

Selective Catalytic Reduction of Diesel Engine NO_x Emissions with NH₃/Urea

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Introduction

The selective catalytic reduction (SCR) of NO_x with NH₃, widely being employed for the removal of NO_x emissions from stationary sources, has recently attracted considerable attention for controlling NO_x emissions from automotive diesel engines. For its application to mobile source, urea may be a convenient NH₃ carrier to resolve NH₃ handling problem for the SCR technology [1-3]. In the present study, a variety of SCR catalysts have been screened for the NH₃-SCR reaction over the wide range of reaction temperatures from 150 to 500 °C as part of the development of an effective urea-SCR catalytic system for the removal of NO_x emissions from automotive diesel engines. The NO conversion activity, stability and NH₃ slip of the candidate catalysts have been investigated under a variety of reactor operating conditions. In addition, the deNO_x performance of the developed catalyst has been also examined with urea as a reductant.

Results and Discussion

A number of SCR catalysts including V₂O₅/TiO₂, V₂O₅-WO₃/TiO₂, Pt/Al₂O₃, CrO_x/TiO₂, MnO_x/TiO₂, and metal ion-exchanged zeolite-based catalysts (e.g., ZSM5, Y, Mordenite, USY and Ferrierite) have been prepared and evaluated in a fixed bed flow reactor system for NH₃-SCR. Among the catalysts, the ZSM5-based catalyst revealed the highest performance of NO removal activity, particularly at reaction temperatures below 250 °C. The catalyst exhibited NO conversion higher than 60% at 150 °C and 100,000 h⁻¹ as well as a wide operating temperature window from 200 to 400 °C over which NO conversion higher than 90% is maintained. V₂O₅/TiO₂ and V₂O₅-WO₃/TiO₂ also showed NO conversion higher than 90% at reaction temperatures above 250 °C, but much lower activity at reaction temperatures below 250 °C compared to the ZSM5 catalyst. Pt/Al₂O₃ revealed high performance of NO removal within the temperature range from 150 to 230 °C. However, NO conversion rapidly falls as the reaction temperature increases further, mainly due to the catalytic oxidation of NH₃ to NO and/or N₂. Contrary to some of the literature claims [4,5], MnO_x/TiO₂ and CrO_x/TiO₂ exhibited relatively low activity at the reaction temperatures covered in the present study with the maximum NO conversions of 93 and 70 % at around 300 °C, respectively. Although Y-type zeolite showed competitive deNO_x activity to ZSM5 at reaction temperatures below 150 °C, its activity still remained lower than that of ZSM5 in the temperature range from 160 to

230 °C. None of the catalysts prepared in the present study reveals better deNO_x performance overall than the ZSM5 catalyst.

The dependence of NO conversion and NH₃ slip of the ZSM5 catalyst on the feed ratio of NH₃/NO varying from 0.8 to 1.0 to the reactor has been examined. The trade-off between NO removal activity and NH₃ slip of the SCR process should be considered in optimizing the appropriate reactor operating conditions to achieve the high deNO_x performance. The effect of reactor space velocity on the NO conversion of the ZSM5 catalyst has also been examined as a strategy of enhancing the low-temperature activity of the ZSM5 catalyst. The increase in the residence time of the feed gas stream through the reactor (or decrease in space velocity) significantly improves NO conversion particularly at low reaction temperatures below 200 °C. At the reaction temperature of 150 °C, the NO conversion of the ZSM5 catalyst increases from 53 % at a space velocity of 100,000 h⁻¹ to 70% at 60,000 h⁻¹ and up to 95% at 30,000 h⁻¹. This suggests that the NO removal activity of the ZSM5 catalyst (especially at low temperatures) can be improved significantly by increasing the reactor size.

The hydrothermal stability of the ZSM5 catalyst has also been investigated. After aging in a reactive mixture (in the presence of 10% H₂O) at 600 °C for 12 h., early-generation ZSM5 catalysts lost about 20% of its fresh NO conversion, particularly at low temperature region from 150 to 200 °C although it still maintained NO conversion higher than 90% from 200 to 300 °C. In contrast, the ZSM5 catalyst optimized in the present study reveals relatively stable NO removal activity after the aging. This is probably due to the distinct state of the metal present on the surface of the optimized ZSM5 catalyst. The activity loss of the aged ZSM5 catalyst is mainly due to the phase transformation of the metal from the ionic state to the oxides during the aging process, as identified by XRD, NMR and XANES.

The deNO_x performance of the ZSM5 catalyst by urea-SCR has been examined in a fixed bed reactor system which is located downstream of a separate reactor for the thermal decomposition of urea. SCR of NO over the ZSM5 catalyst using urea as a reducing agent is quite competitive with its NH₃-SCR performance over the wide operating temperature window from 150 to 450 °C. This strongly suggests that urea can be selectively and effectively decomposed into NH₃ in the present reaction system and can be regarded as an effective reducing agent for the SCR reaction. In conclusion, urea-SCR catalytic systems containing metal ion-exchanged ZSM5 catalysts are promising for the removal of NO_x emissions from automotive diesel engines.

References

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