# LEAN HYDROGEN/AIR OXIDATION OVER PLATINUM IN A 2–DIMENSIONAL MICRO–REACTOR

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**ABSTRACT**   Oxidation of hydrogen in air will produce large amounts of nitric oxides if the temperature of the products is more than about 1800 *K*; the activation of thermal mechanism for NO production is the main cause of this. One environmentally compatible method for low-$NO_x$ combustion of hydrogen is its catalytic oxidation. In this investigation, a two-dimensional micro-reactor for catalytic oxidation of hydrogen over platinum is simulated, and the effects of inlet mixture equivalence ratio on the product temperature and NO production are studied. The reactor dimensions are considered to be 200 *μm* in width and 2 *mm* in length. Governing equations for conservation of mass, momentum, energy and the chemical species are solved using an in-house CFD code. The results form this investigation indicate that for equivalence ratios (φ) of up to 0.3, the amount of NO in the exhaust gases is less than 1 *ppm*. Increasing φ to 0.32 leads to 1.2 *ppm* NO mole fraction, while at φ = 0.34 there will be more than 1000 *ppm* NO in the exhaust gases. In addition, the average reactor wall temperature is 912 *K* at φ = 0.32, that can be used to generate the required heat for fuel processing in small-scale fuel cells.

**Keywords**  Hydrogen-air mixture, catalytic oxidation, lean combustion, low NOx.

## INTRODUCTION

Catalytic oxidation of hydrogen is an emerging method for heat generation in which there can be no or little NOx generation. Nonetheless, heat generation form this reaction will cause the mixture near the reaction zone to heat up. Increased temperature of the mixture will activate NO production mechanisms in the gas phase. In the combustion of fuels that contain no nitrogen, NO is formed by three major chemical mechanisms that involve nitrogen from air including thermal, $N_2O$–intermediate, and Fenimore mechanisms [Turns 2000]; there is new evidence for the possibility of a fourth route for NO production [Bozzeli 1995, Harrington 1996].

The thermal mechanism is significant at high temperatures (over 1800 *K*), while the Fenimore mechanism is important in rich combustion. In addition, the Fenimore mechanism is intimately linked to the combustion of hydrocarbons. The $N_2O$–intermediate mechanism is important in fuel-lean, low temperature combustions [Correa 1992].

Hellsing *et al.* [1991] studied heterogeneous kinetics of hydrogen-oxygen reaction over platinum. Konnov *et al.* [2001] examined NO formation rates for hydrogen combustion in stirred reactors. They used explicit expressions of NO formation rates and modeled hydrogen combustion in the temperature range 1500–2200. Nam *et al.* [2003] studied heterogeneous

ignition temperature of $H_2/O_2/N_2$ mixture on polycrystalline platinum for a wide range of composition at the atmospheric pressure. They proposed a new surface kinetic model of hydrogen oxidation on platinum by modification of the traditional surface reaction model.

Appel *et al.* [2004] investigated catalytic combustion of hydrogen–air mixtures over platinum and validated various hetero/homogeneous chemical reactions.

In the present study, fuel-lean combustion of hydrogen is modelled in a catalytic micro-reactor. The dimensions of the reactor are 0.2 *mm* in width and 2 *mm* in length. The inlet mixture temperature and velocity are considered to be 300 K and 1.6 *m/s*, respectively, which correspond to a Reynolds number of about 80 (based on the channel hydraulic diameter). Air composition in this study is assumed to be 78% nitrogen, 20.74% oxygen and 1.26% argon. Various equivalence ratios are set for the inlet mixture and the effects of this parameter are studied on the wall temperature and NO formation.

## CHEMICAL KINETICS

In this study, two global reactions are considered: hydrogen oxidation (R1) and NO formation (R2).

