Steady-state and dynamic hysteresis effects during lean co-oxidation of CO and C₃H₆ over Pt/Al₂O₃ monolithic catalyst

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Abstract

A global kinetic model is developed for the co-oxidation of CO and C₃H₆ over a Pt/Al₂O₃ diesel oxidation monolithic catalyst based on a recent bench flow reactor study (Abedi et al., Catal. Lett. 2012). A monolith reactor model containing these kinetics is used to elucidate the dynamic and steady state hysteresis behavior observed during oxidation of a CO+C₃H₆ mixture on Pt/Al₂O₃. Dynamic hysteresis is observed during temperature-programmed oxidation which involves ramping the feed gas temperature up and down at a constant ramp rate. The predicted solid temperature spatial profile during ramp-up and ramp-down shows how the catalyst temperature lags behind the inlet temperature change, especially during the ramp-down. The dynamic hysteresis loop, whose width increases with the ramp rate and effective heat Peclet number ($Pe_{h,eff}$), is mainly a result of disparate time scales of thermal front propagation and temperature ramp and will be present even for reactions with negligible heat release. Steady state hysteresis can also be explained based on adiabatic temperature rise (ΔT_{ad}) and $Pe_{h,eff}$, i.e. thermokinetic multiplicity. The region of steady state hysteresis loop expands with an increasing ΔT_{ad} which is proportional to the feed concentrations of CO and C₃H₆. For fixed ΔT_{ad} , the steady state multiplicity disappears as $Pe_{h,eff}$ increases or when there is negligible thermal feedback due to intra or interphase heat transfer. Finally, the model is used to construct a map that may be used to assess the light-off features of multiple reaction systems in monolith reactors.

Keywords: Kinetic Modeling, Propylene, CO, Diesel Oxidation Catalyst, Monolith, Hysteresis;

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1. Introduction

Carbon monoxide (CO) and hydrocarbons (HCs) are primary pollutants from lean burn vehicle engines. For diesel engines, a diesel oxidation catalyst (DOC) is employed to convert CO and HCs to CO₂ and H₂O. Recent advances in low temperature combustion (LTC) diesel engines hold promise for higher net efficiency and lower NO_x and particulate matter (PM) emissions as compared to conventional diesel engine technologies. On the other hand, the LTC engine has lower exhaust temperature which results in higher levels of CO and hydrocarbons (HCs) in the exhaust as compared to today's engines. Hence it is important to understand the light-off behavior of exhaust gas mixtures at lower temperatures and higher levels of these primary pollutants.

The oxidation of CO on Pt has been studied extensively [1-14]. The rate of Pt-catalyzed CO oxidation is known to be self-inhibiting due to the high affinity of CO to Pt. CO oxidation occurs through an established four-step mechanism which involves reaction between the adsorbed CO and oxygen. Both adsorbed molecular O₂ and atomic O species have been suggested as participating in reaction with CO in the CO-inhibition regime. The oxidation of propylene on Pt catalysts has been a popular model reaction for HC oxidation. In a well-cited study, Voltz et al. [7] reported that both CO and C₃H₆ oxidation are self-inhibiting. Furthermore, in a CO+C₃H₆ mixture, CO inhibits C₃H₆ oxidation and vice-versa due to competitive adsorption over active catalytic sites [7, 8, 19, 20]. Complicating this nonlinear kinetic behavior is the potential occurrence of steady state multiplicity and sustained oscillations, particularly for CO oxidation. Processes that cause steady state multiplicity are: (1) high adiabatic temperature rise due to heat generated from exothermic reaction, a reaction rate that depends exponentially on temperature, and low effective heat Peclet number leading to thermal feedback, (2) non-

monotonic (or negative order) kinetics leading to isothermal multiplicity through coupling between the kinetics and mass transfer, and (3) inherent kinetic nonlinearities [2-4, 5-6, 9-13, 21]. It has been shown in the literature that negative-order reaction systems when coupled with transport resistances, can give rise to isothermal steady-state multiplicity. Most of the studies are limited to catalyst pellet. For example, Wei and Becker [3], Roberts and Satterfield [9], Smith et al. [10], have predicted isothermal multiplicity for negative-order reactions under the influence of intra-pellet diffusion resistances. Hegedus et al. [4] have shown that the steady-state multiplicity observed in an isothermal, integral reactor can indeed be well interpreted by diffusion-reaction interactions, and that more than two stable steady states can be generated by appropriate manipulations of the time history of the operating conditions. Oh et al. [11] studied experimentally the presence of multiple steady states during CO oxidation over Pt catalyst particles with various sizes. They showed that the width of the conversion-temperature hysteresis loop goes through a maximum with an increasing catalyst pellet size. The hysteresis loop also shifts along the temperature axis with variation in pellet size. The hysteresis occurred at the lowest temperature when catalyst particles used were of intermediate size and for both smaller and larger particles the multiplicity was observed at higher temperatures. Harold and Luss [12] studied the non-isothermal, steady-state multiplicity features of a self-inhibiting catalytic reaction, CO oxidation on a single Pt/Al₂O₃ pellet. They showed that steady state multiplicity is result of thermokinetic coupling and interparticle transport limitations. Sustained oscillations are thought to result from the involvement of an underlying slow process such as the reversible formation of Pt oxide or the reconstruction of surface structure on particular exposed crystallographic planes such as Pt(100) and Pt(110) [30, 31]. The coupling of such an underlying process, which typically has a slower time constant than the main adsorption, reaction, and

desorption steps, can lead to isothermal periodic and even aperiodic oscillatory behavior. The redox mechanism is considered more likely at atmospheric pressure while the reconstruction mechanism is more common under vacuum conditions.

Salmons et al. [13] reported a series of temperature-programmed oxidation experiments for different inlet CO concentrations (500-2000 ppm) in which the temperature of the feed gas was increased at a rate of 8 K/minute and decreased at 2.3K/minute. Ignition-extinction (light-off) curves demonstrated the presence of clockwise hysteresis behavior. They showed that the width of the hysteresis is smallest for an inlet concentration of 500 ppm and of similar width for higher concentrations. They related the hysteresis to Pt surface coverage with ignition and extinction branches corresponding to the two states of predominantly CO-covered and oxygen-covered. Carlsson and Skoglundh [15] studied CO oxidation on Pt/Al₂O₃ by temperature programmed oxidation (TPO) experiments using heating/cooling ramps of 5°C/min and also observed hysteresis behavior. They explained hysteresis based partly due to inherent kinetic bistability and the interplay between reaction kinetics and diffusion phenomena, together with heat effects. Abedi et al. [19] performed TPO experiments for CO, C₃H₆ and CO+C₃H₆ mixture over Pt/Al₂O₃ monolithic catalyst. The results show that CO and C₃H₆ oxidation exhibit conventional counterclockwise hysteresis. However, in a CO+C₃H₆ mixture, CO and C₃H₆ hysteresis shifts to a clockwise pattern with an increase in the feed C₃H₆ concentration. While dynamic hysteresis has been frequently reported, to our knowledge there has been no satisfactory explanation as to its origins.

