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Effect of Pt:Pd ratio on CO and hydrocarbon oxidation

Sung Bong Kang[a], Melanie Hazlett[a], Vemuri Balakotaiah[a], Christos Kalamaras[b], William Epling[a,*]

[a] *Department of Chemical and Biomolecular Engineering, University of Houston, United States*
[b] *Saudi Aramco Research and Development Center, Dhahran, 31311, Saudi Arabia*

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ABSTRACT

For several reasons, typical diesel oxidation catalysts (DOCs) contain a mixture of Pt and Pd and in this study, the effect of the Pt:Pd ratio on a DOC's ability to oxidize CO and different hydrocarbon types was investigated. The concentrations and types of pollutant species were used to simulate those found in low temperature combustion (LTC) engine exhaust. Representative hydrocarbon species were selected; C_2H_4 (short-chain alkene), C_2H_6 (short-chain alkane), C_6H_{14} (long-chain alkane) and C_7H_8 (aromatic). Two types of experiments were performed, one in which the oxidation of each hydrocarbon or CO reactant was examined individually (simple feed conditions), and the second in which all reactants were added together (full feed conditions). Under the simple feed conditions, CO and C_2H_6 oxidation increased with increasing Pd content, while C_2H_4 and C_6H_{14} oxidation improved with higher Pt content. When the full mixture of CO and hydrocarbons was used, hydrocarbon oxidation light off consistently followed that of CO, regardless of the Pt:Pd ratio, due to strong inhibition by CO. The best CO oxidation activity was observed over the Pd-only catalyst, and performance over the bimetallic samples was a function of both CO inhibition and Pt:Pd ratio. More specifically, as Pd content increased, CO inhibition was dampened, and as Pt content increased its inherent activity toward alkene oxidation became significant. Since inhibition is a function of the Pt/Pd content and the individual metals have different inherent activities toward the oxidation of different hydrocarbons, results obtained from the experiments with the simple feed could not be directly correlated to those from the experiments with the mixture of hydrocarbons.

1. Introduction

Recently, low temperature combustion (LTC) engines have been developed to meet ever tightening fuel economy standards [1,2]; a challenge from the emissions standpoint is the relatively lower exhaust gas temperature and higher concentrations of CO and hydrocarbons [2–4]. This puts emphasis on the need to design and develop improved low temperature oxidation catalysts for LTC engine exhaust treatment. In evaluating such catalysts, often a single pollutant is used but predicting catalytic activity based on such results may be complicated due to the co-existence of multiple reactant species, their mutual inhibition and inhibition via formation of surface intermediate species [4–6]. For example, Patterson et al. [5] reported that the addition of 1% CO in the feed severely inhibited the oxidation activity of hexane, toluene and benzene over a Pt/Al_2O_3 monolith catalyst. The authors attributed this to the competitive adsorption of CO and hydrocarbons onto the catalyst surface. Similarly, Hazlett et al. [4] noted strong CO inhibition of C_3H_6 oxidation, as well as C_3H_6 inhibition of CO oxidation. The former was attributed to the strong adsorption of CO on the precious metal sites, and the latter to C_3H_6 partial oxidation surface intermediates blocking active sites.

The typical oxidation catalyst formulation found in the literature has shifted from a Pt-only precious metal composition to a bimetallic Pt/Pd system. The addition of Pd, when substituted for Pt, of course lowers catalyst cost, but Pd also improves thermal resistance as it has been shown to slow Pt particle sintering [7,8]. And of course it has its own oxidation performance [9,10]. There have been several studies examining the effect of Pt:Pd ratio on CO and hydrocarbon oxidation [11–13]. For example, Skoglundh et al. [11] have shown that for different Pt:Pd ratios, the bimetallic catalysts outperformed the monometallic samples. However, there was not one ratio that proved best for all the species examined; a 1:4 Pt:Pd ratio was best for CO and C_7H_8 oxidation, and the 1:1 for C_3H_6 oxidation. Shakya and coworkers [14] studied a variety of Pt:Pd blends and demonstrated that more Pt led to improved C_3H_6, C_7H_8, $C_{10}H_{22}$

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* Corresponding author.
E-mail address: wsepling@virginia.edu (W. Epling).

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Table 1
Sample content as a function of Pt:Pd ratio.

Sample	Pt:Pd molar ratio	Content of metal atom $(mol/ft^3{}_{\cdot monolith})$		Content of metal mass $(g/ft^3{}_{\cdot monolith})$	
		Pt	Pd	Pt	Pd
Pt-only	100:0	1.42×10^{-1}	–	27.8	–
3:1 Pt:Pd	75:25	1.07×10^{-1}	0.35×10^{-1}	20.8	3.8
1:1 Pt:Pd	50:50	0.71×10^{-1}	0.71×10^{-1}	13.9	7.6
1:3 Pt:Pd	25:75	0.35×10^{-1}	1.07×10^{-1}	6.9	11.4
Pd-only	0:100	–	1.42×10^{-1}	–	15.1

and NO oxidation, whereas CO oxidation was best over the higher Pd content catalysts. Finally, Kim et al. [12] systematically studied Pt:Pd ratio effects and found that better performance for NO and C_3H_6 oxidation, when evaluated as a mixture, was found with a Pt-rich bimetallic catalyst. They also showed that the optimal ratio changes with aging and the addition of other gas components.

