Chemical Engineering Journal 281 (2015) 322–333

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Steady-state and dynamic hysteresis effects during lean co-oxidation of CO and $C_3H_6$ over $Pt/Al_2O_3$ monolithic catalyst

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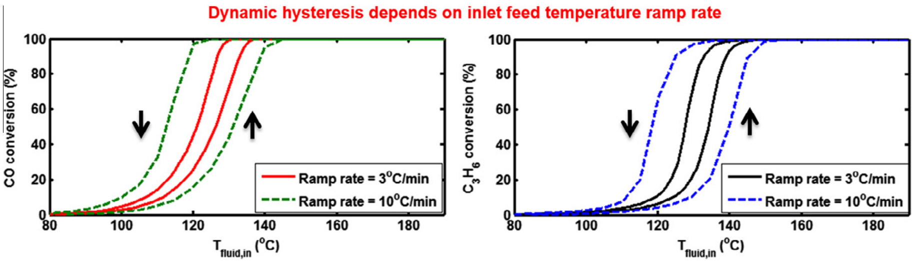
## HIGHLIGHTS

- Kinetic model for co-oxidation of CO and $C_3H_6$ on $Pt/Al_2O_3$ monolith is developed.
- Model predicts the experimentally observed dynamic and steady state hysteresis.
- Dynamic hysteresis is observed due to the transient change in feed temperature.
- Dynamic hysteresis is result of lag between catalyst and feed temperature.
- Coupling between both hysteresis types shifts ignited branch to lower feed temperatures.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 10 March 2015
Received in revised form 9 June 2015
Accepted 10 June 2015
Available online 16 June 2015

*Keywords:*
Kinetic modeling
Propylene
CO
Diesel oxidation catalyst
Monolith
Hysteresis

## ABSTRACT

A global kinetic model is developed for the co-oxidation of CO and $C_3H_6$ over a $Pt/Al_2O_3$ diesel oxidation monolithic catalyst based on a recent bench flow reactor study (Abedi et al., 2012). A monolith reactor model containing these kinetics is used to elucidate the dynamic and steady state hysteresis behavior observed during oxidation of a $CO + C_3H_6$ mixture on $Pt/Al_2O_3$. 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 ($\Delta T_{ad}$) and $Pe_{h,eff}$, i.e. thermokinetic multiplicity. The region of steady state hysteresis loop expands with an increasing $\Delta T_{ad}$ which is proportional to the feed concentrations of CO and $C_3H_6$. For fixed $\Delta T_{ad}$, 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.

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http://dx.doi.org/10.1016/j.cej.2015.06.057
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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 ($W/(m^2 \cdot K)$) |
| $k_{me}$ | 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 ($W/(m \cdot K)$) |
| $L$ | length of the monolith (m) |
| $Nu_\infty$ | 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 |
| $R_{\Omega_1}$ | effective transverse diffusion length for flow area (m) |
| $R_{\Omega_2}$ | 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 |
| $\Delta T_{ad}$ | adiabatic temperature rise (K) |
| $\langle u \rangle$ | average fluid velocity in the fluid phase (m/s) |
| $u_f$ | speed of thermal front (m/s) |
| $Y_{fm,j}$ | 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) |

*Greek letters*

| | |
|---|---|
| $\vartheta_{jr}$ | stoichiometric coefficient of species $j$ for reaction $r$ |
| $\varepsilon_{wc}$ | porosity of washcoat |
| $\rho_f$ | density of gas ($kg/m^3$) |
| $\lambda$ | ratio of fluid phase diffusivity to effective washcoat diffusivity |

## 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 $CO_2$ and $H_2O$. 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 and 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 [1–18]. 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 $O_2$ 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 $C_3H_6$ oxidation are self-inhibiting. Furthermore, in a $CO + C_3H_6$ mixture, CO inhibits $C_3H_6$ 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 the 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 [2–6,9–13,21]. It has been shown 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 pellets. 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 $Pt/A1_2O_3$ 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(1 0 0) and Pt(1 1 0) [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/min and decreased at 2.3 K/min. Ignition-extinction (light-off) curves demonstrated the presence of counter 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 $Pt/Al_2O_3$ by temperature