

Ammonia mediated NO_x SCR and soot oxidation integration for next generation SCR-on-Filter application

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Abstract

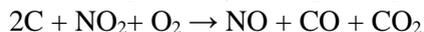
The improvement of soot oxidation performance was investigated for SCR_{oF} applications. The concurrent presence of NO_x SCR reactions significantly inhibited the NO₂ assisted soot oxidation and the main oxidant that could be used was O₂. Complex interaction was observed between the soot oxidation and the SCR reaction. Integrated soot oxidation and NO_x SCR was achieved by mixing different SCR and tailor made soot oxidation catalyst. Most importantly the reductant (NH₃) oxidation has to be prevented on the soot oxidation catalyst as its oxidation prevent the SCR reaction from occurring. For this reason the soot oxidation catalyst was tailored by selectively poisoning the acid sites with potassium which prevented ammonia oxidation. By physically mixing the soot oxidation catalyst and SCR catalyst (in this case Cu and Fe zeolites) comparable or improved NO_x reduction performance could be observed while simultaneously the soot oxidation temperature was lowered by more than 150 °C.

1. Introduction

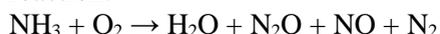
The highly toxic emissions from diesel engines resulted in progressive and ever more stringent regulations to be implemented. The most regulated species are the NO_x and particulate matter (soot) and these require complex and expensive multistage aftertreatment systems. NO_x is difficult to remove due to the net oxidizing conditions in the diesel exhaust, while soot due to the high temperature (>500 °C) required for its combustion. One method to reduce cost and improve performance is to integrate the selective catalytic reduction (SCR) of NO_x and the diesel particulate filter (DPF) on the same device, the so-called SCR on filter (SCR_{oF}). The SCR_{oF} has been well established in practice (BASF has well established commercial system), most commonly zeolite-based Cu chabazite is used as the SCR catalyst, deposited inside the pores of SiC based filter. The disadvantage of the SCR_{oF} system is the inhibition of the soot oxidation by the SCR reaction which consumes the NO₂ [1–4]. This can be represented by the following reaction set where NO₂ is the key reactant:



Fast SCR

NO₂ assisted soot oxidation

For this reason passive regeneration is inhibited and particulate matter accumulates on the SCRof and this results in higher pressure drop and reduced efficiency. To regenerate the SCRof, periodically fuel is injected to raise the temperature (> 600 °C) and burn off the accumulated soot. These harsh conditions consume additional fuel and can easily damage and reduce the lifetime of the filter. The aim of our work was to reduce the regeneration temperature so that the regeneration temperature can be lowered or even brought in the range of working exhaust temperature. This was achieved by physically mixing the SCR catalyst and the soot oxidation catalyst in different ratios. The challenge was to find a soot oxidation catalyst that is compatible with the SCR reactions, i.e. it is oxidative towards soot however not oxidative towards ammonia which is a key reductant in the SCR reaction:



Non-selective ammonia oxidation

2. Materials and methods

Ion exchanged Cu and Fe ZSM5 were used as SCR catalysts. In a typical synthesis the zeolite was added to a 50 mM solution of Cu(II) acetate and Fe(III) nitrate, stirred overnight after which it was washed, dried and calcined.

CeO₂-PrO₂ catalyst was prepared by hydrothermal method, described in detail in [5]. After calcination the catalyst was impregnated by wet impregnation with potassium carbonate so that the final K loading was 1 % wt.

The catalytic tests were conducted in glass tube reactor heated by vertical furnace in the temperature range 200-600 °C with 2 °C/min heating rate. The SCR and soot oxidation catalysts were mixed in different ratios, however the total mass was always 270 mg. The soot was mixed with the catalyst in mass ratio 1:9 with spatula to obtain loose contact. The total gas flowrate was in all cases 600 ml/min with the concentrations 500 ppm NO_x (with NO₂/NO_x = 0 for standard SCR and 0.5 for fast SCR), NH₃, 4% O₂ and balance N₂.

