

New Developments in Diesel Oxidation Catalysts

Tom Paulson, Bethanie Moss, Brandon Todd, Colleen Eckstein, Brent Wise,
Denny Singleton, Svetlana Zemskova and Ron Silver
Caterpillar Inc.

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ABSTRACT

A number of oxidation catalysts have been prepared using different types of advanced support materials such as ceria-zirconia, silica-titania, spinels and perovskites. Active metals such as Pd and Au-Pd were loaded by conventional impregnation techniques and/or deposition-precipitation methods. A liquid hydrocarbon delivery system was designed and implemented for the catalyst test benches in order to simulate the diesel engine exhaust environment. The activity of fresh (no de-greening) catalysts was evaluated with traditional CO and light hydrocarbons (C_2H_4 , C_3H_6) as well as with heavy hydrocarbons such as $C_{10}H_{22}$.

INTRODUCTION

Diesel oxidation catalyst (DOC) is a relatively mature technology and has been used for light and heavy-duty diesel engines since the late 1990s [1]. The first generation of DOCs has also been called "four way" catalysts, with the primary function of decreasing SOF (soluble organic fraction), CO, HC and NO_x [2-4]. Hence, advanced commercial catalysts for diesel vehicles can be composed of (a) oxidation catalyst; (b) HC adsorber (or trap); (c) lean NO_x catalysts. Considering this multi-functionality, the first generations of DOCs were typically Pt formulations on alumina-based supports using Pt loadings as high as 80-100 g/ft³. Rare earth or alkaline earth promoters (La, Ce, Ba, Sr, etc.) were used as well [3]. Zeolite-based hydrocarbon traps also became another standard component in many DOCs [5, 6]. Zeolites are used to enhance the low temperature HC oxidation performance through storage of unburned HCs at low temperatures and release when the temperature is high enough for true catalytic oxidation of hydrocarbons. Some DOCs exhibit a limited NO_x reduction activity (~40%) due to lean NO_x activity of the Pt/ Al_2O_3 system [7]. In applications with high sulfur level diesel fuels, the use of so-called sulfate inhibitors (V_2O_5) or non-sulfating supports (TiO_2 , SiO_2 , ZrO_2) has been proposed [8-9]. Meanwhile, it is known that high Pt loading DOCs generate too much sulfate. Therefore, low (< 5g/ft³) Pt and Pt/Pd DOCs have been developed by Engelhard [10] using alumina-ceria supports that inhibit

sulfate formation and/or exhibit catalytic activity towards the reduction of SOF emissions.

Notable recent developments related to DOCs include: increased HC/CO oxidation activity, soot oxidation activity, and reduced cost (e.g. low PGM (Platinum Group Metal) loadings) [11-14]. This study was focused on three main thrusts: (1) reduction in PGM loading (i.e. cost) while achieving (2) high oxidation of CO and (3) heavy HCs that represent the SOF fraction of particular matter (PM). It should be mentioned that SOF is an important constituent of diesel engine exhaust; meanwhile the majority of research is focused on conversion of light HCs such as C_2 and C_3 . In our first study the most inexpensive, low-loading, Pd catalysts were prepared using various supports and cordierite substrates (1 x 3 inch cores). The oxidation performance was characterized with light (C_2H_4 , C_3H_6) and heavy ($C_{10}H_{22}$) hydrocarbons. In a follow up study, the long term HC/CO performance of the down-selected Pd catalysts will be improved using various strategies such as active metal particles dispersion, alloying, improvement of the sulfur inhibitors, etc.

RESULTS AND DISCUSSION

Table 1 lists the catalysts prepared and tested in this study. Perovskite catalyst powders were provided by Nanox Inc. Commercially available support materials such as alumina MI-200, MI-407, MI-486 (Grace Davison), Ceria-Zirconia (Rhodia) and titania P25 (Degussa) were used for some catalysts, while other supports (alumina-ceria, alumina-zirconia, magnesia-alumina spinels and silica-titania) were prepared in house. Catalyst #1 has a 2%Pt loading (weight % here and after); catalyst #2 contains 1%Pd and was selected as a baseline Pd catalyst. Perovskites #14, #15 contain 1%Pd, perovskites #13, #16 do not have PGM and all other catalysts contain only 0.5% Pd. Catalyst #17 contains 0.5%Pd and 1%Au. Catalysts #1-#16 were calcined in air at 500°C for 2h and catalyst #17 was calcined at 300°C for 1h.

EXPERIMENTAL SET UP – Total surface area (SA), total pore volume (PV) and mean pore diameter (PD)



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measurements for catalyst powders were obtained via N₂ BET analysis and adsorption isotherm using a Micromeritics ASAP 2020.

