NO_x performance of Cu-chabazite SCR catalysts under severe sulfur poisoning from marine diesel engine's fuels

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Introduction

In the last few years Cu-zeolite SCR catalysts have become the catalysts of choice for NO_x abatement in automotive diesel engines due to their durability and high NO_x performance across a large temperature range. More recently, small-pore zeolite Cu-chabazite SCR catalysts have been investigated and show significant promise as the new leading candidate among zeolite formulations. Cu-chabazite exhibits high NH_3 SCR activity in the temperature range from 150-600°C, and shows excellent selectivity towards N_2 when compared with medium-pore zeolite formulations such as Cu-ZSM-5 and Cu-beta [1, 2]. In addition, Cu-chabazite has shown excellent resistance to hydrothermal aging at temperatures up to 850°C, where NO_x performance remains unaffected at evaluation temperatures below 500°C [3, 4]. However, the possible use of Cu-chabazite for NO_x abatement in marine applications poses a unique challenge due to the large sulfur content in the fuel used in marine engines. While automotive ultra-low sulfur diesel (ULSD) fuel typically contains less than 15 ppm sulfur, the current standards for marine diesel fuel allow as much as 3.5% sulfur content by mass in the fuel, which could lead to a concentration in excess of 500 ppm of sulfur in the exhaust gases [5]. Such large concentrations of sulfur could have adverse effects on the NO_x performance and the durability of the Cu-chabazite SCR catalysts.

Materials and Methods

Fresh Cu-chabazite SCR cores of 1-inch diameter and 3-inch length were poisoned using a bench flow reactor (BFR). To simulate the high concentration of sulfur in marine diesel fuel, sulfur poisoning was carried out at 250 and 400°C with the simulated exhaust gases consisting of 500 ppm SO_2, 14% O_2, 5% CO_2, 5% H_2O, and N_2 balance for two hours at a GHSV of 30,000 h^{-1}. The NO_x performance of the fresh and poisoned catalysts were then evaluated at the same GHSV in the temperature range from 150-500°C using a simulated exhaust flow containing 350 ppm NO_x, 350 ppm NH_3, 14% O_2, 5% CO_2, 5% H_2O, and N_2 balance. Following evaluations, the poisoned catalysts were desulfated under lean conditions. The catalysts poisoned at 250°C were desulfated under three different conditions: 30 minutes at 350°C, 10 minutes at 500°C, and 30 minutes at 500°C. Meanwhile, the catalyst poisoned at 400°C was only desulfated once for 30 minutes at 600°C. Performance evaluations were then repeated after desulfation for each catalyst. Materials characterization techniques including electron microprobe analysis (EPMA) and diffuse reflective infrared Fourier transform spectroscopy (DRIFTS) were also performed on the fresh, poisoned, and desulfated catalysts.

Results and Discussion

Figure 1 shows the results of standard and fast SCR performance evaluations on a fresh Cu-chabazite, along with performance of a sulfur-poisoned catalyst at 250°C and later desulfated at 500°C. At temperatures below 250°C the NO_x performance of the poisoned catalyst is severely degraded by as much as 70% when compared to the fresh sample; however, at temperatures above 300°C the NO_x performance of the poisoned catalyst appears to be unaffected (not shown), largely because of desulfation at those temperatures. After desulfation at 500°C for 30 minutes, the NO_x performance of the poisoned catalyst is completely recovered. Similar to the standard SCR performance, the fast SCR performance of poisoned catalyst is significantly impacted at temperatures below 250°C with reduction in performance as high as 50%. However, less desulfation time is required to fully recover fast SCR performance; i.e., 10 minutes at 500°C.

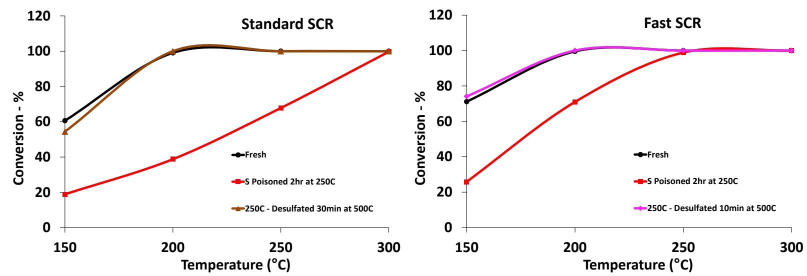

Figure 1. (a) Standard and (b) fast SCR performance of fresh, sulfur-poisoned, and desulfated Cu-chabazite SCR catalysts.

Significance

Under severe sulfur poisoning the NO_x performance of Cu-chabazite catalysts is strongly affected at temperatures below 300°C; however the NO_x performance of the sulfur-poisoned catalysts is completely recovered after being subjected to desulfation at temperatures as low as 500°C. Thus, Cu-chabazite catalysts appear to be the most effective catalysts for NO_x abatement in marine diesel engines.

References

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