**Pd-Promoted Catalysts for Low Temperature Diesel Engine DeNox**

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**Introduction**

The US EPA has put in place Tier 2 Bin 5 emission standards of 0.07 g/mi for NOx and 0.01 g/mi for particulate matter (PM) for model year 2007 and later heavy-duty highway engines. This will require the use of advanced emissions aftertreatments, like PM filters, catalyzed NOx trap and urea selective catalytic reduction (SCR) systems on new diesel engines. These technologies are considered to have the highest potential of meeting these standards. However, urea SCR loses conversion efficiency below 200°C, a temperature where there is also formation of undesirable ammonium nitrate. Also, NOx traps are prone to poisoning by sulfur in diesel fuel and engine lubricating oil.

An alternative approach involves the generation of a H2 rich reformate gas on board by in-cylinder reforming of diesel fuel by post combustion injection [1]. Although there have been studies to use such a reformate gas to periodically regenerate NOx trap systems, there has been little investigation of using it for SCR DeNox. This H2 + CO reformate gas offers the potential of high NOx conversions at low exhaust temperatures due to the high reactivity of H2. We will present NOx conversion data obtained from catalysts using H2 + CO as reductant. These catalysts can also be optimized with metal promoters to improve their reactivity over a broader temperature window while decreasing NOx converted to N2O instead of N2.

**Materials and Methods**

The 80% γ-Al2O3:20% TiO2 support was prepared by the method of Lambert et al. [2]. Sol-gel γ-Al2O3 was coated with titanium isopropoxide, followed by hydrolysis. All catalysts were prepared by incipient wetness using metal nitrates to achieve the nominal concentrations listed in Table 1. The support and catalysts were dried at 120°C for 16 h and calcined at 500°C for 6 h. Characterization was done by BET, XRD and SEM/EDX.

The catalysts were tested in a reactor using a thermal ramp from 450°C to 75°C at gas hourly space velocities of 80,000 h⁻¹ to 110,000 h⁻¹, with a feed flow rate of 1000 mL/min [3]. Gas feed components included: O2, 5 vol%; NO, 500 ppmv; H2O, 5 vol% and helium as balance gas. The reductant was a mixture of H2, 3000ppm, and CO, 1000ppm.

**Results and Discussion**

Figure 1 shows NOx conversions as a function of temperature for the Pd catalysts listed in Table 1 and a typical NH3 SCR Fe-Zeolite catalyst using data from reference [4]. The NH3 SCR catalyst displays conversion greater than 90% at temperatures starting at ~275°C but it decreases dramatically below 250°C. The Pd catalysts can achieve ~80-90% NOx conversion between 170°C and 200°C. However, this activity decreases significantly above 220°C. The CO is converted to CO2 by 180°C. Titania is critical for the formation of NCO on Pd. γ-Al2O3 promotes hydrolysis of NCO to ammonia, which then reduces NOx. There is a need to further optimize the catalysts to extend reactivity over a wider temperature range.

**Significance**

Catalysts can be tailored to use on board generated H2 + CO mixture to reduce NOx emissions by ~90% at lower temperature to meet the upcoming vehicle emissions standards.

**Table 1. Nominal Composition (wt%) of the γ-Al2O3-TiO2 (80%:20%) Catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd</th>
<th>Fe</th>
<th>K</th>
<th>Co</th>
<th>Max. NOx Conversion %</th>
<th>Max. NOx conversion Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td>92%</td>
<td>170-200°C</td>
</tr>
<tr>
<td>Pd/Fe</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
<td></td>
<td>80%</td>
<td>190°C</td>
</tr>
<tr>
<td>Pd/K</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td>80-85%</td>
<td>170-200°C</td>
</tr>
<tr>
<td>Pd/Co</td>
<td>0.5</td>
<td></td>
<td></td>
<td>0.5</td>
<td>97%</td>
<td>200°C</td>
</tr>
<tr>
<td>Pd/K/Co</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td>96%</td>
<td>210°C</td>
</tr>
<tr>
<td>Fe-Zeolite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>97%</td>
<td>300°C-450°C</td>
</tr>
</tbody>
</table>

**Figure 1.** NOx conversion with metal-promoted Pd catalysts as a function of temperature.

**References**