In this study, we develop and apply a global kinetic model for co-oxidation of CO and C₃H₆ on Pt/Al₂O₃ monolithic catalyst using data reported by Abedi et al. [19]. The global kinetic model is developed in steps, starting with CO oxidation, followed by C₃H₆ oxidation and then

the CO+C₃H₆ reaction system. The global kinetic model is used to explain the transient hysteresis behavior that occurs during temperature ramp-up and ramp-down experiments for CO and C₃H₆ mixtures [14-16, 19-20, 22]. In this study we present modeling of dynamic hysteresis observed during co-oxidation of CO and C₃H₆ over Pt/Al₂O₃ monolithic reactor. We show that dynamic hysteresis is result of fast transient change in feed temperature and can exist even in absence of isothermal and non-isothermal steady state multiplicity. We also extend the work of Gundlapally and Balakotaiah[21] in which they studied the effect of the substrate material (ceramic versus metallic) on the steady-state and transient performance of monolith reactors using a one-dimensional two-phase model. They considered linear kinetics (first order reaction) and showed that region of multiplicity depends on the substrate material conductivity and monolith aspect ratio. We also examine the steady state hysteresis behavior for oxidation of CO + C₃H₆ mixture on Pt/Al₂O₃ monolith. In particular, we study the effect of inlet feed composition, adiabatic temperature rise and the effective heat Peclet number on the region of steady state multiplicity. Finally, the model is also used to construct a light-off (ignition) map over range of CO and C₃H₆ inlet concentrations. To this end, this study elucidates the different hysteresis mechanisms as well as the light-off of coupled inhibiting oxidation reactions.

2. Model development

2.1. *Reactor model*

A low-dimensional model of a catalytic monolith channel with washcoat diffusion is used in this study [23]. The model is developed by averaging the convection-diffusion-reaction (CDR) equations in the transverse (radial) direction (in fluid and washcoat phase), i.e. the concept of internal mass transfer coefficients developed by Joshi et al. [23, 24]. It has been shown that the low dimensional model gives comparable results to the detailed numerical solution [23]. Details

of the model development and applications are provided in earlier work [23, 25-29]. The model consists of species and energy balances in the fluid and washcoat phase. The heat and mass transfer in the transverse direction between the bulk of fluid and washcoat are accounted for by the use of overall heat and mass transfer coefficients. The key assumptions in the model are: (i) laminar flow in the monolith channel, (channel Reynolds number $(4\langle u \rangle R_{\Omega 1}/\nu) \sim 12$ to 36), (ii) axial diffusion (and conduction) in the fluid phase is neglected as compared to convection (high axial fluid phase heat and mass Peclet numbers, $\langle u \rangle L/D_m$ or $\langle u \rangle L \rho_f C_{pf}/k_f$ in the range 175 to 1766) and (iii) the reaction mixture is dilute so average values for physical properties may be used (iv) the time scale for the variations in inlet composition and temperature is large compared to the space time so that the traditional two-phase model can be used.

The species balances in the gas phase consist of accumulation, convection and external mass transfer from bulk fluid to washcoat:

$$\frac{\partial Y_{fm,j}}{\partial t} + \langle u \rangle \frac{\partial Y_{fm,j}}{\partial z} = -\frac{1}{R_{\Omega 1}} k_{mo,j} (Y_{fm,j} - \langle Y_{wc} \rangle_j) \quad (2-1)$$

where, $Y_{fm,j}$ and $\langle Y_{wc} \rangle_j$ represent the cup-mixing mole fraction of species j in the fluid phase and volume-averaged mole fraction of species j in the (interstitial space of the) washcoat, respectively; $\langle u \rangle$ is the average fluid velocity, $R_{\Omega 1}$ is the hydraulic radius defined as the ratio of channel area (open to flow) to channel perimeter, and $k_{mo,j}$ is the overall mass transfer coefficient of species j given by:

$$\frac{1}{k_{mo,j}} = \frac{1}{k_{mi,j}} + \frac{1}{k_{me,j}} \quad (2-2)$$

where, $k_{mi,j}$ and $k_{me,j}$ are the internal and external mass transfer coefficients, respectively. The mass transfer coefficients are computed using the following relations:

$$k_{me,j} = \frac{Sh_e D_{f,j}}{4R_{\Omega_1}} \quad (2-3)$$

$$k_{mi,j} = \frac{Sh_{i,\infty} D_{e,j}}{R_{\Omega_2}} \quad (2-4)$$

where, $D_{f,j}$ and $D_{e,j}$ are the fluid phase diffusivity and effective washcoat diffusivity of species j , respectively. The effective diffusivity in the washcoat is estimated by assuming a diffusivity ratio, $\lambda (= \frac{D_{f,j}}{D_{e,j}})$, of 10 based on λ -value reported by Joshi et al. [29] for a Pt/Al₂O₃ washcoat. R_{Ω_2} is the effective transverse diffusion length in the washcoat defined as the ratio of washcoat cross-sectional area to the fluid-washcoat interfacial perimeter (i.e. R_{Ω_2} is the effective/average washcoat thickness). Sh_e is the external Sherwood number obtained by using the correlation given by Ramanathan et al. [24]. Likewise, Sh_i is the internal Sherwood number, the details of which are provided in the works by Joshi et al. [23, 26, 27]. The internal mass transfer coefficient for species j is approximated by using the asymptotic internal Sherwood number $Sh_{i,\infty}$ [23].

The species balances for component j in the washcoat are similarly formulated as follows:

$$\epsilon_{wc} R_{\Omega_2} \frac{\partial \langle Y_{wc} \rangle_j}{\partial t} = k_{mo,j} (Y_{fm,j} - \langle Y_{wc} \rangle_j) + \frac{R_{\Omega_2}}{C_0} \sum_{i=1}^N \vartheta_{ij} R_i (\langle Y_{wc} \rangle_1, \dots, \langle Y_{wc} \rangle_s, T_s) \quad (2-5)$$

where, ϵ_{wc} , ϑ_{ij} and R_i represent the washcoat porosity, stoichiometric coefficients of species j in reaction i and volumetric reaction rate (per unit washcoat volume) of reaction i , respectively. T_s is the solid temperature. The total concentration in the gas phase C_0 is approximated by

neglecting pressure drop in the channel and using the ideal gas law [$C_0 = P_0 / R_g T$, $P_0 = 101.3kPa$].