3. Results and discussion

First the inhibiting effect of the NO_x SCR on soot oxidation was demonstrated. The Cu and Fe-ZSM5 had no effect on soot oxidation with O₂, and the oxidation profile was the same as the non-catalytic one on SiC. When NO_x (with NO₂/NO_x = 0.5) was added to the reaction mixture the soot oxidation initiated at 300 °C as NO₂ is a stronger oxidant than O₂. This improvement was lost however once NH₃ was also added and SCR occurred. The NO₂ was consumed by the kinetically much faster Fast SCR reaction leaving none for soot oxidation. This has a strong implication for the development of the soot oxidation catalyst as the main available oxidant would be O₂.

As can be seen from the reaction system, the non-selective ammonia oxidation has to be avoided as in that case less is available for the NO_x SCR and the fuel penalty

increases. The activation of ammonia on the soot oxidation catalyst was achieved by selectively poisoning the acid sites with small amounts of potassium. By adding small amount of potassium the oxidation of NH_3 was delayed by more than 150 °C compared to the unmodified catalyst (see Figure 2). The deactivation of ammonia adsorption was confirmed by ammonia adsorption/desorption where no adsorption occurred.

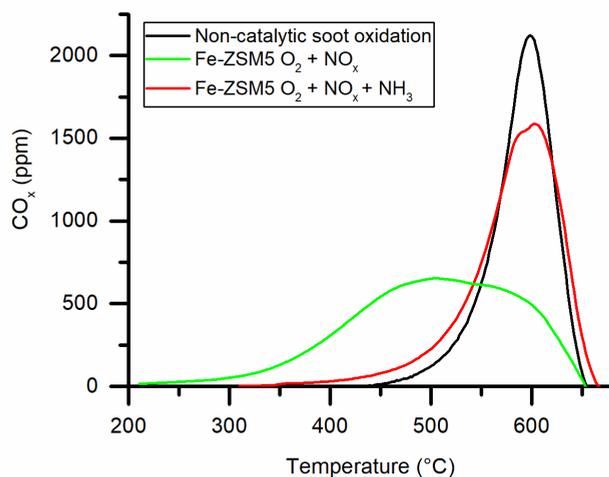


Figure 1. Influence of NO_x and $\text{NO}_x + \text{NH}_3$ on soot oxidation. Reaction conditions: 270 mg of catalyst mixed with 30 mg of soot, total flowrate of 600 ml/min of 500 ppm NH_3 and NO_x (when used), 4% O_2 in N_2 . Heating rate 2 °C/min

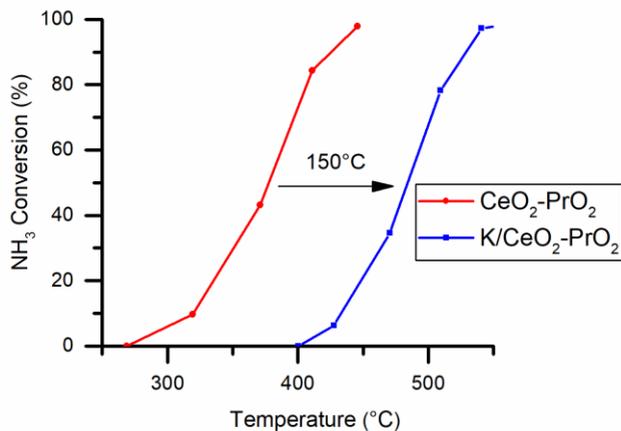


Figure 2. Influence of potassium on the ammonia oxidation deactivation. Reaction conditions: 270 mg of catalyst, 600 ml/min flowrate of 500 ppm NH_3 and 4% O_2 in N_2

