

Deactivation of Cu/Zeolite SCR Catalyst Due To Reductive Hydrothermal Aging

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ABSTRACT

Temperature programmed reduction by CO, H₂, and propylene (C₃H₆), as well as hydrothermal aging in the presence of mixture of NO, HC, CO, H₂ and O₂ were used to study the deactivation of Cu/zeolite SCR catalysts. The presence of CO had no detrimental effect on catalyst activity. Carbonaceous deposit on the catalyst surface from propylene (C₃H₆) reduction suppressed the catalyst activity and burn off of carbonaceous deposit recovered activity, the presence of O₂ suppressed carbonaceous deposit formation. The presence of H₂ under lean conditions had much less effect on catalyst activity than H₂ presence under rich conditions. Rich conditions with O₂ presence represented the most detrimental effect on catalyst activity.

INTRODUCTION

Diesel powered vehicles have a bright future since the diesel engine provides higher fuel efficiency than gasoline powered vehicles. However, diesel engine exhaust streams have to meet future stringent emission regulations, which are especially challenging for nitrogen oxides (NO_x) and particulate matter (PM). Selective catalytic reduction (SCR) of NO_x with aqueous urea is considered as one of the primary approaches for NO_x removal. Diesel particulate filters (DPFs) have been used for PM control. For urea SCR, aqueous urea is injected into the exhaust stream. It undergoes vaporization and hydrolysis to form ammonia for NO_x reduction. For PM removal, a loaded particulate filter needs to be regenerated when it has a high soot loading. Different system configurations containing SCR and DPF for diesel exhaust aftertreatment have been reported. One system that contains a DOC (diesel oxidation catalyst), urea SCR, and DPF has been described (1-3). Another system containing the same catalyst devices, but having the DPF in front of the SCR (DOC-DPF-SCR) is also reported (4, 5). In addition, a combined SCR-DPF single brick system has been disclosed (6, 7). With the single brick system, some of the packaging constraints are relieved and the system is simplified.

Under normal operating conditions, a diesel engine exhaust stream contains high levels of O₂ (lean

conditions). However, there are several situations when O₂ can be low and even depleted, resulting in rich gas conditions. For example, hydrocarbons adsorbed on a catalyst during idling are released during hard accelerations. If the released hydrocarbons are ignited, O₂ is consumed, resulting in low O₂ levels in the gas stream or even rich conditions. This can change the chemistry of the catalyst and cause catalyst deactivation. During the DPF regeneration process, soot combustion results in O₂ depletion and a high exotherm which can potentially cause deactivation of a downstream SCR catalyst or SCR coating on a DPF. In addition, there can also be a small amount of hydrogen in the exhaust stream. Under typical lean conditions CO/H₂ ratio in the diesel engine exhaust stream is 40/1, much lower than the ratio of 3/1 in typical gasoline exhaust. However, under rich conditions, besides hydrocarbons (HC) and carbon monoxide (CO), hydrogen (H₂) is a main reducing agent in engine exhaust stream.

In the present paper, the performance of a typical Cu/zeolite SCR catalyst designed for light-duty vehicle use is studied after aging under reducing conditions. The reducing agents include propylene (C₃H₆), CO, H₂, and their mixtures. The impacts of O₂ and H₂ concentrations are studied. The results elucidate the impacts of various reducing aging conditions on Cu/zeolite SCR catalyst durability.

EXPERIMENTS

1" diameter by 1" long cores were taken from a Cu/zeolite catalyst monolith. The catalyst was fully-formulated and designed for diesel vehicle use by a major catalyst supplier. The cores were aged and tested in a quartz flow reactor. The total flow for aging and testing was 6.44L/min, corresponding to a space velocity of 30,000 hr⁻¹. Temperature was measured at the point of about 3/8" away from the inlet face of the catalyst.

Catalyst degreening was carried out in the flow stream of 5% CO₂, 4.5% H₂O, 14% O₂, and balance N₂ at 650°C for one hour. Hydrothermal aging of catalyst was carried out in the flow of 5% CO₂, 4.5% H₂O, 14% O₂, and balance N₂ at 650°C for 16 hours.

To study the impact of CO and hydrocarbon, catalysts were aged in the reduction gas stream. The temperature was ramped up at 5°C/min to 650°C, held at 650°C for one hour, followed by natural cooling. The reduction gas stream contained 5% CO₂, 4.5% H₂O, balance N₂, and either 3000ppm CO or 1000ppm C₃H₆ respectively.

To study the impact of O₂ level, catalysts were aged in different reductive gas streams at 650°C for 16 hours. The temperature was ramped up at 5°C/min to 650°C, held at 650°C for 16 hours, followed by natural cooling. The gas stream contained 5% CO₂, 4.5% H₂O and specified level of O₂. Reducing agents were added during the time period of 16 hours at 650°C. The reductive gas stream contained 5% CO₂, 4.5% H₂O, 350ppm NO, 1000ppm C₃H₆, 2% CO and O₂, at levels 0, 1% and 3%.