Likewise, the enthalpy balances in fluid and solid phase are given by:

$$\frac{\partial T_f}{\partial t} + \langle u \rangle \frac{\partial T_f}{\partial z} = -\frac{1}{R_{\Omega_a}} \frac{h}{\rho_f c_{pf}} (T_f - T_s) \quad (2-6)$$

$$\begin{aligned} R_{\Omega_w} \rho_w c_{pw} \frac{\partial T_s}{\partial t} = & R_{\Omega_w} k_w \frac{\partial^2 T_s}{\partial z^2} + h(T_f - T_s) \\ & + R_{\Omega_2} \sum_{j=1}^N R_j (\langle Y_{wc} \rangle_1, \langle Y_{wc} \rangle_2, \dots, \langle Y_{wc} \rangle_s, T_s) (-\Delta H_j) \end{aligned} \quad (2-7)$$

where, ρ_f , $c_{p,f}$, h , T_f and T_s are the density of gas, specific heat capacity of gas, heat transfer coefficient, gas phase temperature and solid (washcoat + support) temperature, respectively. The effective solid phase (wall) heat capacity and thermal conductivity are computed as $R_{\Omega_w} \rho_w c_{p,w} = R_{\Omega_2} \rho_c c_{p,c} + R_{\Omega_s} \rho_s c_{p,s}$ and $R_{\Omega_w} k_w = R_{\Omega_2} k_c + R_{\Omega_s} k_s$, respectively. The subscripts c and s refer to catalyst (washcoat) and support, respectively

The initial, inlet and boundary conditions are given below:

$$\begin{aligned} Y_{fm,j}(z, t=0) &= Y_{fm,j0}(z) \\ \langle Y_{wc} \rangle_j(z, t=0) &= \langle Y_{wc} \rangle_{j0}(z) \\ Y_{fm,j}(z=0, t) &= Y_{j,in}(t) \end{aligned} \quad (2-8)$$

$$\begin{aligned} T_f(z=0, t) &= T_{fin}(t) \\ T_f(z, t=0) &= T_{f0}(z) \\ T_s(z, t=0) &= T_{s0}(z) , \\ \frac{\partial T_s}{\partial z}(z=0, L, t) &= 0 \end{aligned} \quad (2-9)$$

where, $Y_{fm,j0}(z)$, $\langle Y_{wc} \rangle_{j0}(z)$, $T_{f0}(z)$, and $T_{s0}(z)$ are initial fluid phase mole fraction of species j , initial washcoat concentration of species j , and initial fluid and solid temperatures,

respectively. $T_{fin}(t)$ is the inlet fluid temperature. The values of parameters used in the simulation are provided in Tables 1 and 2. We have assumed a cell density of 400 cpsi (or a channel hydraulic diameter of 1100 μm before washcoating) and a mean washcoat thickness of 25 μm . The hydraulic diameter of the open channel is 1050 μm . $R_{\Omega w}$ is the effective wall thickness defined as sum of the thickness of washcoat and the half-thickness of the solid wall without washcoat. The solid wall thickness for monolith with ceramic substrate (with 400 cpsi) is 165.1 μm . Hence, the value of $R_{\Omega w}$ is 107.6 μm . The external heat and mass transfer coefficients for fully developed flow in a circular geometry (or rounded square) are taken to be constants because of small values of the transverse mass Peclet number ($P = \frac{\langle u \rangle R_{\Omega 1}^2}{LD_{f,j}} = 0.034$ with $\langle u \rangle = 0.95 \text{ m/s}$, $D_{f,j} = 0.3 \times 10^{-4} \text{ m}^2/\text{s}$; other parameters as listed in Table 1). The value of the asymptotic internal Sherwood number $Sh_{i,\infty}$ is 3 for a thin slab washcoat [23]. The gas-solid heat transfer coefficient appearing in Eqs. (2-6, 2.7) is calculated using a correlation similar to that given by Eq.(2.3).

2.2 Kinetic Model and Parameter estimation

Here we describe a global kinetic model for the simultaneous oxidation of CO and C_3H_6 over Pt/ Al_2O_3 monolithic catalyst. The global reactions are:

The model kinetic parameters were estimated from transient bench-flow reactor studies carried out by Abedi et al. [19]. Although the feed in the experiments contained water, we have assumed that CO and C_3H_6 oxidation are the only reactions that occur at these low temperatures (100°C-200°C). Specifically, the water-gas shift and reforming reactions are ignored because of the

excess O_2 conditions. In these experiments CO and C_3H_6 light-off occurred in the temperature range of 120-140°C [19]. These CO and C_3H_6 light-off temperatures are somewhat lower when compared to other experimental studies [7, 17] employing similar feed concentrations. The lower light-off temperatures observed for these experiments may be attributed to the use of a fresh catalyst with the rather high Pt loading of 95g/ft³, as compared to typical Pt loading of 40-80 g/ft³. The catalyst properties used in the model are listed in Table 3.

In order to estimate the kinetic parameters for the co-oxidation of CO and C_3H_6 , we followed a step-wise approach. Kinetic parameters estimated from the independent single reaction systems (CO and C_3H_6 oxidations) were incorporated into the co-oxidation model. That is, first a global kinetic model for CO oxidation ($CO + O_2$) was developed by fitting the model with data obtained from CO TPO (temperature programmed oxidation) experiments in which temperature was increased at a rate of 3°C/min [19]. Then a global kinetic model of C_3H_6 oxidation reaction ($C_3H_6 + O_2$) was obtained by fitting C_3H_6 conversion data obtained from C_3H_6 TPO experiment [19]. Finally, we fixed the values of kinetic parameters obtained from independent CO and C_3H_6 oxidation global kinetic models and estimated the rest of kinetic parameters by fitting the model with TPO experimental data for CO and C_3H_6 mixture in which temperature was increased at 3°C/min [19]. The Levenberg-Marquardt method was used to converge on the parameter estimates.

It should be pointed out that the model used here is for a single adiabatic channel whereas the experimental data used to determine the kinetic parameters were obtained with a multi-channel monolith placed in a quartz tube that is placed inside a furnace, whose temperature is controlled (ramped up or down). Further, in the experiments [19], the inlet gas temperature was measured close to the center channel while the exit conversion was determined by measuring the

composition of the entire effluent gas. Thus, the assumption of adiabatic (center) channel is reasonable, especially at higher concentrations of reactants, since light-off temperature is insensitive to small heat losses.

2.2.1 *Global kinetic model for CO oxidation*

The rate of CO oxidation is based on a Langmuir-Hinshelwood type mechanism involving the surface reaction between adsorbed CO and adsorbed O₂. The rate expression for CO oxidation is assumed to be of the form

$$R_{CO} = \frac{k_1 Y_{CO} Y_{O_2}}{(1 + K_{CO} Y_{CO})^2} \quad (\text{mol/m}^3\text{-washcoat/s}) \quad (2.10a)$$

This semi-empirical rate expression captures the experimentally-observed reaction orders with respect to CO and O₂. For $K_{CO} Y_{CO} \ll 1$ the rate is first-order with respect to CO, whereas for $K_{CO} Y_{CO} \gg 1$ the rate is negative one order with respect to CO [7]. The rate constant and adsorption equilibrium constant are defined as:

$$k_1 = A_1 \exp\left(\frac{-E_1}{R_g T_s}\right) \quad (2.10b)$$

$$K_{CO} = A_{CO} \exp\left(\frac{-\Delta H_{CO}}{R_g T_s}\right) \quad (2.10c)$$

where E_1 is an effective activation energy for the lumped constant k_1 and $(-\Delta H_{CO})$ is the CO heat of adsorption. The kinetic parameters were estimated by fitting the model with CO conversion data obtained from transient bench flow reactor experiments in which temperature was ramped at a rate of 3°C/min [19].