R1:    $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$          $\Delta H = -242 \ kJ/mol$
R2:    $\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightarrow NO$          $\Delta H = 90.3 \ kJ/mol$

Separate mechanisms for the oxidation of hydrogen (R1) are implemented on the reactor surface and in the gas phase. The one-step mechanism of Schefer [1982] is used for the heterogeneous catalytic reaction, with the corresponding rate equation given by Eq. 1.

$$R_{s,1} = 1.4 \times 10^3 [H_2] \exp(-14900/RT) \tag{1}$$

For the homogeneous reaction, the mechanism suggested by Marinov *et al.* [1995] is implemented which is given by Eq. 2.

$$R_{v,1} = 1.8 \times 10^{13} [H_2][O_2]^{0.5} \exp(-146400/RT) \tag{2}$$

In the above relations, $[H_2]$ and $[O_2]$ are hydrogen and oxygen concentrations in *mol/cm³*, $R$ is the universal gas constant (*8.314 j/molK*), and $T$ is the temperature in *K*.

Since the combustion is fuel-lean and the temperature of the reactor domain is less than 1800 *K*, only the $N_2O$-intermediate mechanism for NO production is expected to occur. Thus, the global rate equation for R2 by this mechanism is adopted from Konnov [2001]. He derived the rate equation for NO formation in a hydrogen/air mixture from 8 elementary reactions which are tabulated in Table 1. In his derivation, he used the steady state assumption for the $N_2O$ concentration and obtained Eq. 3 for NO formation reaction.

$$R_{v,2} = (2k_6 K_2^{1/2}[O_2]^{1/2} + 2k_8 K_1^{1/2}[H_2]^{1/2})$$
$$\times \frac{k_4 k_3 k_2 [H_2][N_2][O_2][M]}{((k_5+k_6)K_2^{1/2}[O_2]^{1/2} + (k_7+k_8)K_1^{1/2}[H_2]^{1/2})[H_2O]} \quad (3)$$

In this equation $k_i$ is the reaction rate of reaction $i$ in Table 1, and $K_j$ is the equilibrium constant of reaction $j$ ($j=1,2$).

Table 1
Elementary reactions for NO formation, units are $cm^3$-mole-cal-K, $k=AT^n\exp(-E_a/RT)$

| No. | Reaction | A | n | $E_a$ | Source |
|-----|----------|-----|-----|-------|--------|
| 1 | $O + H_2 = OH + H$ | $5.06\times10^6$ | 2.67 | 6,285 | [Baulch et al. 1992] |
| 2 | $H + O_2 = OH + O$ | $1.0\times10^{14}$ | 0 | 14,843 | [Baulch et al. 1994] |
| 3 | $H_2 + OH = H_2O + H$ | $1.0\times10^8$ | 1.6 | 3,300 | [Baulch et al. 1992] |
| 4 | $N_2 + O + M = N_2O + M$ | $4.0\times10^{14}$ | 0 | 56,640 | [Rohrig et al. 1996][1] |
| 5 | $N_2O + O = N_2 + O_2$ | $1.0\times10^{14}$ | 0 | 28,200 | [Hanson et al. 1984] |
| 6 | $N_2O + O = NO + NO$ | $6.92\times10^{13}$ | 0 | 26,630 | [Hanson et al. 1984] |
| 7 | $N_2O + H = N_2 + OH$ | $2.2\times10^{14}$ | 0 | 16,750 | [Bozzelli et al. 1994] |
| 8 | $N_2O + H = NH + NO$ | $6.7\times10^{22}$ | -2.16 | 37,155 | [Bozzelli et al. 1994] |

[1]Enhanced third body efficiencies (relative to Ar): $O_2$=1.4, $N_2$=1.7, NO=3.0, $H_2O$=12.

## GOVERNING EQUATIONS AND SOLUTION METHOD

**Model Assumptions** The flow regime in this article is assumed to be steady, incompressible and laminar. The gas mixture is treated as an ideal gas with variable properties based on the local composition. The gas flow mixture consists of 6 species: $H_2$, $O_2$, $N_2$, $H_2O$, Ar and NO. Furthermore, Dufour and Soret effects are neglected in the species mass diffusion.