To study the impact of H₂, catalysts were aged in reducing gas streams containing hydrogen. The temperature was ramped up at 5°C/min to 650°C, held at 650°C for 16 hours, followed by natural cooling. The gas stream contained 5% CO₂, 4.5% H₂O and a specified level of O₂. Reducing agents were added during the time period of 16 hours at 650°C. The reductive gas stream contained 5% CO₂, 4.5% H₂O, 350ppm NO, 1000ppm C₃H₆, 2% CO, H₂ and O₂. Two O₂ levels, i.e. 1% and 3% were studied. At each O₂ level, three H₂ levels, i.e. 0, 500ppm and 0.67% were included. 1% O₂ is equivalent to a rich condition of $\lambda=0.98$. 3% O₂ is equivalent to a lean condition of $\lambda=1.1$.

After aging, all catalysts were evaluated for steady state activities. The testing gas stream contained 350ppm NO, 350ppm NH₃, 5% CO₂, 4.5% H₂O, and balance N₂. The testing was performed from low temperature to high temperature (up to 600°C). After the first test (Run1), the catalyst was cooled down in a gas flow with 14% O₂. Then, the activity testing was repeated and called Run2. No special cleaning procedure was used between two runs.

RESULTS AND DISCUSSIONS

1. Impact of CO reduction on catalyst deactivation

Figure 1 shows the activities of a degreened catalyst, catalyst as-reduced by 3000ppm CO at 650°C for 1 hour (Run1) and the repeat steady state testing (Run2). The results show that CO as-reduced catalyst had comparable activity to the degreened catalyst. The consecutive repeat testing shows no apparent activity change.

Reduction of Cu/ZSM5 catalyst by CO at high temperature has been reported in literature (8, 9). Though Cu²⁺ can be reduced to Cu¹⁺ by CO in inert atmosphere, Cu¹⁺ is readily oxidized into Cu²⁺ once O₂ is available. This process is reversible and it has no negative impact on Cu²⁺ dispersion. As a result, CO reduction has no impact on catalyst deactivation.

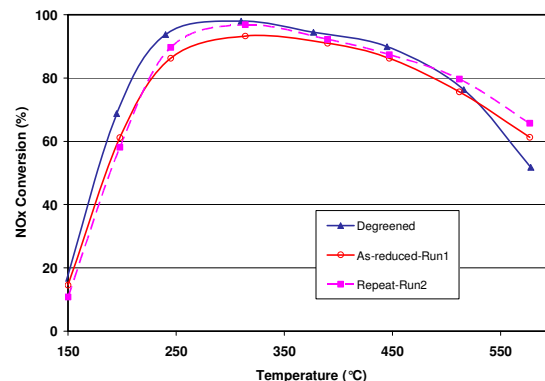


Fig. 1. SCR activities of fresh catalyst and catalyst reduced by 3000ppm CO

2. Catalyst deactivation due to carbonaceous coke formation

Figure 2 shows the catalytic activities of the degreened catalyst and catalyst reduced by 1000ppm C₃H₆ at 650°C for 1 hour. The as-reduced catalyst sample was dark in color and had lower activity than the degreened catalyst (Run1). After Run1 test, the color of the catalyst became lighter and turned to grey. As shown in Figure 2, the second run (Run2) catalyst activity was almost identical to the degreened catalyst.

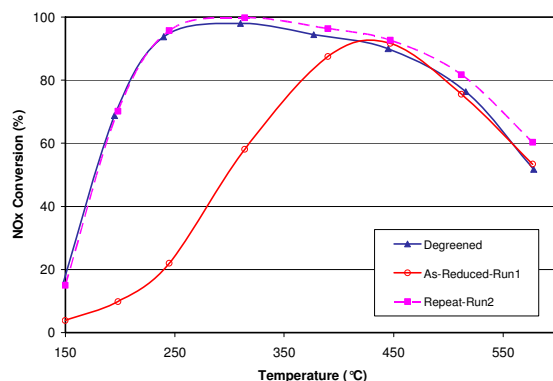


Fig. 2. SCR activities of fresh catalyst and catalyst reduced by 1000ppm C₃H₆

The results indicated that the reduction of Cu/zeolite catalyst by C₃H₆ results in the formation of carbonaceous coke formation on the catalyst surface. The surface carbonaceous deposit blocked the active sites and suppresses the catalyst activity. These results were consistent with literature report (10). During the Run1 activity testing, 14% O₂ was present and the highest temperature was up to 600°C. As a result, the carbonaceous deposit was burned off and activity was recovered. Therefore, the catalyst deactivation due to carbonaceous coke formation is recoverable once the deposit is burned off.

3. Impact of O₂ presence on catalyst deactivation

Catalysts were aged under reaction conditions in the presence of NO, C₃H₆, CO and O₂. Without the presence