Light-off Characteristics for Diesel Oxidation Catalysts in Monolith Reactors: Effects of Catalyst Distribution Schemes

Neeti Kapur, Ligen Wang, Timothy J. Truex, Kyle L. Fujdala and John B. Nicholas

Nanostellar Inc., Redwood City, CA, USA, jnicholas@nanostellar.com

ABSTRACT

We present a mathematical model utilizing experimentally derived reaction rate laws for CO oxidation on platinum that includes variations in the catalyst distribution along both the axial and radial washcoat directions. The light-off temperature for CO oxidation is reduced by distributing the catalyst along the axial direction under steep inlet temperature ramp rates. The steep temperature ramp rates emulate transient exhaust gas temperatures. Thus, the effects of catalyst zoning are applicable under cold start conditions. We also report the corresponding reduction in CO emissions with varied catalysts distributions within a two-zone washcoat. Varying the catalyst distribution along the radial washcoat direction influences the net CO emissions from the reactor under mass transfer limited conditions. A modest increase in outlet conversion is obtained by redistributing the catalyst within washcoat layers in the radial direction at elevated inlet gas temperatures.

Keywords: monolith, catalyst distribution, CO oxidation, light-off, reactor model, diesel emissions

1 INTRODUCTION

In order to fulfill the EPA emission standards for diesel automobiles, platinum-coated catalytic converters are commonly employed for CO and hydrocarbon oxidation. Nanostellar is currently developing catalyst materials to reduce diesel emissions and improve the effectiveness of precious metal catalysts using a Rational Catalyst Design methodology. As part of this effort, we have been developing a monolith reactor model to study the effects of washcoat variables, such as zones, layers, and catalytic components. Such models are useful tools as they can potentially shorten catalyst development time and provide optimized formulations for specific applications. It is known that catalytic performance can be optimized with respect to catalyst distribution on a monolithic substrate[1-4]. Previous studies of axial parabolic catalyst distributions suggest shorter warm-up times in comparison to uniform catalyst distributions for CO oxidation[1]. CO emissions are reported to be significantly reduced in a two-zone model including simultaneous CO, hydrocarbon and hydrogen oxidation for an optimal axial catalyst distribution[2]. This two zone model includes the synergistic effects between competitive oxidation reactions and therefore, does not reflect the impact of zoning on an individual reaction. In this study, we report the influence of catalyst distribution on monolith reactor performance with CO oxidation only.

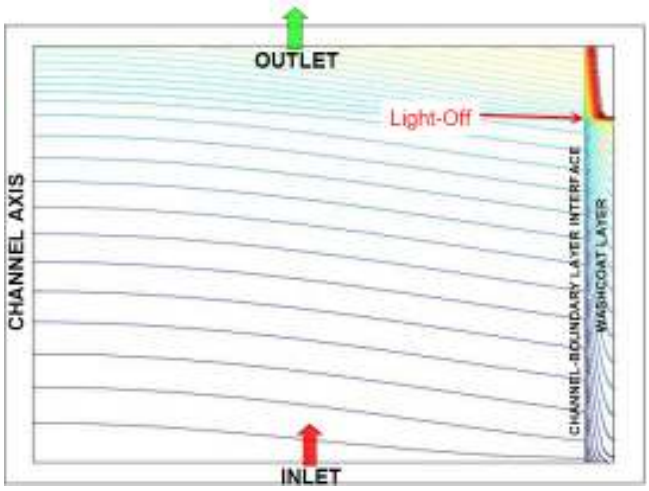

Figure 1: Contour plot for CO conversion for axisymmetric reactor model at inlet gas temperature of 425 K.

2 COMPUTATIONAL METHODOLOGY

Monolith reactor behavior can be effectively modeled with a single monolith channel with adjoining washcoat. We represent the channel and adjoining washcoat by a two dimensional axisymmetric model such that the effect of the catalyst distribution in both the axial and radial washcoat directions can be investigated. The model includes three computational domains, channel, boundary layer and washcoat, as shown in Figure 1. The parameters for the monolith model and the balance equations are detailed in Table 1.