**Governing Equations** The governing equations are conservations of mass, momentum, energy and chemical species, as well as the ideal gas mixture equation.
The continuity equation for a steady-state flow in a Cartesian coordinate is given by Eq. 4.

$$\frac{\partial(\rho u_i)}{\partial x_i} = 0 \quad (4)$$

The Conservation of momentum is the Navier-Stokes equation, given in Eq. 5.

$$\frac{\partial(\rho u_i u_j)}{\partial x_i} = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_i}\left(\mu \frac{\partial u_i}{\partial x_j}\right) \quad (5)$$

Eq. 6 gives chemical species conservation for the $i$th species. The term $\omega_i$ in Eq. 6 is the molar production rate of species $i$ which is different on the surface of the reactor and in the gas phase region according to Eqs. 1-3.

$$\frac{\partial(\rho u_i Y_k)}{\partial x_i} = \frac{\partial}{\partial x_i}\left(\rho D_{eff,i} \frac{\partial Y_k}{\partial x_j}\right) + \omega_k MW_k \quad (6)$$

Conservation of energy is implemented to calculate the teperature , and is given in Eq. 7.

$$\frac{\partial(\rho u_i c_p T)}{\partial x_i} = \frac{\partial}{\partial x_i}\left(k \frac{\partial T}{\partial x_j}\right) + \sum_{i=1}^{2} \Delta H_i R_{r,i} \tag{7}$$

In this equation $R_r$ is $R_s$ on the reactor surface, and $R_v$ in the internal computational cells, and $i$ ($i$=1,2) is the reaction number.

Gas mixture density is computed using the ideal gas relationship for a multi-component mixture, given in Eq. 8.

$$\rho = \frac{P\,MW_{mix}}{R_u T} \tag{8}$$

The mixture molecular weight in the above equation is computed from the following.

$$MW_{mix} = \sum_i \chi_i\,MW_i = \frac{1}{\sum_i \dfrac{Y_i}{MW_i}} \tag{9}$$

The effective mass diffusion coefficient, $D_{eff}$, in Eq. 6 is computed using the following.

$$D_{eff,i} = \frac{1-\chi_i}{\sum_{\substack{\forall j \\ j\neq i}} \dfrac{\chi_j}{D_{ij}}} \tag{10}$$

Here $D_{ij}$ is the binary diffusion coefficient. The binary mass diffusivity is calculated by the relationships given by Reid *et al.* [1987]. The methodology is based on the Chapman-Enskog theoretical description of a binary mixture of gases at low to moderate pressures. In this theory, the binary diffusion coefficient for the species pair $i$ and $j$ is given by Eqs. 11-15.

$$D_{ij} = \frac{0.0266\,T^{3/2}}{P\,MW_{ij}^{1/2}\,\sigma_{ij}^2\,\Omega_D} \tag{11}$$

$$MW_{ij} = 2\left[(1/MW_i) + (1/MW_j)\right]^{-1} \tag{12}$$

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \tag{13}$$

$$\Omega_D = \frac{1.06036}{\left(T^*\right)^{0.15610}} + \frac{0.19300}{\exp\left(0.47635\,T^*\right)} + \frac{1.03587}{\exp\left(1.52996\,T^*\right)} + \frac{1.76474}{\exp\left(3.89411\,T^*\right)} \tag{14}$$

$$T^* = k_B T\Big/\left(\varepsilon_i\,\varepsilon_j\right)^{1/2} \tag{15}$$

Table 2 gives the values of hard-sphere collision diameter, $\sigma$, as well as Lennard-Jones energy, $\varepsilon$, for various species involved in our calculations.

The constant pressure specific heat, dynamic viscosity, and thermal conductivity of the gas mixture are computed using Eqs. 16-18.

$$c_{p,eff} = \sum_i c_{p,i} Y_i \tag{16}$$

$$\mu_{eff} = \sum_i \mu_i Y_i \tag{17}$$

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$$k_{eff} = \sum_i k_i \chi_i \tag{18}$$

It is noted that the values of constant specific heat of each species varies with temperature because of the high temperature gradients across the reactor.