Figure 1 shows the fitted result which indicates that the model is able to capture reasonably well the experimental light-off trend. The fitted values of kinetic parameters $\frac{E_1}{R_g}$ and $\frac{-\Delta H_{CO}}{R_g}$ are 14421K and 1166K, respectively. For comparison, the estimated values of $\frac{E_1}{R_g}$ and $\frac{-\Delta H_{CO}}{R_g}$ for CO oxidation by Voltz et al. [7] were 10825K and 961K, respectively. These moderate differences may be attributed to differences in the catalyst loading and other factors; e.g. Voltz et al. [7] performed the kinetic studies on a pelleted platinum–alumina catalyst, whereas our model is fitted to data for Pt/Al₂O₃ monolithic catalyst. Figure 2 shows the dependence of CO oxidation rate on CO mole fraction at different temperatures. The CO oxidation rate exhibits a maximum at ~700 ppm and ~1400 ppm of CO mole fraction at 400K and 500K, respectively.

2.2.2 Global kinetic model for C₃H₆ oxidation

The rate of C₃H₆ oxidation can also be described by a Langmuir-Hinshelwood type mechanism with the surface reaction between adsorbed C₃H₆ and adsorbed O₂. The rate expression for C₃H₆ oxidation is expressed as follows:

$$R_{C_3H_6} = \frac{k_2 Y_{C_3H_6} Y_{O_2}}{(1 + K_{C_3H_6} Y_{C_3H_6})^2} \quad (2.11a)$$

It has been observed experimentally that C₃H₆ is also self-inhibiting [17]. Hence, the empirical rate expression is consistent with the experimentally observed reaction orders with respect to C₃H₆. For $K_{C_3H_6} Y_{C_3H_6} \ll 1$ the rate is positive order with respect to C₃H₆, whereas, for $K_{C_3H_6} Y_{C_3H_6} \sim O(1)$ and higher the rate is negative order with respect to C₃H₆ [29]. The rate constant and adsorption equilibrium constant are defined as:

$$k_2 = A_2 \exp\left(\frac{-E_2}{R_g T_s}\right) \quad (2.11b)$$

$$K_{C_3H_6} = A_{C_3H_6} \exp\left(\frac{-\Delta H_{C_3H_6}}{R_g T_s}\right) \quad (2.11c)$$

Following the same approach as for CO oxidation, the kinetic parameters were estimated by fitting the reactor model with data obtained from C₃H₆ TPO experiment in which temperature was ramped at a rate of 3°C/min in the presence of 10% O₂ [19]. Fig. 3 shows the fitted result and the model values agree well with the experimental data. The estimated values of the parameters $\frac{E_2}{R_g}$ and $\frac{-\Delta H_{C_3H_6}}{R_g}$ are 11306K and 117K, respectively. Again, for comparison, the estimated values of $\frac{E_2}{R_g}$ and $\frac{-\Delta H_{C_3H_6}}{R_g}$ for C₃H₆ oxidation by Voltz et al. [7] are 11427K and 361K, respectively. Figure 4 shows dependence of C₃H₆ oxidation rate on C₃H₆ mole fraction at different temperatures. The C₃H₆ oxidation rate is negative order with respect to C₃H₆ above 300 ppm and 400 ppm of C₃H₆ mole fraction at 400K and 500K, respectively.

2.2.3 Global kinetic model for CO + C₃H₆ oxidation

It has been shown experimentally [19] that C₃H₆ inhibits CO oxidation and CO inhibits C₃H₆ oxidation. In order to account for this mutual inhibition effect the rate expressions for both CO and C₃H₆ oxidation were modified by adding an extra inhibition term in their respective denominators. The modified expressions are given by

$$R'_{CO} = \frac{k_1 Y_{CO} Y_{O_2}}{(1 + K_{CO} Y_{CO} + K_{I,C_3H_6} Y_{C_3H_6})^2} \quad (2.12a)$$

$$R'_{C_3H_6} = \frac{k_2 Y_{C_3H_6} Y_{O_2}}{(1 + K_{C_3H_6} Y_{C_3H_6} + K_{I,CO} Y_{CO})^2} \quad (2.12b)$$

To account for the inhibition on the rate of CO oxidation by C₃H₆, the term $K_{I,C_3H_6} Y_{C_3H_6}$ is added to the denominator of CO oxidation rate. Similarly, to account for the inhibition of C₃H₆ oxidation by CO, the term $K_{I,CO} Y_{CO}$ is added to the denominator of C₃H₆ oxidation rate. The temperature dependence of the inhibition constants is assumed to be of the form

$$K_{I,CO} = A_{I,CO} \exp\left(\frac{-\Delta H_{I,CO}}{R_g T_s}\right) \quad (2.12c)$$

$$K_{I,C_3H_6} = A_{I,C_3H_6} \exp\left(\frac{-\Delta H_{I,C_3H_6}}{R_g T_s}\right) , \quad (2.12d)$$

The constants were estimated by fitting the TPO data obtained for a CO and C₃H₆ mixture [19]. Fig. 5 show the measured and predicted results.

In order to validate the kinetic models, we compared the CO conversion and C₃H₆ conversion obtained using additional TPO data set and model predictions without any further adjustment in the parameters. Figure 6 show that the model predicts well the CO and C₃H₆ light-off. Figure 7a shows the comparison between R_{CO} (CO = 1000 ppm, O₂ = 10%) and R'_{CO} (CO = 1000 ppm, C₃H₆ = 500 ppm, O₂ = 10%). R'_{CO} is about 1/4th that of R_{CO} showing strong C₃H₆ inhibition on CO oxidation. Similarly, Figure 7b shows the comparison between $R_{C_3H_6}$ (C₃H₆ = 1000 ppm, O₂ = 10%) and $R'_{C_3H_6}$ (C₃H₆ = 1000 ppm, CO = 500 ppm, O₂ = 10%). $R'_{C_3H_6}$ is about half that of $R_{C_3H_6}$. The various fitted global kinetic parameters are listed in Table 4.

3. Results and Discussion

3.1. Simulation of Dynamic Hysteresis

As described earlier, dynamic hysteresis may be encountered when a catalytic reaction is carried out in a tubular flow reactor with an imposed temperature ramp. The CO and C₃H₆ co-

oxidation experiments exhibited hysteresis in the conversion versus temperature when the temperature was ramped up and down at a constant rate. In order to understand this dynamic hysteresis behavior we simulated the co-oxidation of CO and C₃H₆ mixture at different ramp rates and nearly isothermal conditions as a result of the low feed concentrations of CO and C₃H₆. Specifically, the CO and C₃H₆ inlet mole fractions were fixed at low values such that the adiabatic temperature rise was low (<25°C). For example, the adiabatic temperature rise for co-oxidation of 500 ppm CO and 300 ppm C₃H₆ is 24°C. In order to confirm that for 500 ppm CO, 300 ppm C₃H₆ and 10% O₂ there is no steady state multiplicity, a simulation was carried out in which the inlet fluid temperature was first increased from 80°C to 190°C in steps of 5°C which was followed by a decrease in the feed fluid temperature from 190°C to 80°C in steps of 5°C. At each inlet temperature steady state solution was obtained. Figure 8 shows the steady state CO and C₃H₆ conversions with the varying fluid inlet temperature. The exit CO and C₃H₆ conversions follow the same path during temperature ramp-up and ramp-down. Hence, this CO+C₃H₆ mixture does not exhibit steady state hysteresis.