The velocity profile is solved within the channel using the Navier-Stokes equation. The local velocity within the boundary layer and washcoat domains is taken as zero. For any species *i*, the mole balance is given by

$$\nabla.(-D_i.\nabla c_i + c_i u) - R_i = \varepsilon \frac{\partial c_i}{\partial t} \quad (1)$$

The diffusion coefficients (D_i) are calculated for bulk diffusion in the channel using the Fuller equation. Knudsen diffusion dominates in the washcoat and effective diffusion coefficients are given by

$$(D_{eff})_i = \frac{\varepsilon}{\tau} 4850 d_p \sqrt{\frac{T}{M_i}} \quad (2)$$

where M_i represents the molecular weight for species *i*. No homogeneous reaction occurs in the gas phase. The experimentally derived reaction rate for CO oxidation on platinum (A. Allian & E. Iglesia 2007) in the washcoat domain is described by

$$-R_{CO} = \frac{A e^{\frac{-E_a}{RT}} c_{O_2} (Catalyst.Loading)}{c_{CO} + Z} \quad (3)$$

The reaction rates are constrained using smoothed step functions to avoid negative concentrations within the reactor. An artificial factor (*Z*) is added to the denominator in order to prevent reaction rate from approaching infinity.

The energy balance in all the domains is given by

$$\nabla.(-k\nabla T) - (\rho C_p) u.\nabla T = \rho C_p \frac{\partial T}{\partial t} \quad (4)$$

The simulated inlet gas stream consists of 1000 ppm CO, 10% O_2 and remaining N_2 for all cases considered. We used the properties of air for the density, viscosity, thermal conductivity and heat capacity of the inlet gases. The diffusion coefficients and thermal conductivity for the gases in the boundary layer domain are calculated using asymptotic Nusselt numbers for flow in ducts. The inlet gas temperature is ramped up from 350 K to 500 K at a ramp rate of 0.5 K/s unless otherwise specified.

These balance equations are solved alongside the boundary conditions using finite element method in COMSOL[5]. The finite element mesh is increased near the reactor outlet and at the interface between the channel-boundary layer and the washcoat. This dense grid helps to capture the light-off behavior accurately with respect to the position in the monolith reactor.

3 RESULTS & DISCUSSION

The light-off temperature for CO oxidation within a monolith reactor with uniform catalyst loading corresponds to 422 K under the simulated conditions as detailed in Table 1. As the inlet gas temperature is ramped up at the rate of 0.5 K/s, CO conversion within the reactor changes as a function of time. Figure 1 shows the contour plot for CO conversion within the reactor at an inlet gas temperature of 425 K. A jump in CO conversion is observed within the washcoat which represents the light-off

Reactor Length	2 in
Reactor diameter	1.1 in
Channel radius	0.76 mm
Washcoat thickness	0.0353 mm
Boundary layer thickness	0.00353 mm
Average channel velocity	1.25 m/s
Porosity, ε	0.8
Tortuosity, τ	3
Pore diameter, d_p	100 Å
Washcoat density	1300 kg/m^3
Washcoat specific heat	800 J/kg-K
A	6.87E7 s^{-1}
E_a	88 kJ/mol
Total catalyst loading	100 g Pt/ ft^3 reactor volume

Table 1: Input parameters for monolith reactor model.

within the current model. Herein, we examine the effects of catalyst redistribution in the axial and radial washcoat direction on the light-off temperature and net CO emissions from the monolith reactor.

3.1 Effect of Axial Catalyst Distribution

Results reported so far on axial catalyst distribution include one dimensional mathematical models[1-4] for catalytic converters either with a parabolic distribution or a two zone distribution model. The conclusions drawn from two zone washcoat models are applicable under normal operating conditions to a greater extent than the parabolic catalyst distribution. To this end, we divided the washcoat into two equal halves in the axial direction, with high catalyst loading for the zone near the reactor inlet (Case 1) and high catalyst loading in the zone near the reactor outlet (Case 2). The corresponding catalyst loading ratios were 3:1 and 1:3 for Case 1 and 2 respectively.