Table 2
Hard–sphere collision diameter and Lennard–Jones energy parameter for each species

| Species | $\sigma \left( \overset{\circ}{A} \right)$ | $\varepsilon/k_B$ (K) |
|---|---|---|
| $H_2$ | 2.827 | 59.7 |
| $O_2$ | 3.467 | 106.7 |
| $H_2O$ | 2.641 | 809.1 |
| $N_2$ | 3.798 | 71.4 |
| Ar | 3.542 | 93.3 |
| NO | 3.492 | 116.7 |

**Numerical Approach**  The non-linear, coupled governing equations are solved using a finite volume method based on the SIMPLE algorithm. The convective terms are discretized using the power-law scheme, and the diffusion terms using a second-order central difference scheme. The resulting algebraic equations are solved by a point-by-point iteration method.
The inlet boundary conditions are the velocity, temperature and composition of the mixture. The reactor walls are assumed adiabatic. At the outlet, the pressure is fixed.

**RESULTS AND DISSCUSSION**

In this article, simulation results for a two dimensional, steady-state, micro-reactor for catalytic oxidation of hydrogen are presented. The computational domain consists of 3,150 finite volume cells with 150 × 21 uniform grid nodes. However, to select this final domain discretization, a grid study is performed for the base-line condition on three different grids: a fine grid of 300 × 43 nodes (12,900 cells), a medium grid of 150 × 21 nodes (3,150 cells) and a coarse grid of 110 × 15 nodes (1,650 cells).
The simulation results for the wall temperature along the reactor using these three grids are compared in Fig. 1. These results indicate that the medium and fine grids predict temperatures that are virtually indistinguishable on this diagram. It is therefore admissible to use the medium grid in the subsequent simulations.
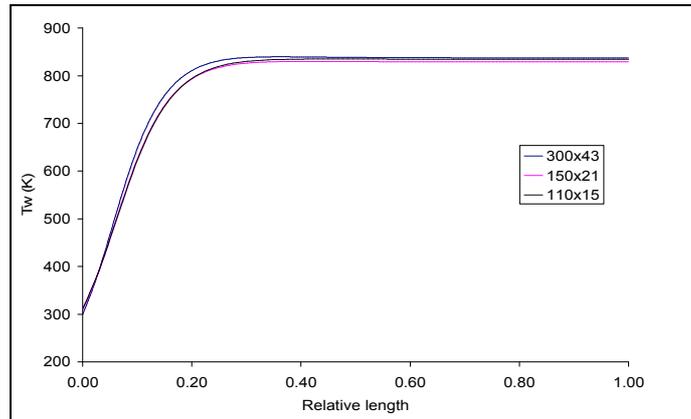
Figure 1. Grid study of the simulation results

In order to validate the present code, a comparison is made in Fig. 2 between the predicted wall temperature and the corresponding experimental data by Appel *et al*. [2004]. The inlet velocity in this case is set to 1.6 *m/s*, inlet temperature 313 *K*, inlet equivalence ratio 0.28, and the channel hydraulic diameter and length are 13.1 *mm*, 300 *mm*, respectively. The numerical results exhibit a good agreement with the corresponding experimental data.
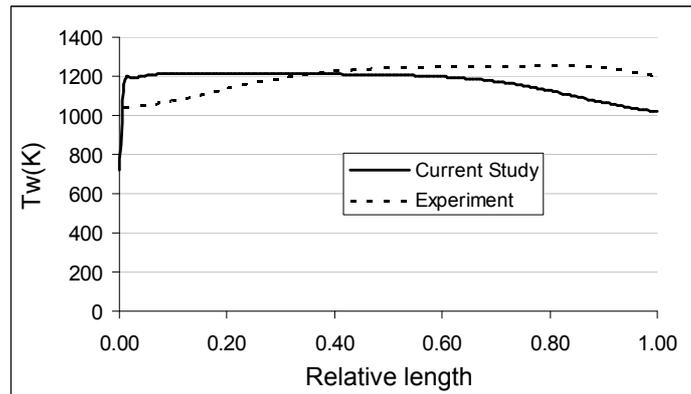


Figure 2. Validation of the simulation results

Simulation results for catalytic oxidation of hydrogen-air mixture are given now for the base-line conditions which are shown in Table 3.

