Bifunctional Catalyst for the Selective Catalytic Reduction of NO by Diesel Fuel

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Introduction

The reduction of nitrogen oxides from diesel emission streams is becoming an increasingly important problem due to pending governmental regulations. The use of selective catalytic reduction (SCR) with hydrocarbons under lean conditions is a promising solution, and can typically be performed over a wide range of catalysts with Cu-exchanged ZSM-5 being a strong candidate [1]. Cu-ZSM-5, however, does not perform well in the presence of water, which is ubiquitous in any exhaust stream. Recent studies have shown that the physical combinations of metal oxides and metal-exchanged zeolites have comparable or improved performance under wet conditions compared with that of Cu-ZSM-5 [2,3]. We have developed a new ceria coated Cu-ZSM-5 catalyst (CeO_2/Cu-ZSM-5) which shows high hydrothermal stability along with high activity and selectivity for converting NO to N_2 using hydrocarbons as the reductant [4-6].

Materials and Methods

Catalysts were synthesized using standard ion exchange methods for the metals addition, and the impregnation of nanoparticle sols (Nyacol) for the addition of metal oxides. The resulting materials show that the sol remains in nanoparticle form and is dispersed across the surface of the zeolite. Variations in addition order and catalyst preparation can be used to further alter the surface functionality.

SCR testing was performed using a standard plug-flow reactor with 1000 ppm NO, 1000 ppm of either C_3H_6 or diesel fuel, 2-10 vol% O_2, 10 vol% H_2O at a space velocity of 30,000 hr^{-1}.

Engine tests run by Integrated Fuels Technology were done on a John Deere model 4045 diesel engine running a constant speed. The catalyst was coated on to a standard cordierite monolith (8-14 wt %) and then mounted downstream of a diesel particulate filter.

Results and Discussion

There is strong evidence for interaction between the metal and the metal oxide phase, as observed by additional ex situ and in situ spectroscopy techniques; both the metal and metal oxide show additional reduction peaks at temperatures much lower than observed for the individual materials themselves, suggesting the formation of a mixed-metal oxide phase on the catalyst.

Activity and selectivity for the CeO_2/Cu-ZSM-5 in bench scale tests are shown in Table 1. The catalyst not only exhibits high deNOx activity, but its selectivity to CO and HC's is very low as compared to the uncoated material.

Two improvements in NOx reduction activity were seen for these catalysts compared with Cu-ZSM-5: a lower temperature of maximum NOx conversion activity (as low at 250°C), and an enhancement of activity when water was present in the system. The use the CeO_2 coating provides a way to further tune the properties of the catalyst in order to achieve mechanistic conditions necessary to maximize NOx remediation. Figure 1 shows the activity of the catalyst using a variety of diesel fuels as the reductant including FT diesel, ultralow sulfur diesel, and biodiesel is optimal at 350°C.

Table 1 – deNOx activity with and without CeO2 coating at 300°C

	Cu-ZSM-5	Coated CeO_2/Cu-ZSM-5
NO Conversion	17.6%	64.2%
NO_2 & N_2O Selectivity	3.8% (11 ppm)	0.1% (14 ppm)
CO Selectivity	11.0% (120 ppm)	0.0% (67 ppm)
C_3H_6 Slippage	51.7% (517 ppm)	0.1% (1.4 ppm)

The catalyst was coated on to a series of ceramic monolithic supports and tested for the reduction of diesel emissions. The catalyst demonstrated a constant 60% conversion with excursions to 90%. The fuel penalty was less than 1 % of total feed. Hydrocarbon and CO emissions were comparable to those for the bench scale tests (<10 ppm of each). Accelerated aging tests show that the catalyst retains most of its activity (>65%) over 450,000 miles of operation.

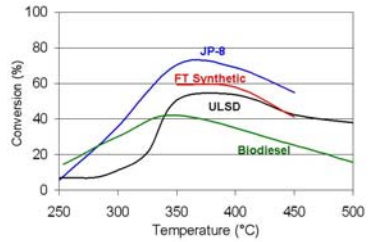

Figure 1 – Conversion efficiency of CeO_2 coated ZSM-5 using various diesel feedstocks as reductants.

Significance

This catalyst will be the first of its type to reach commercial development. If successful it could eliminate the need of additional tankage as required by urea based systems.

References

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