Simulations were then performed for the same CO (500 ppm) and C₃H₆ (300 ppm) inlet concentrations while the feed temperature was increased and decreased at different ramp rates. Figures 9a and 9b shows CO and C₃H₆ conversions when the feed temperature was increased from 80°C to 190°C and then decreased from 190°C to 80°C at a rate of 3°C/min and 10°C/min, respectively. This plot shows widening of hysteresis loop with increase in the ramp rate. The calculated feed gas temperatures corresponding to 50% CO and C₃H₆ conversion, T₅₀, during the ramp-up and ramp-down at different ramp-rates are listed in Tables 5 and 6, respectively. The temperature during ramp-up at which 50% conversion is reached, T_{50-u}, is found to be much less sensitive to the ramp rate than the temperature at which conversion drops to 50% during ramp

down, T_{50-d} . [Remark: The temperature T_{50-u} is often referred to as the light-off or ignition temperature in some aftertreatment literature studies. We do not use this terminology here as ignition or light-off in our definition means the existence of a limit point in the bifurcation diagram of conversion versus inlet temperature, see [24]]. The difference between T_{50-u} and T_{50-d} values (ΔT_{50}) defines the width of the dynamic hysteresis loop. It is observed that ΔT_{50} increases with the ramp rate. These results show that during ramp-down higher CO and C₃H₆ conversions are obtained at lower feed temperature as compared to the ramp-up.

The root cause for the dynamic hysteresis is a catalyst temperature response that lags behind the feed temperature during the ramp-down. We note that the speed of the thermal front is given by [21]

$$u_f = \langle u \rangle \frac{\rho_f C_{pf} R_{\Omega f}}{\rho_w C_{pw} R_{\Omega w}} \quad (3-1)$$

For the values of the parameters listed in Table 1 (and $\langle u \rangle = 0.95 \text{ m/s}$), this value is about 0.06 m/min. Thus, the difference in the front and back temperatures of a monolith of length 6.35cm at a ramp rate of 10°C/min is about 10°C. This is confirmed in the simulations shown in Figures 10a and 10b, where the solid temperature spatial profiles are shown during both ramp-up and ramp-down at a rate of 10°C/min. The solid temperature is almost linear along the monolith length during the ramp-up until ignition occurs at the front (between 6 and 7 minutes). After ignition and before ramp-down starts, this temperature difference reaches about 34°C (which is the sum of adiabatic rise and ramping delay). During the ramp-down, the back of the monolith remains hot even when the front end is below the ignition temperature. At a feed temperature of 120°C (6 minutes into ramp-down), 1/4th of the monolith back-end is still at or above 140°C.

Thus, the part of the monolith length with higher temperature results in higher CO and C₃H₆ conversions.

In order to confirm that the dynamic hysteresis is mainly due to transport delays and not due to heat generation, a temperature ramp-up and ramp-down simulations was again carried out at a rate of 10°C/min but the heats of reaction were set to zero. The result in Figures 11a and 11b shows that the dynamic hysteresis is sustained, confirming that the phenomenon is principally due to the transient heat transfer process. To our knowledge this fact has not been shown in the open literature.

3.2. Steady state hysteresis

Hysteresis that is observed at steady state, also called steady-state multiplicity, is typically a consequence of the coupling between reaction and transport processes. The existence of thermo-kinetic multiplicity depends on both the adiabatic temperature rise (ΔT_{ad}) and the effective heat Peclet number ($Pe_{h,eff}$). The adiabatic temperature rise is proportional to the heat of the reaction and reactant inlet concentrations while the effective heat Peclet number depends on the axial heat Peclet number (intra-phase or solid conduction) and transverse Peclet number (inter-phase or gas to solid heat transfer). The adiabatic temperature rise and the effective heat Peclet number are defined for the current reaction system as follows [21]:

$$\Delta T_{ad} = \frac{(-\Delta H_{R,CO})Y_{CO}}{\langle C_P \rangle} + \frac{(-\Delta H_{R,C_3H_6})Y_{C_3H_6}}{\langle C_P \rangle} \sim 9433Y_{CO} + 64200Y_{C_3H_6} \quad (3-2)$$

$$\frac{1}{Pe_{h,eff}} = \frac{1}{Pe_{hs}} + \frac{P_h}{Nu_{\Omega\infty}} \quad (3-3)$$

$$Pe_{hs} = \frac{\langle u \rangle L \rho_f C_{pf} R_{\Omega 1}}{k_w R_{\Omega w}}, P_h = \frac{\rho_f C_{pf} R_{\Omega 1}^2 \langle u \rangle}{k_f L}, Nu_{\Omega \infty} = \frac{Nu_{\infty}}{4}, \quad (3-4)$$

where, Pe_{hs} is the solid axial heat Peclet number which is a monotonically decreasing function of the product $k_w R_{\Omega w}$. Steady state hysteresis occurs due to a sufficiently high adiabatic temperature rise coupled with thermal feedback resulting from axial intra and/or interphase heat transfer, and the nonlinear dependence of the rate on temperature (overall activation energy). We note that $Pe_{hs} \ll 1$ for either very large values of solid conductivity (e.g. metallic supports), low velocity, and/or short reactor length. Similarly, $Pe_{hs} \gg 1$ for low solid conductivity (e.g. ceramic support), high velocity, and/or or length of the monolith. The transverse heat Peclet number (P_h) is the ratio of transverse heat diffusion (or gas to solid heat transfer) time to convection (residence) time. It determines the interphase temperature gradients within the monoliths. When $P_h \ll 1$, the temperature difference between gas and solid is small while it is significant for P_h values of order unity. For a constant adiabatic temperature rise (ΔT_{ad}), the effective heat Peclet number determines the size of the multiplicity region [21]. For parameter values listed in Table 1 (with $L=6.35\text{cm}$), we have $P_h=0.026$ and $Pe_{hs}=63.9$ so that $Pe_{h,eff}=25.3$ [Remarks: (i) As shown in [21], $Pe_{h,eff}$ is not a monotonic function of velocity; (ii) in the simulations (and experiments) the velocity is not constant but varies with temperature; and (iii) the numerical values of the Peclet numbers quoted here correspond to a typical velocity of 0.95 m/s and or temperature of 400K].