The light-off temperature curves for the uniform and axial catalyst distribution cases are plotted in Figure 2 for inlet gas temperature ramp rate of 0.5 K/s. The total catalyst loading within the washcoat is equal for all the three cases considered. Both of the non-uniform axial catalyst distribution cases show a decrease in the light-off temperature by ~ 2 K from the uniform catalyst distribution scenario. Case 1 with high catalyst loading near reactor inlet translates to an early 100% CO conversion while Case 2 corresponds to delayed 100% conversion with respect to uniform catalyst distribution. Although the light-off temperature for Case 1 and 2 are similar, the CO emissions for the two cases differ. The net CO emissions for Case 1 decrease by 2.9%, while Case 2 shows negligible variations as compared to the uniform catalyst distribution scenario. The variance in the net CO emissions from the reactor for

Clean Technology 2008, www.ct-si.org, ISBN 978-1-4200-8502-0

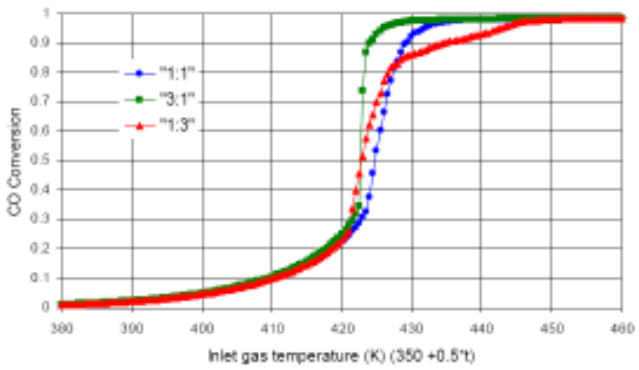

Figure 2: Light-off characteristics for uniform (1:1), Case 1 (3:1) and Case 2 (1:3) axial catalyst distributions for 0.5 K/s temperature ramp rate.

Case 1 and 2 comes into play once light-off occurs in the reactor. Overall, Case 2 takes 20% longer time to attain negligible CO emissions as compared to Case 1. The improvement in reactor performance with higher catalyst loading near the reactor inlet (Case 1) results from the changes in the washcoat temperature profile.

The washcoat temperature is assumed to be uniform at 350 K initially. As the inlet gas temperature is ramped up to simulate the transient behavior of exhaust gas stream, the washcoat heats up and reaction rate for CO oxidation increases. The washcoat temperature is in turn affected by the heat generated from the increased CO conversion. Due to the presence of more catalyst in the first washcoat zone (Case 1), higher CO conversion occurs with respect to the uniform catalyst distribution. CO consumption is accompanied by heat generation and hence, the washcoat (catalyst) attains higher temperature with axial conduction in the washcoat. The reaction rate for CO oxidation includes an Arrhenius expression and therefore, the rate of CO consumption is further enhanced with higher washcoat temperatures for Case 1. In other words, the time required for heating the washcoat is reduced with the presence of more catalyst near the reactor inlet. Thus, even though less catalyst is present in the second washcoat zone for Case 1, CO consumption continues to be higher than with the other catalyst distribution schemes. The temperature profiles along the reactor length as shown in Figure 3 confirm that higher temperatures (~4-5 K for 1000 ppm CO) can be attained in the reactor with more catalyst near the reactor inlet when the inlet gas temperature is 425 K for all cases.

For Case 2, on the other hand, the light-off occurs near the reactor outlet. The additional reaction heat generated due to the presence of three times more catalyst near the reactor outlet cannot be used to heat the entire washcoat as in Case 1. Hence, the washcoat temperature for Case 2 shows a sharp jump only in the second zone as confirmed in Figure 3.

