Hydrothermal Stability of Fe/Zeolite SCR Catalyst for NOx Reduction of Diesel Engine Exhaust Gas

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Introduction

Selective Catalytic Reduction (SCR) of NOx technology is considered as one of the leading candidates for meeting 2010 EPA diesel exhaust emissions regulations [**1**, **2**]. Zeolite-based catalysts, in particular the iron- and copper-exchanged ones, are among the primary candidates for diesel engine applications of the Urea-SCR technology. However, all zeolite-based catalysts are inherently prone to degradation when exposed to high temperatures in the presence of water vapor, via the process called de-alumination, whereby the Al^{+3} ion in the SiO_2-Al_2O_3 tetrahedral framework migrates out of the structure. This leads to irreversible deactivation and, in extreme cases, collapse of the crystalline structure. Therefore, hydrothermal stability of the SCR catalyst at the temperatures experienced in the normal engine operation and during active regeneration of Diesel Particulate Filters is one of the vital factors for the SCR catalyst selection and application.

In this study, hydrothermal stability of Fe-exchanged zeolite catalysts was explored using pilot reactor, with the focus on the following areas: 1) Effects of reaction temperature, space velocity, and NO_2/NOx ratios on SCR performances; 2) Effects of hydrothermal aging on catalyst functions including SCR activity, isothermal NH_3 storage, the product distribution of SCR reaction, NH_3 oxidation by O_2, and NO oxidation to NO_2; 3) Thermal aging (without steam) effects on SCR performance. Finally, Fe/zeolite catalyst degradation was correlated to ammonia storage degradation as well as the degradation of NH_3 and NO oxidation by oxygen due to hydrothermal aging.

Materials and Methods

A commercially available Fe-ZSM5 SCR catalyst was used as a model catalyst for this study. The Fe-zeolite powder was coated on a cordierite honeycomb with a cell density of 400 cpsi. For the catalytic investigation, the cordierite monolith was cut into cores of the size 2.5 cm (in diameter) x 7.6 cm (in length) fitting to the sample holder of the tube reactor. The gas hourly space velocity (GHSV) was 40,000 hr^{-1}. For tests of the standard SCR reaction, the composition of diesel exhaust gas was simulated by a gas mixture containing 10% O_2, 8% CO_2, 6.5%H_2O, 200 ppm of NOx and balance N_2. Ammonia to NOx ratio (ANR) was 1 in this study. Catalytic NH_3 and NO oxidation by O_2 was conducted under the same reaction conditions as SCR reaction using the same gas mixture but no NO for NH_3 oxidation and no NH_3 for NO oxidation. The thermal and hydrothermal stability of the Fe/zeolite catalyst coated on cordierite was tested by ageing at 700 ^{0}C in the presence of 20% oxygen in nitrogen for 50 h (thermal aging) and by ageing at 700 ^{0}C in 10% water and 20% oxygen in nitrogen for 10 to 50 hrs (hydrothermal aging), respectively. The ammonia adsorption capacities of the fresh, the aged catalysts were measured at different temperatures between 200 and 400 ^{0}C by combination of physical desorption and NO titration of pre-adsorbed ammonia according to the literature [**3**]: 1) catalyst was adsorbed using a nitrogen gas flow containing 10% O_2, 8% CO_2, 6.5 % H_2O and 200 ppm of NH_3, at a given temperature until the saturated ammonia adsorption on catalyst was reached; 2) subsequently, the chemically accessible ammonia was removed by stopping the ammonia dosage, and meanwhile, dosing 10% O_2, 8% CO_2, 6.5% H_2O and 200 ppm of NO at the same temperature until the NO consumption ceased. The physically desorbed ammonia was measured in parallel. GHSV is kept at 40,000 hr^{-1}. Oxygen and water were necessary in order to obtain realistic ammonia storage capacities for diesel exhaust gas conditions. The concentrations of NO, NO_2, N_2O, NH_3 and H_2O in the gas phase were measured by a MKS's FT-IR (2030 MultiGas Analyzer).

Results and Discussion

Our test results indicate that hydrothermal aging at high temperature has a significant effect on the performance of Fe-exchanged zeolite SCR catalyst including ammonia storage, ammonia oxidation by O_2, NH_3-SCR reactions, which all are thought to be related to BrØnsted acid sites. More remarkable effects can be observed at low reaction temperatures, in particular at around 250 ^{0}C. Lower NO_2/NO ratio, greater loss in NOx reduction efficiency. In particular, our results showed a good agreement between ammonia oxidation by O_2 and SCR performance degradations, implying that hydrothermal aging leads to the loss of active sites (BrØnsted acid sites) for NH_3 molecule activation. In addition, it was also observed that there was no significant difference in NO oxidation by O_2 between un-aged and aged catalyst. Zeolite dealumation is a major contributor to Fe-zeolite catalyst deactivation. Finally, no thermal aging impact on SCR performance was observed on the studied catalyst in our tests.

Significance

This study is of importance for NOx reduction of diesel engine exhaust gas.

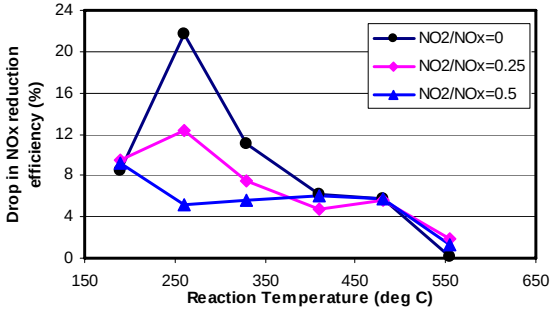

Figure 1. Drop in NOx reduction efficiency due to hydrothermal aging at 700 ^{0}C for 50 hrs.

References

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