To illustrate the impact of the heat Peclet numbers, a simulation was carried out for a feed mixture containing 2000 ppm CO, 1200 ppm C_3H_6 and 10% O_2 ($\Delta T_{ad} = 96^\circ\text{C}$ and $Pe_{h,eff} \approx 5.48$ obtained by reducing the length to 2.0 cm but keeping the same space velocity or P_h). In

order to compute the ignition and extinction points the feed temperature was increased from 90°C to 200°C in steps of 2°C (and held constant until a steady-state is reached) and then decreased from 200°C to 90°C with the same step size. Figures 12a and 12b show the steady-state bifurcation diagram of conversion versus inlet temperature (and ignition and extinction points) for a feed consisting of both CO and C₃H₆. Close to the ignition point of 140°C the CO conversion is 42% whereas the C₃H₆ conversion is 5%. Both CO and C₃H₆ ignite between 140°C to 142°C as both CO and C₃H₆ conversions are 100% at 142°C. This feature suggests that at low temperature the catalyst is poisoned by both CO and C₃H₆. With an increase in temperature the rate of CO desorption increases enabling the adsorption of O₂ onto the surface. This results in an increase in the reaction rate as the adsorbed CO and O₂ react to CO₂, freeing up additional sites for O₂ adsorption. Once there is sufficient oxygen on the surface it will react with C₃H₆. Table 7 shows the extinction and ignition temperatures for CO and C₃H₆ for different feed compositions. The region of steady state multiplicity expands with increases in the CO and C₃H₆ inlet concentrations. Figures 13a and 13b show the CO and C₃H₆ ignition and extinction curves for 2000 ppm CO, 2000 ppm C₃H₆ and 10% O₂. The heat of reaction of C₃H₆ oxidation is much higher than the heat of reaction of CO oxidation. As a result, an increase in the C₃H₆ inlet mole fraction moves the extinction point to much lower temperature. Figure 14 shows the solid temperature spatial profile when the temperature is decreased from 200°C to 70°C in steps of 2°C. The extinction is between 90°C and 88°C as conversion is almost zero at 88°C. Above 90°C both CO and C₃H₆ conversions are 100% as the downstream section of the monolith is at a temperature exceeding the ignition temperature (146°C). Thus, steady state hysteresis observed here is due to both high adiabatic temperature rise that leads to increase in the rate of reaction

during extinction as the catalyst is at higher temperature compared to measured inlet gas temperature and lower effective heat Peclet number value.

Under dynamic conditions, the combination of thermokinetic multiplicity and the transient lag mechanism can contribute to the observed hysteresis behavior. To illustrate this, we consider a feed mixture containing 2000 ppm CO, 1200 ppm C₃H₆ and 10% O₂. A simulation was carried out in which the inlet temperature was first increased from 90°C to 200°C at a rate of 3°C/min and then decreased from 200°C to 90°C at the same rate. Figures 15a and 15b show there is increase in the width of hysteresis loop as compared to steady state hysteresis. This suggests that for this case hysteresis is due to the combined effect of both thermal effect and transport delay due to ramping.

The simulations discussed in this section so far were performed with a monolith length of 2 cm, which has an effective heat Peclet number of 5.48. In order to illustrate the dependence of steady state multiplicity on the effective heat Peclet number, a simulation was performed for 2000 ppm CO, 1200 ppm C₃H₆ and 10% O₂ but for a larger value of the effective heat Peclet number of 25.3. The effective heat Peclet number was increased from 5.48 to 25.3 by increasing the axial heat Peclet number from 6.3 to 63.9 while keeping the transverse heat Peclet number (P_h) constant. Figures 16a and 16b show that for the same adiabatic temperature rise of 96°C the steady state multiplicity disappears for this case of a higher effective heat Peclet number. This clearly shows the impact of effective heat Peclet number on steady state multiplicity.

For $Pe_{h,eff} = 25.3$ and 2000 ppm CO, 1200 ppm C₃H₆ and 10% O₂, simulation was performed in which temperature was first increased from 90°C to 200°C at a rate of 3°C/min and then decreased from 200°C to 90°C at a same rate. Figures 17a and 17b show there is transient

hysteresis due to ramping even when there is no steady state hysteresis. This further confirms that dynamic hysteresis can exist even when there is no steady state multiplicity.

3. Light-off behavior during co-oxidation of CO and C₃H₆

A question of some practical importance that arises during the design and operation of the diesel oxidation monolithic converters is “how does the light-off temperature depend on various design and operating conditions”? For the case of a single reaction, this has been addressed in earlier studies [21, 24], though most of theory and simulations were confined to monotonic kinetics. It is well known that for negative order kinetics such as that considered here, higher inlet concentrations of reactants can increase the light-off temperature, while the higher adiabatic temperature rise can reduce it. Which of these effects dominates depends on the specific kinetics and range of inlet concentrations considered. Table 8 shows the steady state CO and C₃H₆ conversion at ignition temperature for two different feed compositions. In both the cases C₃H₆ conversion is less than 10% below ignition temperature whereas, the CO conversion is in range of 40-50% at ignition temperature. This difference in CO and C₃H₆ conversion is attributed to C₃H₆ adsorption which is stronger than CO adsorption. Above the ignition temperature C₃H₆ conversion is 100%. Similarly, there is sharp increase in CO conversion to 100% within the same temperature range. The steep increase in CO conversion is attributed to both the availability of empty sites for O₂ adsorption and also due to increase in solid temperature during C₃H₆ oxidation.

Finally, we present some simulations that examine the dependence of the inlet temperature at which a conversion of 99% or higher is obtained during the co-oxidation of CO and C₃H₆. [As remarked earlier, this is not ignition or light-off temperature as we do not use the

limit point criterion. However, this temperature, which is analogous to T_{50} , is useful in assessing the performance of the diesel oxidation catalysts with different inlet concentrations of hydrocarbons and CO. Further, we present this calculation with a temperature ramp so that it simulates the cold-start behavior]. Figures 18a and 18b show the T_{99+} for both CO and C_3H_6 for varying CO and C_3H_6 inlet concentrations. T_{99+} corresponds to the lowest calculated feed gas temperature corresponding to nearly 100% CO and C_3H_6 conversion. The 2D plots show that the for the inlet CO mole fraction in range of 1000-4000 ppm and for the inlet C_3H_6 mole fraction of 200-3000 ppm, T_{99+} for both CO and C_3H_6 lies between 130-165°C.

4. Conclusions

The main contribution of this work is a study of dynamic and steady-state hysteresis using global kinetic model for co-oxidation of CO and C_3H_6 over Pt/ Al_2O_3 monolithic catalyst. This work focuses on elucidation of the transient as well as steady-state hysteresis that occurs in laboratory scale TPO experiments (or in full scale monolith reactors in which temperature excursions occur).