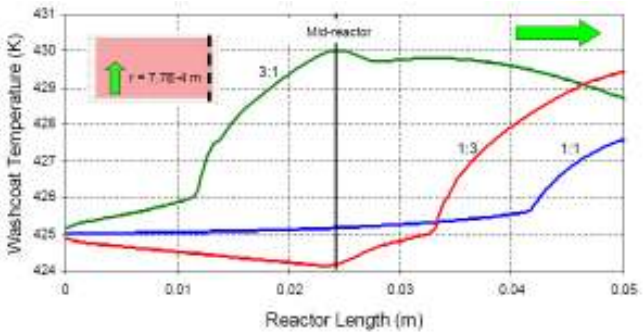

Figure 3: Axial washcoat temperature profiles for uniform (1:1), Case 1 (3:1) and Case 2 (1:3) axial catalyst distributions for 0.5 K/s ramp rate. Inset shows the reactor model and radial cutoff for the axial temperature profiles. Arrows point out the flow direction in the reactor.

The role of the washcoat temperature profile on the net CO emissions is further established by including a steep inlet temperature ramp rate of 4 K/s. The steep temperature ramp rates (4-16 K/s) are representative of the transient behavior of exhaust gases under normal exhaust conditions and during vehicle emission test procedures. The washcoat temperature profiles along the reactor length are plotted in Figure 4 for different axial catalyst distribution schemes at an inlet gas temperature ramp rate of 4 K/s for an inlet gas temperature of 432 K. The washcoat temperature profiles show a linear decrease with the reactor length since the variations in the inlet gas temperature are faster than the time required to stabilize the washcoat temperature through axial conduction. The washcoat temperature buildup will depend on the reaction rate for CO oxidation, which in turn depends on the initial catalyst bed temperature and catalyst loading. The catalyst loading in the first washcoat zone is highest for Case 1 followed by uniform loading case and lowest for Case 2. Thus, the resultant washcoat temperature profiles follow the catalyst loading trend in the first washcoat zone. The catalyst loading variations in the second washcoat zone compensate the initial washcoat temperature trends. Therefore, all the catalyst distribution cases correspond to similar temperatures near the reactor outlet in Figure 4.

The light-off temperature for the uniform catalyst distribution with a 4 K/s inlet temperature ramp rate increases to 435 K (not shown here) as compared to 422 K for 0.5 K/s ramp rate. These light-off temperatures are defined as the inlet gas temperatures for which 50% CO conversion is achieved at the monolith reactor outlet. Since the temperature buildup in the reactor with a 4 K/s inlet temperature ramp rate is slower than for 0.5 K/s, 50% conversion corresponds to a higher light-off temperature. As expected, high catalyst loading near reactor inlet (catalyst loading in 3:1 ratio between zones) corresponds to a lower light-off temperature of 431 K. This 4 K decrease in light-off temperature corresponds to a 4.5 % decrease in the net CO emissions from the reactor.

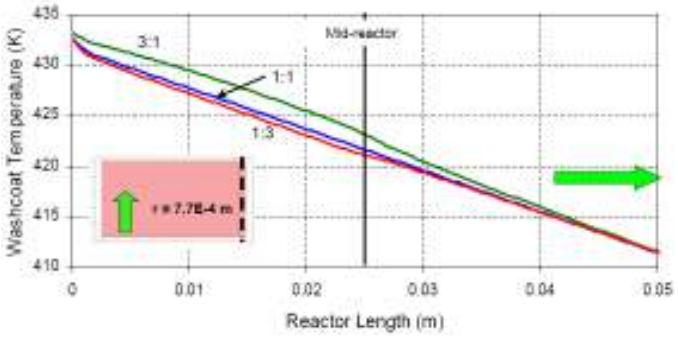

Figure 4: Axial washcoat temperature profiles for uniform (1:1), Case 1 (3:1) and Case 2 (1:3) axial catalyst distributions for 4 K/s ramp rate. Inset shows the reactor model and radial cutoff for the axial temperature profiles. Arrows point out the flow direction in the reactor.

Thus, net CO emission from the monolith reactor can be reduced by redistributing more catalyst near the reactor inlet even with variant exhaust gas temperature ramp rates.

