Aging environment and lean redispersion effects on Pd catalysts

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Introduction

An automotive three-way catalyst (TWC) deteriorates as a function of temperature, time and aging environment. While much effort has gone into formulating durable exhaust catalysts, relatively little attention has been paid to controlling the aging environment on the vehicle, and techniques currently in use to protect the catalyst act counter to increasing demands for higher fuel economy (e.g., overfueling to reduce exhaust temperatures). Thus, new engine control methods are needed to minimize the extent of catalyst deactivation and provide a lean environment capable of redispersing the precious metal particles [1].

Materials and Methods

Two Palladium-based model catalysts, 1.5wt% Pd on γ-Al_2O_3 (Pd/Al) and 1.5wt% Pd on $Ce_{0.5}Zr_{0.5}O_2$ (Pd/CZO), were prepared by a Ford OEM supplier. A quartz j-tube was loaded with a bed of 0.3 grams of model catalysts supported between beds of quartz wool. A flow reactor was used to run probe reactions of oxygen storage capacity (OSC) and water gas shift (WGS) through the bed at 1 L/min across a temperature range of 100°C - 400°C upstream of an electron ionization mass spectrometer. The OSC gas feed was 2% CO_2 and argon with 1 minute alternating pulses adding in 2% CO or 1% O_2, each spaced 1 minute apart, with at least five CO pulses collected in fixed temperature steps every 50°C. The WGS gas feed was 2% CO, 2% CO_2, 2.5% H_2O and Argon, with a temperature ramp of 10°C/min. Pd dispersion was measured with H_2 chemisorption. Pd particle size was calculated from XRD line broadening and also imaged with Scanning Transmission Electron Microscopy (STEM). Surface areas were measured by nitrogen adsorption at 77K and calculated by the BET method. Model catalysts were exposed to 10% water and nitrogen carrier gas at 700°C for 16 hours plus either 1% CO/H_2 (rich-only), 0.5% O_2 (lean-only) or a cycling of both (redox) in 10 minute pulses. A lean treatment of air at 700°C for 2 hours was later applied to determine the significance of WGS and OSC activity improvement over the redox aged Pd catalysts. The Pd metal dispersion (D) from XRD or STEM was estimated using the equation D (%) = 111 / d (nm) [2], where the Pd particle size (d) assumes spherical shapes.

Results and Discussion

Table 1 shows that the redox aging method was the most severe of the three modes with the most surface area lost and the lowest Pd dispersion. The redox environment rich-to-lean transitions contributed exothermic reactions over the catalysts that raised the temperature, which likely caused the conditions to be the harsher than rich-only. The lean-only aging Pd dispersion was just slightly deteriorated compared to fresh samples. A 700°C/2h lean treatment applied after redox aging increased the Pd dispersion, as measured by H_2 chemisorption, of both Pd/Al and Pd/CZO samples from undetectable (u/d) to 6% and 4%, respectively. The Pd dispersion determined by XRD line broadening agreed with H_2 chemisorption for the fresh samples and redox aged samples with 700°C/2h lean treatment.

Table 1: Characterization of Fresh and Aged Catalysts (u/d = undetectable)

Sample	Condition	Surface Area [m^2/g]	Pd Dispersion [%]		
Pd/Al	Fresh	209	9%[a]	8%[b]	18%[c]
	Redox 700°C/16h	164	1%[a]	9%[b]	
	+ air 700°C/2h	157	6%[a]	7%[b]	
Pd/CZO	Fresh	91	22%[a]	u/d[b]	
	Lean-only 700°C/16h	49	15%[a]	u/d[b]	
	Rich-only 700°C/16h	41	u/d[a]	9%[b]	
	Redox 700°C/16h	35	u/d[a]	6%[b]	
	+ air 700°C/2h	35	4%[a]	3%[b]	

[a] from H_2 Chemisorption, [b] from XRD Pd peak broadening, [c] from STEM image number-average Pd particle diameter

The generation of CO_2 over the Pd/CZO samples is shown in Figure 1 for the OSC test and in Figure 2 for the WGS test. The trends observed for aging method severity were the same between the WGS and OSC tests and were as follows: redox > rich-only > lean-only. The lean treatment showed a large benefit for the redox aged sample and had comparable results to the lean-only aged sample for both tests. The two samples with the lowest activity in both tests had Pd particles that were undetectable by H_2 chemisorption as shown in Table 1.

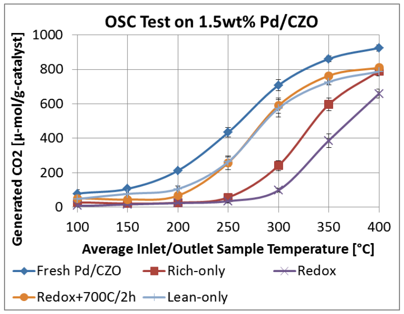

Figure 1: OSC Test on Pd/CZ

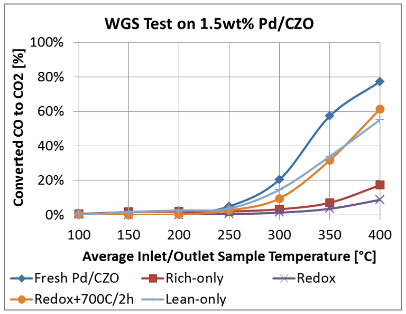

Figure 2: WGS Test on Pd/CZ

Significance

The significance of this research would be to identify the most severe TWC aging modes and conditions for reversing TWC deactivation. The results will assist in developing methods to track (or infer) the aging process on the vehicle and either avoid severe aging modes or actively intervene at various points to preserve or regenerate the catalyst.

References

1. Lieske, H., Völter, J., *Journal of Physical Chemistry* **1985**, 89, 1841-1842
2. Baylet, A., Royer, S., Marécot, P., Tatibouët, J., Duprez, D., *Applied Catalysis B: Environmental* **2008**, 81, 88–96