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Experimental and modeling study of CO and hydrocarbons light-off on various Pt-Pd/γ-Al_2O_3 diesel oxidation catalysts

Keyvan Daneshvar [a], Rama Krishna Dadi [a], Dan Luss [a], Vemuri Balakotaiah [a,*], Sung Bong Kang [a], Christos M. Kalamaras [c], William S. Epling [b]

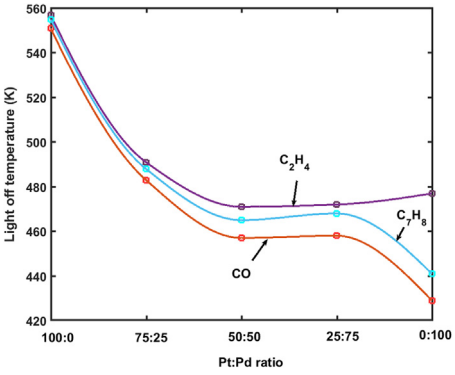
[a] Deptartment of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, USA
[b] Deptartment of Chemical Engineering, University of Virginia, Charlottesville, VA 22904-4741, USA
[c] Fuel Technology R&D Center, Saudi Aramco Research and Development Center, Dhahran 31311, Saudi Arabia

HIGHLIGHTS

- A global kinetic model is developed for the oxidation of CO and HC mixtures.
- Model is validated with the experiments and captures the light-off behavior.
- Light-off temperatures of CO and HCs are presented and modeled with varying Pt/Pd.
- Catalyst with Pt/Pd (50:50) ratio is found to be optimal.

GRAPHICAL ABSTRACT

Variation of CO and hydrocarbons light-off temperature (T_{50}) with Pt/Pd molar ratios.



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ABSTRACT

A global kinetic model is developed for the oxidation of mixtures of CO, C_2H_4 (ethylene), C_7H_8 (toluene), C_6H_{14} (hexane), and C_2H_6 (ethane) over Pt-Pd/γ-Al_2O_3 diesel oxidation catalysts with different Pt/Pd molar ratios (100:0, 75:25, 50:50, 25:75, 0:100). The kinetic model is based on bench flow reactor data obtained by temperature-programmed oxidation, ramping up the feed gas temperature at a fixed rate of 8 °C/min. The kinetic model is developed in stages starting with pure CO oxidation, followed by oxidation of the individual hydrocarbons (HCs) and then mixtures over all Pt/Pd ratios. Examination of the inhibition terms containing the effect of CO, HCs, and NO shows that CO has the most dominant inhibition effect on light-off over the range of conditions investigated. The kinetic model is validated with experimental data at different feed concentrations and is found to simulate the light-off behavior for all catalyst compositions with acceptable accuracy. Comparison of the light-off temperatures and trend investigation for kinetic parameters of CO, C_2H_4, and C_7H_8 in the mixture over all Pt/Pd ratios is also presented. Considering trade-offs between having a low light-off temperature, low deactivation impact on the catalyst, and higher conversion of HCs within the temperature domain of interest, the Pt/Pd (1:1) molar ratio is found to be the optimal catalyst under the conditions examined.

* Corresponding author.
E-mail address: bala@uh.edu (V. Balakotaiah).

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Nomenclature

Symbols definition

a	pore radius (m)
A	pre-exponential factor (mol/m^3.s)
C_p	specific heat capacity (J/kg.K)
C_{Total}	total concentration of gas phases species (mol/m^3)
$\boldsymbol{D}$	diffusivity (m^2/s)
E	activation energy (kJ/mol)
h	heat transfer coefficient (W/m^2.K)
$\Delta\boldsymbol{H}$	vector of reaction enthalpies (kJ/mol)
$\boldsymbol{k_{me}}$	external mass transfer coefficient matrix (m/s)
$\boldsymbol{k_{mi}}$	internal mass transfer coefficient matrix (m/s)
$\boldsymbol{k_{mo}}$	overall mass transfer coefficient matrix (m/s)
L	length of the monolith channel (m)
M	molecular weight (g/mol)
Nu	Nusselt number
p	pressure (Pa)
P	transverse Peclet number
P_h	transverse Peclet heat number
$\boldsymbol{r}$	vector of reaction rates (mol/m^3.s)
$\boldsymbol{R}$	vector of net rate of production (mol/m^3.s)
R_g	universal gas constant (J/mol.K)
R_Ω	hydraulic radius of monolith channel (m)
$\mathbf{Sh}_e$	external Sherwood number matrix
$\mathbf{Sh}_i$	internal Sherwood number matrix
SV	space velocity (h^{-1})
t	time (s)
T	temperature (K)
$\langle u\rangle$	average feed gas velocity (m/s)
x	coordinate along the length of the monolith channel (m)
z	dimensionless axial co-ordinate
$\mathbf{Y}$	vector of mole fractions
$\boldsymbol{Y_{fm}}$	vector of cup-mixing mole fractions in fluid phase
$\langle\boldsymbol{Y_{wc}}\rangle$	vector of volume averaged mole fractions in washcoat