Table 3
Base-line conditions at the inlet of the reactor

| Inlet condition | Value |
|---|---|
| $T_{in}$ | 300 $K$ |
| $\varphi$ | 0.3 |
| $u_{in}$ | 1.6 $m/s$ |
| $\chi_{H_2}$ | 11.19 % |
| $\chi_{O_2}$ | 18.65% |

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| | |
|---|---|
| $\chi_{H_2O}$ | 0.0 |
| $\chi_{N_2}$ | 69.27% |
| $\chi_{Ar}$ | 0.89% |
| $\chi_{NO}$ | 0.0 |

Contours of $H_2$, $O_2$, $H_2O$ and NO mole fractions for these conditions are presented in Fig. 3, and those for the temperature are given in Fig 4. It is obvious from these results that the hydrogen oxidation reaction mostly occurs by the heterogeneous reaction on the reactor surface, where the catalyst exists.
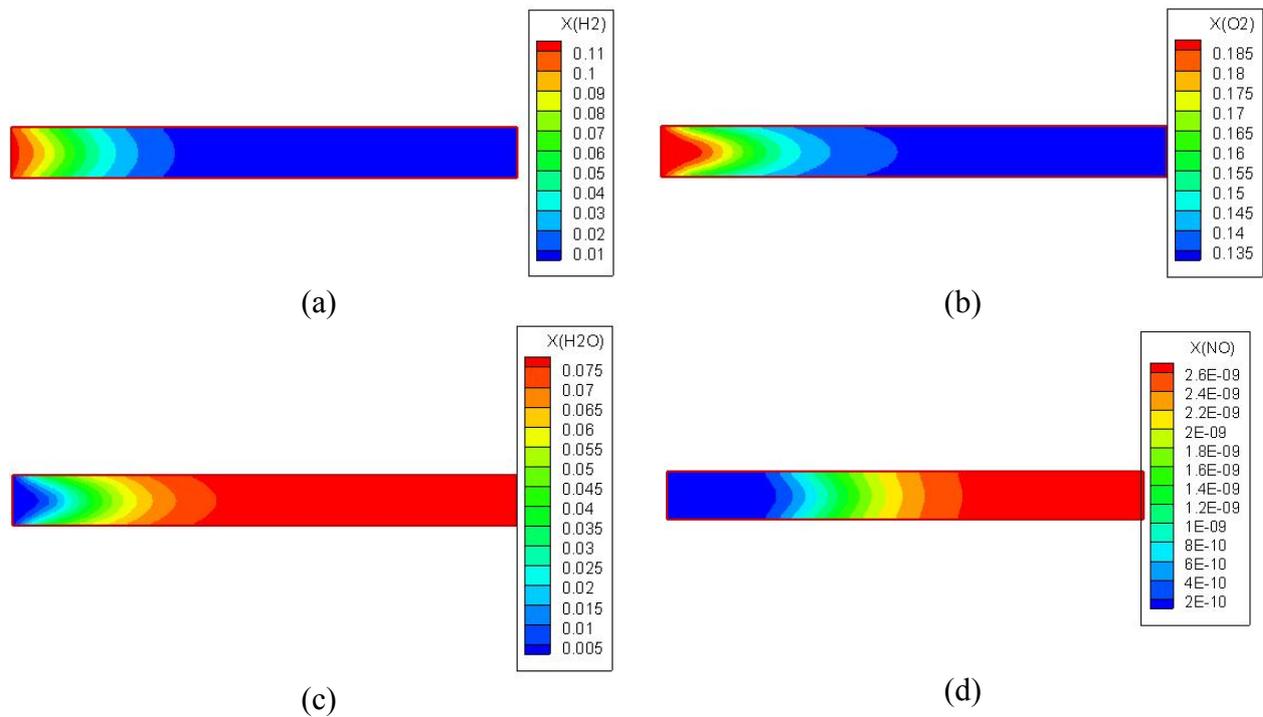