3.2 Effect of Radial Catalyst Distribution

The monolith reactor undergoes a change in operating conditions from a kinetically limited regime to a mass transfer limited regime as the reaction proceeds towards completion. Under kinetic limitations, the reactant (CO) concentration is within 10% of the bulk reactant concentration. The reaction rate is limited by low rate constants due to the low washcoat (catalyst) temperature. As the reaction proceeds through light-off, the washcoat temperature increases beyond the inlet gas temperature and higher CO conversion occurs. The reaction rate at this stage is limited by the amount of reactant diffusing to the catalyst surface. The CO concentration profile along the radial washcoat direction under such mass transfer limited conditions is shown in Figure 5. In this case, the CO concentration decreases sharply within the boundary layer by ~ 90% of the bulk CO concentration. Hence, variations in catalyst distribution along the radial washcoat direction affect the net CO emission from the monolith reactor under mass transfer limited conditions only.

Since diffusion of reactants to the catalyst surface drives the reaction rate under the mass transfer limited regime, a high concentration of catalyst near the boundary layer-washcoat interface improves the outlet conversion. The conversion can be improved by ~ 1.3% by redistributing the catalyst within the washcoat layers in the radial direction in the ratio 3:1 at inlet gas temperatures that are greater than the light-off temperature. The effect of catalyst redistribution in the radial washcoat direction can be enhanced either by using different catalyst formulations in washcoat layers or by employing thin washcoats within monolith reactors.

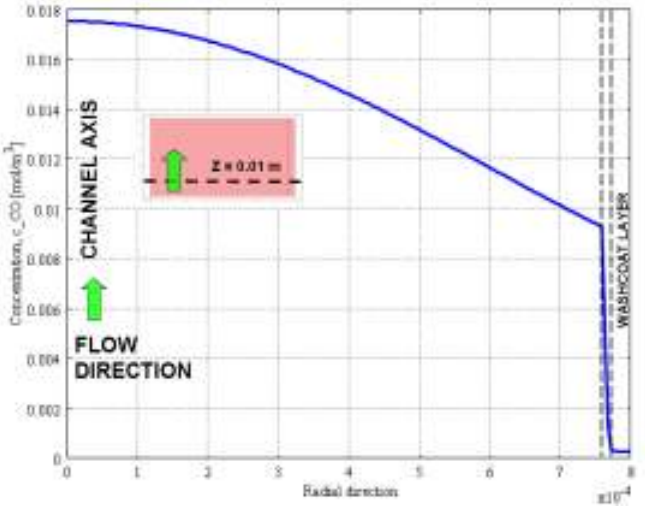

Figure 5: CO concentration profile at an axial cutoff of 0.01 m from reactor inlet at inlet gas temperature of 440 K. Inset shows the reactor model and axial cutoff for the concentration profile. Arrows represent the flow direction within reactor.

4 CONCLUSION

A two-dimensional axisymmetric model was used to demonstrate that catalyst distribution in axial and radial washcoat directions can have a significant effect on the light-off temperatures for CO oxidation. The axial catalyst distribution with high catalyst loading in the zone near the reactor inlet shows improvements in reactor performance in terms of light-off temperatures and net CO emissions. The improved performance is related to the elevated washcoat temperatures within the reactor with catalyst redistribution in the axial washcoat direction. The net CO emissions decrease up to 4.5% under transient inlet gas temperatures with the axial catalyst distribution schemes. The catalyst distribution along the radial washcoat direction influences the net CO emissions under mass transfer limited conditions. CO outlet conversion can be increased by redistributing the catalyst such that reactants come into contact with a higher amount of catalyst near the washcoat interface.

REFERENCES

[1] A. Psyllos and C. Philippopoulos, App. Math. Modelling 17, 459, 1993.
[2] S. Tronci, R. Baratti and A. Gavriilidis, Chem. Eng. Comm. 173, 53, 1999.
[3] S. Oh and J. Cavendish, Ind. Eng. Chem. Res. Dev. 21, 29, 1982.
[4] K. Ramanathan, D. West and V. Balakotaiah, Ind. Eng. Chem. Res. 43, 4668, 2004.
[5] COMSOL 3.4 (http://www.comsol.com/)

Clean Technology 2008, www.ct-si.org, ISBN 978-1-4200-8502-0