Two-Stage Lean NO$_x$ Reduction with Methane on Pd and Co Catalysts

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Introduction

The increasingly stringent regulations on NOx emissions make it vital to develop materials to address this area. In the last decade a significant amount of research has examined the use of hydrocarbons as reducing agents for NOx emission control. Hydrocarbons, particularly methane, are attractive choices as reductants due to their availability either in combustion exhaust, or through the natural gas infrastructure. Diesel and natural gas engines are the applications that would be most likely to benefit from catalysts that use hydrocarbons as reducing agents. The excess oxygen that gives these engines their high efficiency also poses a challenge due to the combustion of hydrocarbons with oxygen, leading to decreased NOx conversion to N$_2$.

Studies examining a two-stage catalytic system of NOx reduction with methane in lean conditions are presented. In the first stage, NO is oxidized to NO$_2$. Because NO$_2$ is a more easily reduced species than NO, we predicted and observed that the reduction of NO$_2$ gave higher N$_2$ yields than the reduction of NO. This observation is attributed to NO$_2$ being better than NO at competing with oxygen for reaction with the reducing agent. Our studies have examined each of the stages individually, as well as catalyst mixtures for the combined two-stage system.

Materials and Methods

Catalysts have been prepared using incipient wetness impregnation and sol-gel techniques. Cobalt-based catalysts supported on ZrO$_2$ and TiO$_2$ have been studied for the NO oxidation reaction. Reduction stage catalysts are comprised of Pd supported on sulfated-ZrO$_2$ (SZ), which has shown high activity [1,2]. The effects of synthesis techniques and parameters on activity have been investigated. Steady-state activity measurements were recorded between 200-600°C using gas chromatography and chemiluminescent NOx analysis. Typical reactant concentrations were 1000ppm NO or NO$_2$, 3000ppm CH$_4$, 10% O$_2$, (0-10% H$_2$O), in He at 1 atm and 30,000 h^{-1}. Structural and mechanistic characterization was performed using BET surface area measurements, laser Raman spectroscopy (LRS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction and desorption (TPR, TPD), and *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

Results and Discussion

Oxidation catalysts capable of reaching equilibrium conversion of NO to NO$_2$ below 300°C, providing over 90% NO$_2$ yield, in 10% O$_2$ have been developed. These catalysts also showed high activity in the presence of 10% H$_2$O. In the literature Co has been shown to be active for the NO oxidation, with loading being an important factor in observed activity. The most active formulations in this study have been 10% Co/TiO$_2$ and 10% Co/ZrO$_2$. The support is shown to have a significant role in the oxidation reaction, as better performance is obtained over the ZrO$_2$. Characterization by LRS, XPS, XRD, and TPR indicate that the Co$_3$O$_4$ phase can more easily form on ZrO$_2$ than TiO$_2$, leading to higher NO oxidation activity.

Pd-loaded sulfated ZrO$_2$ catalysts have been studied for NOx reduction and showed that higher N$_2$ yields were obtained when NO$_2$, rather than NO, was the NOx species in the feed. Various metal and sulfate loadings, and synthesis parameters were examined. Physical mixtures of oxidation and reduction catalysts were used to reduce NO and showed similar N$_2$ yields as when only the reduction catalyst was used to reduce NO$_2$.
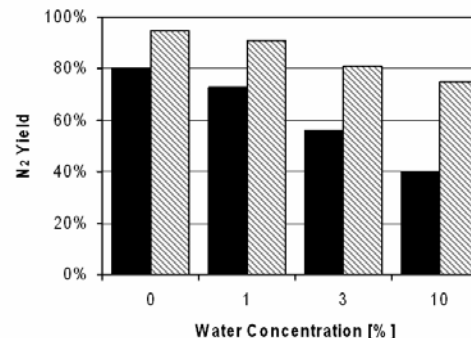

Figure 1. N$_2$ yield at 400°C over mixed catalyst beds with different sulfate loadings. Reaction conditions: 1000ppm NO, 3000ppm CH$_4$, 10% O$_2$, and (0-10% H$_2$O). Catalyst bed composition: 10%Co/ZrO$_2$ and (Left/Black) 0.3%Pd/(5%SO$_4$)-ZrO$_2$, (Right/Shaded) 0.3%Pd/(15%SO$_4$)-ZrO$_2$.

By changing the nominal sulfate loading from 5% to 15% on the Pd/SZ catalysts, we were able to improve the observed N$_2$ yield over a catalyst mixture and significantly enhanced the performance in the presence of water, as shown in Figure 1. Further reaction studies examining the ratio of oxidation to reduction catalysts, the nature of the adsorbed species, and other composition modifications have also been conducted.

Significance

An effective NOx reduction system for lean exhaust would find widespread use in engine and distributed energy systems.

References

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2. Ohtsuka, H., *Appl. Catal. B* 33 (2001) 325.