The experimental data analyzed in this work is typical of laboratory studies in which TPO experiments are used to investigate the light-off characteristics of diesel oxidation (and other monolith) catalysts [13, 15, 19]. During TPO of CO+ C_3H_6 mixture, hysteresis is observed when temperature is first increased and then decreased with a constant ramp-rate. In order to explain this we performed simulations for feed composition with low CO and C_3H_6 inlet fractions ($(\Delta T_{ad} < 25^\circ C)$) in which temperature is ramped up and down with a constant rate. As heat generated is negligible so dynamic hysteresis observed is only due to the lag between catalyst temperature change and inlet fluid temperature change. Hence, hysteresis observed is result of a transient

change in feed temperature. We also performed simulations to show the effect of dynamic change in feed temperature on the steady state multiplicity region. We showed that a change in feed temperature at constant rate increase the width of hysteresis loop as compared to steady state multiplicity region. Therefore, due to the coupling between dynamic and steady state hysteresis the ignited branch extends to lower inlet gas temperatures. We also studied the effect of inlet feed composition, adiabatic temperature rise and effective heat Peclet number on steady state multiplicity for nonlinear self-inhibiting reaction kinetics ($\text{CO} + \text{C}_3\text{H}_6 + \text{O}_2$). For given adiabatic temperature rise, the region of steady state multiplicity depends on effective heat Peclet number. The region of multiplicity shrinks with increase in effective heat Peclet number. Similarly, for constant effective heat Peclet number the width of steady state hysteresis loop depend on heat generated or adiabatic temperature rise. Hence, increase in inlet mole fractions of CO and C_3H_6 lead to shifting the ignition branch at lower feed temperatures. This study provides useful insight into the cause of dynamic hysteresis and how it relates to the thermokinetic multiplicity.

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Nomenclature:

C_0	total concentration in gas phase
$c_{p,f}$	specific heat capacity of gas (J/kg/K)
$c_{p,w}$	effective solid phase heat capacity (J/kg/K)
$D_{f,j}$	diffusivity of species in the fluid phase (m ² /s)
$D_{e,j}$	effective diffusivity of species in the washcoat (m ² /s)
h	heat transfer coefficient
k_{me}	external mass transfer coefficient (m/s)
k_{mi}	internal mass transfer coefficient (m/s)
k_{mo}	overall mass transfer coefficient (m/s)
k_w	effective thermal conductivity
L	length of the monolith (m)
Nu_∞	asymptotic Nusselt number
P	transverse Peclet number
Pe_{hs}	solid axial heat Peclet number
P_h	transverse heat Peclet number
$Pe_{h,eff}$	effective heat Peclet number
R_{Ω_1}	effective transverse diffusion length for flow area (m)
R_{Ω_2}	effective transverse diffusion length for washcoat area (m)
R_i	volumetric reaction rate (mol/m ³ of washcoat/s)
Sh_e	external Sherwood number
Sh_i	internal Sherwood number
$Sh_{i,\infty}$	asymptotic internal Sherwood number
t	time (s)
T_f	gas phase temperature (K)
T_s	solid temperature

ΔT_{ad}	adiabatic temperature rise
$\langle u \rangle$	average fluid velocity in the fluid phase (m/s)
u_f	speed of thermal front
$Y_{fm,j}$	cup-mixing mole fraction of species j in fluid phase
$\langle Y_{wc} \rangle_j$	volume averaged mole fraction of species j in washcoat
z	axial coordinate (m)
<i>Greek letters</i>	
ν_{jr}	stoichiometric coefficient of species j for reaction r
ϵ_{wc}	porosity of washcoat
ρ_f	density of gas (kg/m ³)
λ	ratio of fluid phase diffusivity to effective washcoat diffusivity

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Table 1 Constant parameters used in the simulation

Parameter	Value
R_{Q1}	262.5 μm
R_{Q2}	25 μm
L	2cm or 6.35cm
Sh_e	4.36
$Sh_{i,\infty}$	3.0
Nu	4.36
ε_{wc}	0.4
λ	10
R_{Qw}	107.55 μm
ρ_f	0.856 kg/m^3
C_{pf}	1014 J/kg/K
$\langle C_p \rangle$	30 J/mol/K
k_f	0.0343 W/m/K
ρ_w	2000 kg/m^3
C_{pw}	1000 J/kg/K
k_w	2 W/m/K
R_g	8.314 J/mol/K
Pe_{hs}	63.5 or 6.3
Pe_h	0.0259
P	0.0338
ΔH°_{CO}	-283.0 kJ/mol
$\Delta H^\circ_{C_3H_6}$	-1925.9kJ/mol

Table 2 Temperature dependent parameters used in the simulation

Parameter	Value / Expression
$\langle u \rangle$	$0.645 \times (T_f/273.15) \text{ m/s}$
D_{f,CO_2}	$0.825 \times 10^{-9} \times T_f^{1.7148} \text{ m}^2/\text{s}$
D_{f,O_2}	$1.13 \times 10^{-9} \times T_f^{1.7019} \text{ m}^2/\text{s}$
D_{f,C_3H_6}	$4.237 \times 10^{-10} \times T_f^{1.7844} \text{ m}^2/\text{s}$
D_{f,H_2O}	$1.62 \times 10^{-9} \times T_f^{1.7033} \text{ m}^2/\text{s}$
$D_{f,CO}$	$1.13 \times 10^{-9} \times T_f^{1.7148} \text{ m}^2/\text{s}$

Table 3 Catalyst properties

Catalyst	Components	Pt loading (g/ft ³)
DOC	Pt/Al ₂ O ₃	95

Table 4 Kinetic parameters used in the simulation

Parameters	Value (moles/ m ³ /s)/(-)	Parameters	Values (K)
A ₁	1.28×10 ²¹	$\frac{E_1}{R_g}$	14421.46
A _{CO}	88.59	$\frac{-\Delta H_{CO}}{R_g}$	1161.88
A ₂	1.36×10 ¹⁷	$\frac{E_2}{R_g}$	11306.24
A _{C₃H₆}	2508.28	$\frac{-\Delta H_{C_3H_6}}{R_g}$	117.0
A _{ICO}	2090.13	$\frac{-\Delta H_{ICO}}{R_g}$	300.0
A _{IC₃H₆}	323.06	$\frac{-\Delta H_{IC_3H_6}}{R_g}$	1100.0

Table 5 T₍₅₀₎ for CO conversion during ramp-up and ramp-down at different ramp-rates

CO (ppm)	C ₃ H ₆ (ppm)	Ramp rate (°C/min)	T _{50-u} (°C)	T _{50-d} (°C)	ΔT(°C)
500	300	3	126	121	5
500	300	5	128	119	11
500	300	8	129	116	13
500	300	10	131	113	18
500	300	15	134	104	30
500	300	0.5	124	123	1

Table 6 T₍₅₀₎ for C₃H₆ conversion during ramp-up and ramp-down at different ramp-rates

CO (ppm)	C ₃ H ₆ (ppm)	Ramp rate (°C/min)	T _{50-u} (°C)	T _{50-u} (°C)	ΔT (°C)
500	300	3	134	127	7
500	300	5	136	125	11
500	300	8	137	123	14
500	300	10	140	118	22
500	300	15	143	110	33
500	300	0.5	130	128	2