Greek symbols

δ_w	effective wall thickness (m)
δ_s	half-thickness of wall (m)
δ_c	washcoat thickness (m)
ε_w	porosity of washcoat
$\boldsymbol{v}$	matrix of stoichiometric coefficients
v_j	diffusion volumes
ρ	density (kg/m^3)
τ	tortuosity

Subscripts

j	gaseous component index
f	fluid phase
s	solid phase
w	wall/washcoat
∞	asymptotic

Superscripts

in	inlet condition
0	initial condition

1. Introduction

Diesel oxidation catalysts (DOCs) are used in the treatment of hydrocarbon and CO emissions from diesel and lean burn engines. An accurate prediction of the DOC performance is important for the simulation of the entire after-treatment system [1]. The major functions of the DOC are oxidation of CO, Total Hydrocarbons (THCs) and NO. While monolith reactors with ceramic substrates are usually used in DOCs, metallic monoliths may sometimes be used. Precious Group Metals (PGMs) are used as catalyst materials in DOC as they have good oxidation performance and high thermal durability. An efficient DOC design requires knowledge of the light-off behavior of CO and hydrocarbons mixtures as a function of inlet temperature and concentration [2]. Temperature programmed experiments are usually used to determine the activity of the catalysts and estimate the kinetic parameters. These experiments involve heating or cooling of the feed gas temperature and are used to define the light-off curves for various species at different temperature ranges. With strong inhibition effects, it is important to know if the ignition temperatures of the species are either similar or are quite different to each other. An example of a system in which the light-off temperatures are close is the CO + C_2H_4 + C_7H_8 mixture. In contrast, during the oxidation of a CO + C_2H_6 mixture, CO ignites at a low temperature while C_2H_6 ignites at a much higher temperature [3].

Extensive previous studies reported the oxidation of CO and hydrocarbons on Pt, Pd and Pt:Pd catalysts in monolith reactors. Salomons et al. [4] predicted the ignition and extinction behavior using different models for the CO oxidation reaction on Pt/γ-Al_2O_3. This was based on data obtained from temperature-programmed oxidation (TPO) experiments for different inlet CO concentrations in which the feed gas temperature was ramped-up at a rate of 8 K/min and ramped down at a rate of 2.3 K/min. Garetto et al. [5] compared Pt-supported catalysts performances during oxidation of ethane, propane, and butane [2]. CO inhibits HC oxidation in CO and HC mixtures, and HCs inhibit CO oxidation due to competitive adsorption on active catalytic sites [6–9]. Carlsson et al. [10] studied CO oxidation on Pt/γ-Al_2O_3 using TPO experiments. Abedi et al. [8] performed TPO experiments for CO, C_3H_6, and CO + C_3H_6 mixtures over a Pt/γ-Al_2O_3 monolithic catalyst [11]. Diehla et al. [12] investigated the catalytic oxidation of many heavy hydrocarbons including hexane and toluene over a Pt/γ-Al_2O_3 catalyst. The selected HCs were among those which are usually detected in diesel exhaust gases. Grbic et al. [13] studied the oxidation of *n*-hexane and toluene mixtures in air over Pt/γ-Al_2O_3 catalysts. The goal of their work was to explain which hydrocarbons in a mixture influence others over Pt/γ-Al_2O_3 catalysts.

Pt catalysts are very active, but they are expensive and have poor thermal durability [14]. One of the reasons for the deactivation is the sintering of Pt crystallites [15], while Pd leads to better thermal durability with catalyst aging, compared to Pt [16–18]. Chen et al. [19] reported that Pt/Pd alloys sinter at a much lower rate than pure Pt in oxidative atmospheres. Hydrothermal sintering of Pt can be decreased by the addition of Pd [15,20]. One issue though is that substituting Pt with Pd can be tricky for NO oxidation since the rate of conversion of NO to NO_2 is lower on the Pd surface [21–22]. Several prior studies reported catalytic behaviors of Pt:Pd systems considering many reactions [17,23–24]. Morlang et al. [15] and Persson et al. [25] have found that a Pt:Pd alloy increases the hydrocarbon oxidation rate [14]. Khosravi et al. [26] determined global kinetic models for Pt and Pt:Pd diesel oxidation catalysts. Han et al. [18] reported that among the three DOCs evaluated, the one with (Pt/Pd) had the best light-off efficiency, followed by (Pt-Pd + CeO_2), and Pt-only, regardless of exhaust mixture. Global kinetic models have been used to explain the light-off behavior during temperature ramp-up for CO and HC