ. This value holds under the assumption that no energy is lost during the application of the pulse, which in practice will be the case. In the next section it is shown that for this design the simulation predicts an actual rise of 500 K which the authors find satisfactory.
- (3) Determine the maximum available voltage. The voltage is limited mostly by the switching devices needed to open and close the current loop. In this design a MOSFET type device will be used for switching. Even high voltage MOSFETs can typically not deal with voltages greater than 1000 V. This will be the voltage used. For higher voltages spark gap switches can be applied if necessary. The voltage determines the size of the capacitance C needed by the basic relation of (11).

$$E = \frac{1}{2} C U_{C0}^2 \quad (11)$$

In this case the capacitance needed is 14 nF. Using this capacitance value, the corresponding inductance can be computed from (10) to get the proper quality factor for the resonance circuit. The natural frequency that corresponds to this network can be computed using (9), in this case it is 1.32 Mrad/s. That means the period length is approximately 4.75μ s, which is excellent for this application. If the natural frequency would have been too low, the applied voltage would have to be increased further.

Table 1 summarizes the choices made using this design procedure.

3. HEAT SIMULATION MODEL

The previous section introduced the design of a pulsed reactor, and in this section the heat distribution within that design is simulated. Since the design is developed in such a way that heat loss to the sides should be negligible in comparison to the heat loss to the support of the catalytic layer, only the vertical dimension is simulated. Figure 3 schematically shows the layers (not drawn to scale), with their respective sizes in one dimension which is named the x dimension.

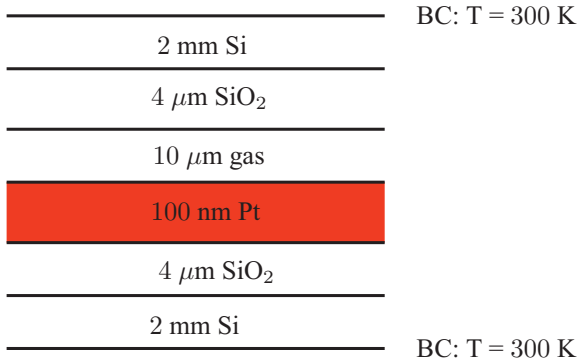


Fig. 3. Schematic view of the layers in the vertical dimension. In this dimension the heat distribution will be simulated. BC stands for boundary condition.

Heat distribution by conduction and diffusion in the model is simulated, as a lower limit to the cooling. The partial differential equation that is being solved is the standard heat diffusion equation given as (12), where κ is the local thermal conductivity [m^2/s].

$$\frac{dT}{dt} = \kappa(x) \frac{\partial^2 T}{\partial x^2} \quad (12)$$

Since this is a very straightforward geometry, the pseudo spectral method is used for collocation (Trefethen (2000); Weideman and Reddy (2000)) to get the benefit of spectral accuracy. Each of the layers is collocated separately, with energy preserving von Neumann boundary conditions at the layer boundaries. Only at the very top and bottom there are fixed temperatures (Dirichlet boundary conditions). Initially, all the layers have a temperature of 300 K. When heat enters the system in the catalytic layer, conduction will transport the heat through the other layers to the outer boundary where it is eventually lost to the surroundings.

After collocation, a system of ordinary differential equations which pose an initial value problem that is solved in Matlab using the built-in stiff ODE solvers.

3.1 Simulation Results

An RLC circuit is also simulated in parallel with the heating simulation. The RLC parameters are chosen identical to those found using the design procedure described in the previous section. The capacitor discharges via the inductance into the catalytic layer. The power that is released as heat into the catalytic layer is shown in figure 4. The peak power is about 5 kW which creates an enormous temperature gradient in the thin catalyst layer.

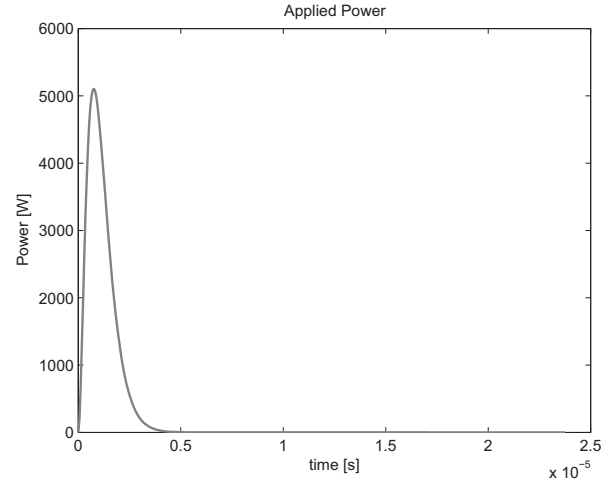


Fig. 4. Power supplied to the catalytic layer by the resonant circuit. The shape is very much like a pulse, with the peak power at about 5 kW.

