200c Dual-Catalyst System for Lean Exhaust Aftertreatment

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Energy production through lean combustion has several benefits, particularly higher efficiencies and lower emission levels out of the engine. Natural gas-fired engines are particularly gaining in popularity for distributed energy and pipeline service applications. However nitrogen oxide reduction from these exhaust streams remains a significant barrier to their more widespread adoption. Three-way catalysts developed for automotive applications are not active for NOx reduction in excess oxygen, and ammonia SCR suffers from additional cost and control barriers. Effective use of hydrocarbon reducing agents, particularly methane, is seen as the ideal solution. The main challenge to this approach is that hydrocarbon combustion is favored over nitric oxide reduction in excess oxygen conditions.

To approach this problem a dual-catalyst NOx reduction system was proposed in which nitric oxide is first oxidized to nitrogen dioxide, a more reducible species that can better compete with oxygen for the hydrocarbon reducing agent. Specific catalysts for the NO oxidation and the NO2 reduction reaction were developed. Cobalt loaded on titania and zirconia supports have been shown to be highly active for the oxidation reaction, while palladium on sulfated zirconia is able to reduce NO2 with methane in high oxygen concentrations. Additionally, the NO2 reduction was shown to give much higher nitrogen yields than the reduction of NO. Initial tests on mixed catalyst beds have shown promising results, exceeding the direct reduction of NO2, and achieving nitrogen yields of above 60%. Reaction testing with a simulated exhaust has also demonstrated that the dual-catalyst system has potential as a complete exhaust aftertreatment system. High conversions in the oxidation of methane, ethane, propane, as well as carbon monoxide have been observed.

Catalysts are prepared through both incipient wetness and sol-gel techniques, with extensive reaction testing performed in a bench-scale flow reactor. Kinetic experiments include extensive testing in simulated lean exhaust conditions. Structural and chemical characterization is performed using BET surface area measurements, in-situ X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis combined with differential scanning calorimetry. Mechanistic studies by temperature programmed desorption (TPD), laser Raman spectroscopy (LRS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) are also presented.