In this study, we used both simple feed flows (CO or hydrocarbon and O_2) as well as more complex mixtures in order to (i) understand the role of the precious metal ratio on oxidation activity, including inhibition characteristics, and (ii) evaluate the reliability of simplified simulated mixtures in determining the performance under more realistic conditions. The hydrocarbon species selected were a short-chain alkene (ethylene, C_2H_4), a short-chain alkane (ethane, C_2H_6), a long-chain alkane (hexane, C_6H_{14}) and an aromatic (toluene, C_7H_8) species as representative hydrocarbon molecules. CO and NO were also included in the feed gas.

2. Experimental

2.1. Catalyst preparation and characterization

A series of five catalyst samples were prepared: 1:0, 3:1, 1:1, 1:3 and 0:1 Pt:Pd supported on an Al_2O_3 washcoated cordierite monolith (1.59 g/in^3 Al_2O_3, 400 cpsi). The total Pt and Pd metal content was kept constant, 1.42×10^{-1} mol/ft^3 of monolith, regardless of the Pt and Pd ratio. All the values are listed in Table 1. The Al_2O_3 washcoated monolith was provided by Johnson Matthey. The Pt and Pd precursors, $Pt(NH_3)_4(NO_3)_2$ and/or $Pd(NO_3)_2$ (Sigma-Aldrich), were mixed to form aqueous solutions, into which the Al_2O_3 washcoat monoliths were dipped. The monolith samples were dried at 80 °C for 24 h and subsequently calcined at 550 °C for 4 h in air. All monolith catalysts were hydrothermally aged in a flowing mixture of 14% O_2, 5% H_2O and N_2 balance at 700 °C for 24 h.

Pulsed CO chemisorption was used to measure metal dispersion and particle size, with the sample scraped off from the cordierite. The powder was pretreated in 10% H_2/Ar at 500 °C for 1 h, then the temperature was lowered to 35 °C in an Ar flow. CO pulses, (1.12×10^{-6} mol) were injected until no CO uptake was observed. The metal dispersion and mean particle sizes were calculated using standard dispersion and particle size calculations [15,16], and specific metal surface areas were taken from references [17,18]. A 1:1 adsorption stoichiometry was assumed and for the bimetallic samples, a weighted average for the metals based on ratio was used for density and weight. Identical Pd and Pt interatomic distances were assumed for simplification, and the resulting dispersions and mean particle sizes are summarized in Table 2. Samples with higher Pd content had higher dispersions/smaller particle sizes, attributed to the thermal stability found with Pd addition to Pt under oxidizing conditions [8,19].

2.2. Catalytic performance test

A monolith catalyst (3/4" diameter and 2" long) was wrapped in insulation to prevent gas bypass and was placed in a quartz tube reactor. Four thermocouples were placed in the reactor to measure the gas temperature ~2 cm upstream of the catalyst, front and back temperatures of the monolith core, and the reactor wall at the catalyst inlet. The data are plotted versus inlet gas temperature. The gas mixture used for the "complex" feed contained 5500 ppm CO, 150 ppm C_2H_4, 150 ppm C_2H_6, 260 ppm C_6H_{14} and 50 ppm C_7H_8, 30 ppm NO, 10% O_2, 5% CO_2, and 5% H_2O in a N_2 balance. Similar experiments, but with respect to a single reactant (CO or hydrocarbon) were also performed to compare the catalytic oxidation activity of the individual components to its oxidation in the more complex mixture. The reactor space velocity of both full mixture and simple feed conditions was 50,000 h^{-1}. Water and liquid hydrocarbons, C_6H_{14} and C_7H_8, were vaporized and introduced into the reactor using Bronkhorst CEM liquid delivery systems. The reactor effluent concentrations were monitored using a MKS MultiGas 2030 FTIR analyzer. A pretreatment was used prior to each test, with a feed containing 14% O_2, 5% H_2O and N_2 balance at 600 °C for 1 h.

Table 2
Dispersion and particle size.

Sample	Dispersion (%)	Particle size (nm)
Pt-only	5.8	19.4
3:1 Pt:Pd	15.6	7.2
1:1 Pt:Pd	21.7	5.2
1:3 Pt:Pd	23.5	4.8
Pd-only	26.4	4.3

3. Results and discussion

3.1. Simple feed conditions

Simple feed conditions refer to the experiments where a single pollutant reactant was considered, i.e. CO oxidation, or ethylene oxidation, etc. CO and individual hydrocarbon species oxidation were evaluated as a function of the Pt:Pd ratio. As shown in Fig. 1a, CO oxidation consistently improved with increasing Pd content in the catalyst, ultimately resulting in the best reactivity observed over the monometallic Pd catalyst. This is consistent with previous work that has shown CO oxidation T_{50} (temperature at which 50% conversion is observed) values monotonically decreased with increasing Pd levels [20]. This is also consistent with Pd being less sensitive to CO self-poisoning compared to Pt [21,22]. Moreover, the addition of the smallest amount of Pd had the most significant impact, with the largest change in T_{50} occurring between the monometallic Pt sample and the 3:1 Pt:Pd sample. Note, although there was also a significant difference in particle size between the monometallic Pt samples and the bimetallic samples, the overall performance was not solely due to this parameter, as otherwise light off would have been observed at similar temperatures, which was not the case. Conversion was observed at lower temperature with the addition of Pd.

The opposite trend was observed in C_2H_4 oxidation as a function of Pt:Pd ratio (Fig. 1b), where a higher relative Pt content led to