Table 7 Steady state ignition and extinction temperatures for C₃H₆ conversion

CO (ppm)	C ₃ H ₆ (ppm)	Ignition T (°C)	Extinction T (°C)	ΔT (°C)
2000	1200	140	120	20
3000	1200	140	110	30
2000	2000	146	90	55

Table 8 Steady state CO and C₃H₆ conversion at ignition temperature

CO (ppm)	C ₃ H ₆ (ppm)	Ignition T (°C)	CO conversion (%)	C ₃ H ₆ conversion (%)
2000	1200	140	42	5
2000	2000	146	47	6

Figures

Figure 1 Fitted light-off curve of CO (Abedi et al. [15], CO = 1000 ppm, 10% O₂, 10% H₂O, 10% CO₂; Space velocity of 25,000 h⁻¹ at STP; Temperature ramp = 3°C/min)

Figure 2 Predicted CO oxidation rate versus CO mole fraction (a) 400 K (b) 500 K (CO = 100-5000 ppm, 10% O₂; Space velocity of 25,000 h⁻¹ at STP)

Figure 3 Fitted light-off curve of C_3H_6 (Abedi et al. [15], $C_3H_6 = 800$ ppm, 10% O_2 , 10% H_2O , 10% CO_2 ; Space velocity of $25,000\text{ h}^{-1}$ at STP; Temperature ramp = $3^{\circ}\text{C}/\text{min}$)

Figure 4 Predicted C_3H_6 oxidation rate versus C_3H_6 mole fraction (a) 400 K (b) 500 K ($C_3H_6 = 100\text{-}5000 \text{ ppm}$, 10% O_2 ; Space velocity of $25,000 \text{ h}^{-1}$ at STP)

Figure 5 Fitted light-off curve of CO and C_3H_6 (Abedi et al. [13], CO = 1000 ppm, C_3H_6 = 800 ppm, 10% O_2 , 10% H_2O , 10% CO_2 ; Space velocity of $25,000\ h^{-1}$ at STP; Temperature ramp = $3^\circ C/min$)

Figure 6 Comparison between measured and predicted CO conversion and C_3H_6 versus inlet fluid temperature (Abedi et al. [13], CO = 1000 ppm, C_3H_6 = 500 ppm, 10% O_2 , 10% H_2O , 10% CO_2 ; Space velocity of $25,000\ h^{-1}$ at STP; Temperature ramp = $3^\circ C/min$)

Figure 7 (a) Comparison between predicted CO oxidation rates in absence and in presence of C₃H₆ in the feed (CO = 1000 ppm, C₃H₆ = 0 or 500 ppm, 10% O₂) (b) Comparison between predicted C₃H₆ oxidation rates in absence and in presence of CO in the feed (C₃H₆ = 1000 ppm, CO = 0 or 500 ppm, 10% O₂)

Figure 8 Predicted steady state CO and C_3H_6 (CO = 500 ppm, C_3H_6 = 300 ppm, 10% O_2 ; Space velocity of $25,000 \text{ h}^{-1}$ at STP)

Figure 9 (a) Predicted CO conversion versus inlet fluid temperature with temperature ramp of $3^{\circ}\text{C}/\text{min}$ and $10^{\circ}\text{C}/\text{min}$ (b) Predicted C_3H_6 conversion versus inlet fluid temperature with temperature ramp of $3^{\circ}\text{C}/\text{min}$ and $10^{\circ}\text{C}/\text{min}$ ($\text{CO} = 500 \text{ ppm}$, $\text{C}_3\text{H}_6 = 300 \text{ ppm}$, $10\% \text{ O}_2$; Space velocity of $25,000 \text{ h}^{-1}$ at STP)

Figure 10 (a) Predicted spatial profile of solid temperature during ramp up from 80°C to 190°C (b) Predicted spatial profile of solid temperature during ramp down from 190°C to 80°C (CO = 500 ppm, C₃H₆ = 300 ppm, 10% O₂; Space velocity of 25,000 h⁻¹ at STP; Temperature ramp = 10°C/min)

Figure 11 (a) Predicted CO conversion versus inlet fluid temperature (b) Predicted C_3H_6 conversion versus inlet fluid temperature (CO = 500 ppm, C_3H_6 = 300 ppm, 10% O_2 ; Space velocity of $25,000 \text{ h}^{-1}$ at STP; Temperature ramp = $10^{\circ}\text{C}/\text{min}$; Heat of reaction = 0 kJ/mol)

Figure 12 (a) Predicted steady state CO conversion versus inlet fluid temperature (b) Predicted steady state C_3H_6 conversion versus inlet fluid temperature (CO = 2000 ppm, C_3H_6 = 1200 ppm, 10% O_2 ; Space velocity of $25,000 \text{ h}^{-1}$ at STP, $\text{Pe}_{\text{h,eff}} = 5.48$)

Figure 13 (a) Predicted steady state CO conversion versus inlet fluid temperature (b) Predicted steady state C_3H_6 conversion versus inlet fluid temperature (CO = 2000 ppm, C_3H_6 = 2000 ppm, 10% O_2 ; Space velocity of $25,000 \text{ h}^{-1}$ at STP, $\text{Pe}_{\text{h,eff}} = 5.48$)

Figure 14 Predicted steady state spatial profile of solid temperature when inlet fluid temperature is decreased in steps of 5°C ($\text{CO} = 2000 \text{ ppm}$, $\text{C}_3\text{H}_6 = 2000 \text{ ppm}$, $10\% \text{ O}_2$; Space velocity of $25,000 \text{ h}^{-1}$ at STP, $\text{Pe}_{\text{h,eff}} = 5.48$)

Figure 15 (a) Predicted CO conversion versus inlet fluid temperature (b) Predicted C_3H_6 conversion versus inlet fluid temperature (CO = 2000 ppm, C_3H_6 = 1200 ppm, 10% O_2 ; Space velocity of $25,000 \text{ h}^{-1}$ at STP; $\text{Pe}_{\text{h,eff}} = 5.48$; Temperature ramp = 3°C/min)

Figure 16 (a) Predicted steady state CO conversion versus inlet fluid temperature (b) Predicted steady state C_3H_6 conversion versus inlet fluid temperature (CO = 2000 ppm, C_3H_6 = 1200 ppm, 10% O_2 ; Space velocity of 25,000 h^{-1} at STP; $Pe_{h,eff}$ = 25.3)

Figure 17 (a) Predicted CO conversion versus inlet fluid temperature (b) Predicted C₃H₆ conversion versus inlet fluid temperature (CO = 2000 ppm, C₃H₆ = 1200 ppm, 10% O₂; Space velocity of 25,000 h⁻¹ at STP; $Pe_{h,eff}$ = 25.3; Temperature ramp = 3 °C/min)

Figure 18 (a) Predicted T_{99+} for CO (b) Predicted T_{99+} for C_3H_6 ($\text{CO} = 1000\text{-}4000$ ppm, $\text{C}_3\text{H}_6 = 200\text{-}3000$ ppm, 10% O_2 ; Space velocity of $25,000\text{ h}^{-1}$ at STP, Temperature ramp = $3^{\circ}\text{C}/\text{min}$)