This heat will result in a temperature rise of the catalytic layer, which will therefore have a temperature gradient with respect to the other layers. Transport of heat to the other layers will result. The temperature at the boundary between the catalytic layer and the gas layer is the surface temperature, which is critical for the catalytic reactions taking place. The simulated surface temperature resulting from the energy pulse is shown in figure 5. The surface temperature rises by about 500 K and not with the 1000 K for which this amount of energy (7.1 mJ) was computed in the previous section. This is due to the loss of energy to the other layers while the pulse is still in progress. About half the energy is lost to the other layers before the pulse is finished, so the heating and cooling time constants are approximately equal. If this is undesired, raising the voltage used in the design procedure will give a smaller capacitance and a faster resonance frequency. The applied energy pulse will then be shorter and higher. For the current laboratory application losing half of the 7.1 mJ is not a problem so the design is left as it is.

The heat will quickly spread into the gas layer and the SiO₂ (silica) layer supporting the catalyst. Figure 6 shows how the heat spreads through the silica supporting layer in time. The conduction within the metal layer that lies beneath the silica layer is so fast that, even though the Si layer is 2 mm thick, it does not allow for high internal temperature gradients. The whole Si layer remains at approximately 300 K and has a maximum at the boundary with the silica layer of only 301.5 K. The whole temperature gradient between the Si layer and the catalyst layer exists in the supporting silica layer, which very quickly builds up a linear temperature profile, due to the fact that the silica has a much lower thermal conductivity than the catalyst or Si layer.

The other side of the catalyst layer loses heat to the gas layer. Figure 7 shows the heat profile within the gas layer. The heat conductivity for gas is even lower than the one for the top silica layer and thus much lower than that of the metallic catalyst layer. Just like with the supporting silica layer at the bottom, the majority of the temperature gradient at the top side of the catalyst will be in the layer

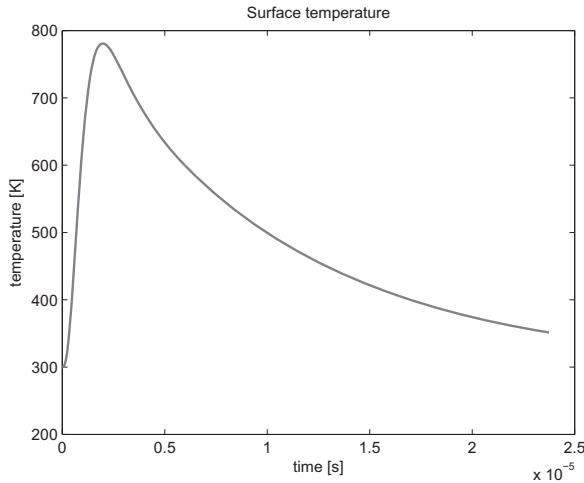


Fig. 5. Surface temperature when pulse is applied. The pulse causes the temperature to rise by about 500 K. The cooling time constant and the heating time constant are approximately equal for the parameters of table 1.

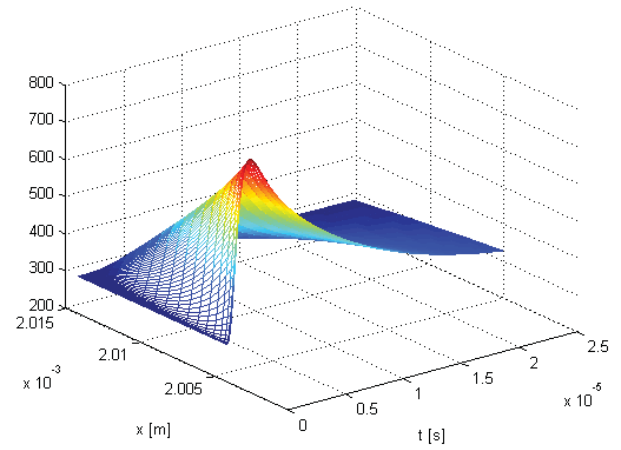


Fig. 7. The gas layer temperature profile over time. Like with the supporting SiO_2 layer a gradient leads to a linear profile, but the time taken for the linear profile to build up is longer.

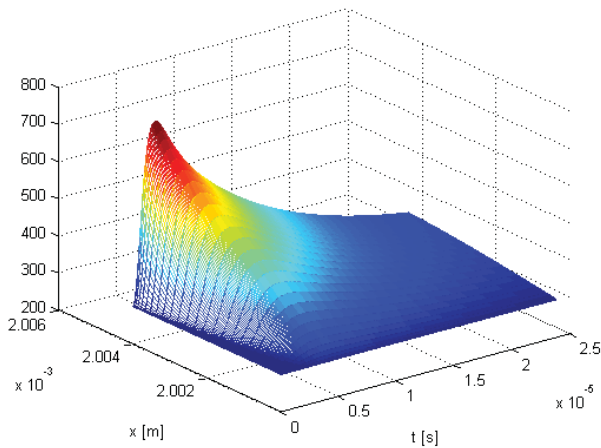


Fig. 6. Heat profile of the SiO_2 layer supporting the catalyst. A large temperature gradient over this layer quickly leads to a linear temperature profile.

with the poorest heat conductivity which is the gas layer. Since the gas layer is thicker than the silica layer and even poorer in conducting heat, it takes a bit longer for the linear profile to build up. Due to the low conductivity of the gas, much less heat is lost to the gas than is lost through the supporting silica layer.