(a)

(b)

(c)

(d)

Figure 3. Mole fraction contours for base-line conditions: (a) $H_2$, (b) $O_2$, (c) $H_2O$, (d) NO

Fig. 3(d) indicates that the NO concentration is negligible in the first half of the reactor length, but it increases in the second half-length of the reactor where the temperature rises above 800 K.



Figure 4. Temperature contours for the base-line conditions

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It is seen in Fig. 4 that the temperature is increased on the reactor wall surfaces since the surface reactions are dominated.

Fig. 5 shows the outlet NO mole fraction versus the inlet equivalence ratio. NO mole fraction is approximately zero up to an equivalence ratio of 0.3; it then increases considerably as the equivalence ratio is increased further. The reason for this behaviour is that by increasing $\varphi$, the temperature of the mixture in the reactor will increase, as shown in Fig. 6. Hence, the NO formation rate will increase rapidly for $\varphi > 0.3$.
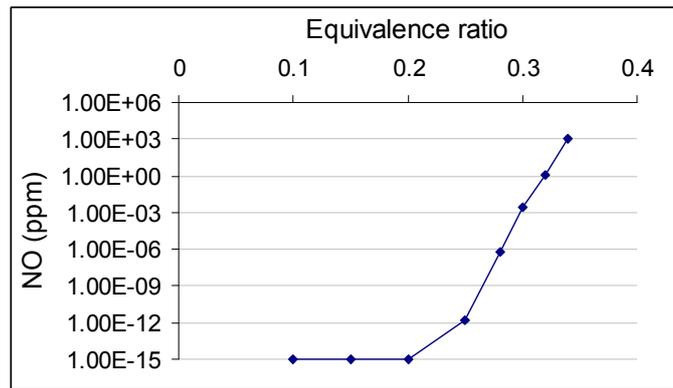


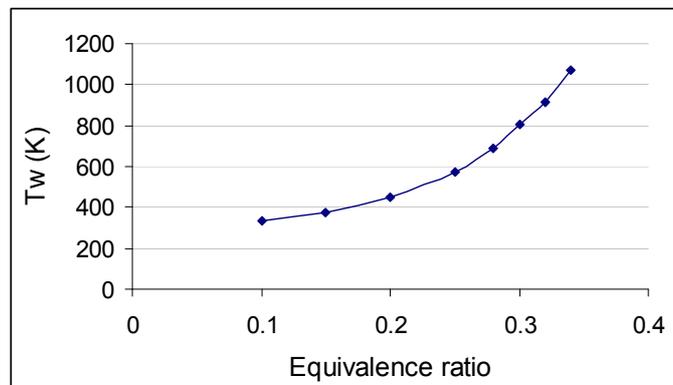Figure 5. Variation of NO mole fraction versus inlet equivalence ratio



Figure 6. Variation of the average wall temperature versus inlet equivalence ratio

**CONCLUSION**

In this investigation, a two-dimensional, steady-state, micro-reactor for hetero/homogeneous oxidation of lean hydrogen-air mixtures is modelled. The behaviour of the results from this numerical simulation has a good agreement with the experimental data.

The results from this simulation indicate that in order to reduce the NO mole fraction in the exhausted gases, equivalence ratio of the inlet feeding gas should not be more than 0.3. In this condition, the NO mole fraction is less than 3 *ppm*. The average wall temperature, which is achieved at this equivalence ratio, is 912 *K* and can be used generate the required heat for a micro-scale fuel reformer of a fuel cell system.

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