

Selective Catalytic Reduction of NO_x with Diesel as Reductant

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Introduction

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) under lean conditions using higher alkanes and fuels such as diesel as reductants has been found to be effective over catalytic systems such as silver on alumina [1, 2]. This type of hydrocarbon SCR is of special interest in diesel and lean-burn engines where the use of a foreign onboard storage reductant such as urea is an inconvenient solution.

We have reported the development of bifunctional catalysts based on metal-exchange zeolites coated with metal oxide phases at the nanoscale level [3, 4]. In the case of C₃H₆-SCR, the application of the oxide coating lowers the NO reduction temperature by approximately 100-150°C. These novel materials also show higher activity under wet feeds. It was concluded that the catalyst is able to lower the temperature of oxidation of NO to NO₂, matching it to that of the activation of the light hydrocarbon. Since kerosene fuels activate and coke at relatively low temperatures, it was thought that the coated CeO₂/Cu-ZSM-5 system could be active for diesel SCR. Results of deNO_x studies over this catalyst using middle-distillate fuels as reductants will be presented in this talk.

Materials and Methods

Cerium oxide was added to partially exchanged Cu-ZSM-5 by incipient wetness impregnation of a nanoparticle sol, dried and calcined at 500°C. A microscale plug flow reactor was used to test the catalyst activity. Gas flow rates were controlled to achieve nominal gas concentration of 2-8% O₂ and 1000 ppm NO in balance He at 100 cc/min. The introduction of fuels (gasoline, JP-8, diesel, aromatic liquids) and water (when used) into the feed was controlled through syringe pumps to achieve different fuel penalty levels (2-10%) and a 10% H₂O concentration in the feed. The sample mass was typically 150 mg, diluted up to 2 g using SiC. A clamshell furnace was used to maintain reaction temperatures between 150 and 600 °C. The NO and NO₂ concentrations were monitored on-line with a California

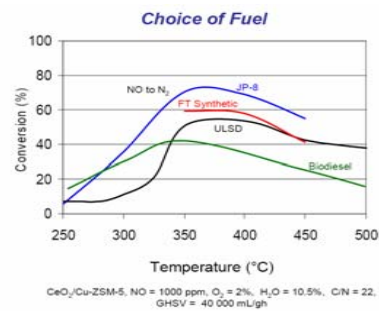


Figure 1. NO to N₂ conversion for CeO₂/Cu-ZSM-5 with various diesel feeds as the reductant.

Analytical Instruments Model 400-HCLD Chemiluminescence NO/NO_x analyzer. An on-line GC was used to analyze the other components of the effluent gas stream such as N₂, O₂, CO, CO₂, N₂O, hydrocarbons and water.

Results and Discussion

The CeO₂/Cu-ZSM-5 system shows significant activity for NO to N₂ conversion when diesel fuels are used as reductants (Figure 1). The unusual enhancement in activity observed in C₃H₆-SCR by the addition of water to the feed is also observed with this type of reductant. Unlike the C₃H₆ system, however, the middle distillate fuels increase the temperature window of activity while exhibiting no NO₂ breakthrough.

In situ XANES shows that a controlling factor in the catalyst is the ratio of Cu²⁺ to Cu¹⁺ (Figure 2). At the optimal temperature (350°C) this ratio is nearly 1. No evidence of Cu⁰ is observed at reaction temperatures as high as 500°C.

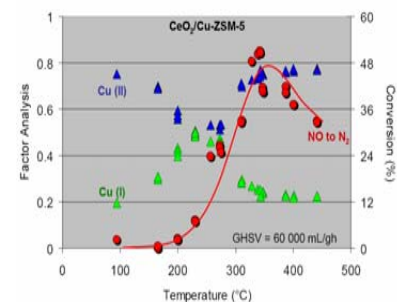


Figure 2 Amount of Cu²⁺ and Cu¹⁺ in the CeO₂/Cu-ZSM-5 catalyst by operando XANES.

Significance

The use of a slip of fuel as reductant for NO_x abatement in diesel and lean-burn engines is an attractive alternative to adding an onboard storage reductant as in the case of NH₃ or light hydrocarbon SCR.

References

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