Table 1. List of the catalysts

ID	Support	Promoters	SA, m ² /g	PV, cm ³ /g	PD, Å
1	alumina MI 200	n/a	250	0.87	139
2	*alumina MI 200	n/a	245	0.91	145
3	silica-titania	n/a	15	0.126	379
4	TiO ₂ P25	n/a	36	0.285	308
5	alumina MI407	15%K, 15%Mg	33	0.235	292
6	alumina MI407	30%Ni, 25%Mg	146	0.578	132
7	alumina MI486	25%CeOx	70	0.37	190
8	alumina MI486	25%ZrO ₂	93	0.492	207
9	CeOx: ZrO ₂ (88:12)	none	73	0.161	88
10	CeOx: ZrO ₂ (53:47)	none	60	0.167	104
11	CeOx: ZrO ₂ (30:60)	10%La	75	0.222	103
12	CeOx: ZrO ₂ (25:75)	none	60	0.282	187
13	LaSrCoOx	n/a	82	0.246	114
14	*LaCeCoOx	n/a	20	0.063	123
15	*LaCeFeOx	n/a	48	0.127	98
16	LaMnCuOx	n/a	13	0.05	155
17	TiO ₂ P25	n/a	57	0.426	285

*Contains 1%Pd

The catalytic performance of the powder samples was measured using a catalyst powder test bench system. The samples were placed in a quartz micro reactor (25mm diameter, coarse quartz frit, 0.2g powder, no inert diluents), heated with a split tube furnace using a temperature ramp 25-300°C. The feed gas composition for all tests was nominally: 65 ppm C₂H₄, 375 ppm CO, 9% O₂, 8% CO₂, 5% H₂O (added via heated saturator with He flow), balance He with a total flow rate of 200sccm. The CO and C₂H₄ conversions were measured using a Haysep D and Mol Sieve 5Å columns on an Agilent 6890 GC with Thermal Conductivity Detectors. The tests for decane (C10) oxidation were performed as following: the C10 saturator was kept at 30°C and He flow was 55 ml/min, 8% O₂, and 7% H₂O with balance He at a total flow rate of 200sccm. C10 oxidation was estimated via CO₂ formation over a catalyst bed at 300°C. CO₂ was measured on a Haysep D column. No CO formation was observed during C10 oxidation. The temperatures for 50% (T50) and 90% (T90) conversion were used as a measure of catalyst activity. Catalyst performance data are shown in Table 2 and Table 3.

Catalyst powders were washcoated in-house using various ceramic 1 x 3 inch core substrates. Cell density, wall thickness and porosity of cordierite substrates type A, B, and C provided by Corning Inc. are listed in Table 4. These substrates were coated with 1%Pd/alumina MI-200 catalyst powder to study the effect of substrate characteristics on catalyst performance. Catalyzed cores were tested on the high flow "Altamira BenchCAT" test

bench provided by Altamira Instruments. Test gases include 100ppm C10 (as C1), 50ppm C₂H₄ (as C1), 100ppm CO, 260ppm NO, 9% O₂, 8% CO₂, 7% H₂O and balance N₂ at 32K hr⁻¹ space velocity. Liquid C10 was delivered into the system using a KDS 200 syringe pump with a Hamilton gastight 10μL syringe. The sample furnace ramped from 120°C to 500°C at a rate of 10°C/min. Heated lines throughout the system maintained the gas temperature at 180°C. The exhaust gases were analyzed using MKS Type MultiGas Analyzer Model 2030.

CATALYST PERFORMANCE – Palladium oxidation catalysts with 40-60g/ft³ were developed previously and are known to be less active for diesel applications than for gasoline [3, 15]. This has been attributed to the difference in chemical composition of gasoline and diesel exhaust HCs. Gasoline HCs have short carbon chains and contain many unsaturated compounds, while diesel HCs are characterized by long carbon chains (C6-C16) with mostly saturated bonds [16-18]. Several studies have shown that catalytic oxidation of heavy HCs proceeds via catalytic cracking over the base metal oxide support and appear to be the dominant HC conversion mechanism [10, 19-21]. HC storage properties of the catalyst can also contribute to the overall HCs conversion mechanism. The CO/HC conversion activities of various catalyst powders prepared in this study are summarized in Table 2.

Table 2. CO and C₂H₄ oxidation activity of the catalyst powders (where noted, >300 indicates that the T50/T90 were above test temperature range of 25-300°C).

ID	CO T50	CO T90	C2H4 T50	C2H4 T90
1	62	91	63	91
2	61	90	182	246
3	190	>300	>300	>300
4	65	96	244	>300
5	137	>300	>300	>300
6	74	131	>300	>300
7	69	115	220	>300
8	150	136	214	>300
9	114	213	>300	>300
10	69	104	215	>300
11	66	95	159	247
12	67	156	156	297
13	164	209	270	>300
14	132	186	286	>300
15	65	96	226	>300
16	189	203	>300	>300
17	90	130	170	240

As mentioned above, the "baseline" catalyst #2 and perovskites #14, #15 contain 1% Pd, perovskites #13, #16 do not have PGM, and all other catalysts contain 0.5% Pd. The goal of this study was to achieve CO/HC