Figure 8 shows the top silica layer, which is heated through the gas layer. The maximum rise of temperature in the top silica layer is only 10 K even though the catalyst surface was heated by almost 500 K. The heat that ends up in the top silica layer is quickly lost to the top Si layer.

Just to confirm the results, the heat distribution within the platinum catalyst layer is shown in figure 9. From this figure it is clear that there exists almost no gradient within the catalyst layer, due to the superior heat conductivity of platinum.

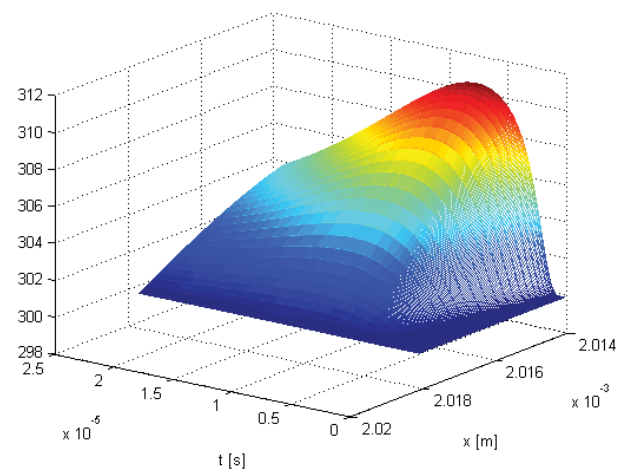


Fig. 8. Temperature profile within the top SiO_2 layer over time. The peak temperature is only about 10 K above the ambient temperature. Heat entering this layer from the gas layer is quickly transported to the top Si layer.

The heating of the platinum layer is achieved through ohmic heating a resonant circuit with a high natural frequency and a low quality factor. By using higher voltages and adjusting the capacitance and inductance accordingly the heating can be made as fast as parasitic effects allow for. The cooling of the catalyst layer however cannot be forced, and the cooling time constant is created as an interplay between the different layers thicknesses and their values for thermal conductivity. By manipulating the thickness of the catalyst layer and the supporting silica layer the time constant for cooling can be shaped. A thickness of 100 nm for the catalyst layer and 4 μm for the supporting silica layer give a feasible time constant in this design.

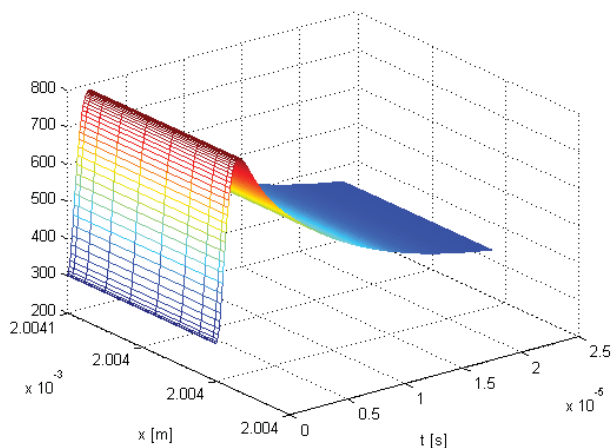


Fig. 9. The temperature profile within the catalytic layer. There exists almost no gradient within the catalyst layer, resulting in a flat profile.

4. POTENTIAL PITFALLS

Apart from the design variables already considered there are some miscellaneous design considerations that need to be included. This section mentions the most important ones.

4.1 Mechanical Strength

The heated metal layer will go up and down in temperature by hundreds of Kelvin. Metals normally expand when they become hot, and shrink when they cool down again. Unfortunately it is difficult to say whether this will physically break the layer or not. Since nobody ever tried this before there is no data on such high gradients in such thin supported metal layers. If mechanical strength is found to be a problem the pulses will need to be less intense.

4.2 Discharge Through SiO_2 Support

In the current design there is a $4 \mu\text{m}$ SiO_2 layer between the catalytic layer and the silicon support. The silicon support is electrically grounded for safety reasons. The catalytic layer is subjected to a high voltage. This voltage should not become so high that discharge occurs straight through the quartz layer because this will not only lead to pulse energy loss, but also break the device.

4.3 Electro Migration

When extremely high current densities are applied to any material, a phenomenon called electro migration will occur. The atoms of the metal start to physically move to one of the contacts, which in time will break the catalyst layer. To prevent this effect the current direction should be reversed between pulses.

4.4 Electromagnetic Interference

The high frequency currents are associated with a high frequency electromagnetic field. For any industrial application this field should be contained to such values that

other electronic devices are not disturbed, and the radio spectrum is not polluted.

5. CONCLUSION

A new prototype reactor is presented to create extremely fast temperature pulses in heterogeneous catalysis. The authors intend to use this prototype to improve understanding of the effects of temperature pulsing on complex reaction schemes. The availability of such a reactor can help understanding the results of microwave enhanced catalysis as well. There appear to be no fundamental problems preventing a temperature pulse of 1000 K in less than 10^{-5} s, which is orders of magnitudes faster than what is known from literature.

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