On Figure 3 the performance of the simultaneous NO_x reduction and soot oxidation

of the physical mixture of Cu-ZSM5 and K/CeO₂-PrO₂ is shown. As the total catalyst mass was always 270 mg Cu-ZSM5 and K/CeO₂-PrO₂ was mixed in different ratios, namely 2:1 and 4.5:1. A slight decrease in the NO_x conversion was observed in the low temperature region (<300 °C) due to the lower amount of SCR catalyst and the resulting higher relative GHSV. Above 300 °C there was a slight 5% improvement as the NO oxidation as the soot oxidation catalyst enhanced the SCR activity by partially transforming the standard SCR to fast SCR by enhancing NO oxidation. In general, however the SCR chemistry and activity remained mostly unaffected by the addition of a soot oxidation catalyst. The soot oxidation profiles in the mixture mostly resembled the catalytic soot oxidation in O₂ alone, confirming that in the presence of SCR reaction NO₂ does not contribute significantly to soot oxidation. A portion of the soot was also oxidized non-catalytically as in the mixture a portion of soot was segregated by the SCR catalyst from the soot oxidation catalyst. As the proportion of the soot oxidation catalyst in the mixture was reduced the proportion of the non-catalytically oxidized soot increased.

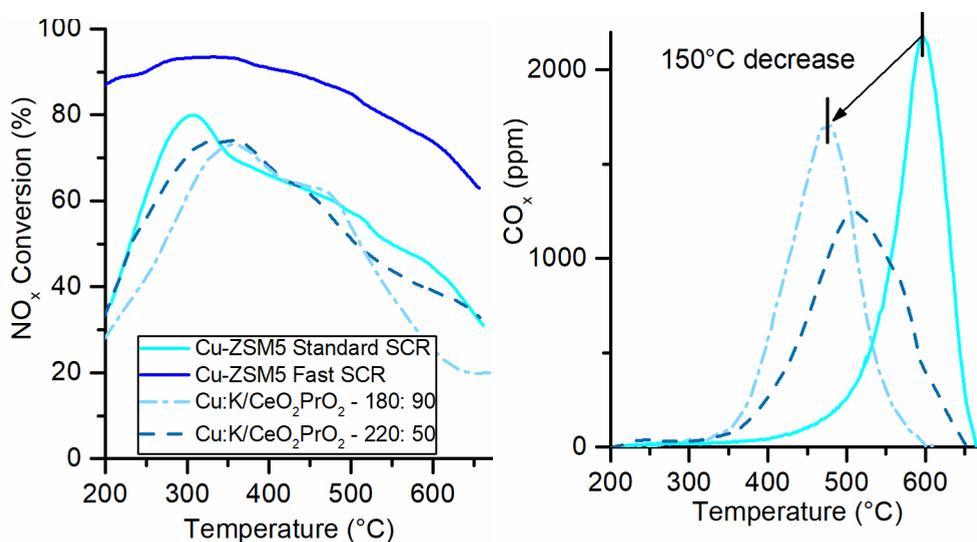


Figure 3. Integrated NO_x SCR and soot oxidation over Cu-ZSM5 and K/CeO₂-PrO₂ mixtures. Reaction conditions: 270 mg of catalyst mixed with 30 mg of soot, total flowrate of 600 ml/min of 500 ppm NH₃ and NO, 4% O₂ in N₂. Heating rate 2 °C/min

Fe-ZSM5 benefited more from the combination with soot oxidation catalyst as it has synergistic effect. As Fe based zeolites are more sensitive to NO₂/NO_x ratio the performance was enhanced by the K/CeO₂-PrO₂ oxidizing NO to NO₂. In contrast to Cu-ZSM5, with Fe-ZSM5 more soot oxidation catalyst in the mixture resulted in better performance. From the Fe-ZSM5: K/CeO₂-PrO₂ ratios of 1:1 and 2:1 the 2:1

offered the optimized performance. As the SCR reaction system was partially transformed to fast SCR the NO_x conversion increased by more than 20 % relative to the case when Fe-ZSM5 was used only. The soot oxidation was also improved and the same conclusions can be drawn as in the previous case.

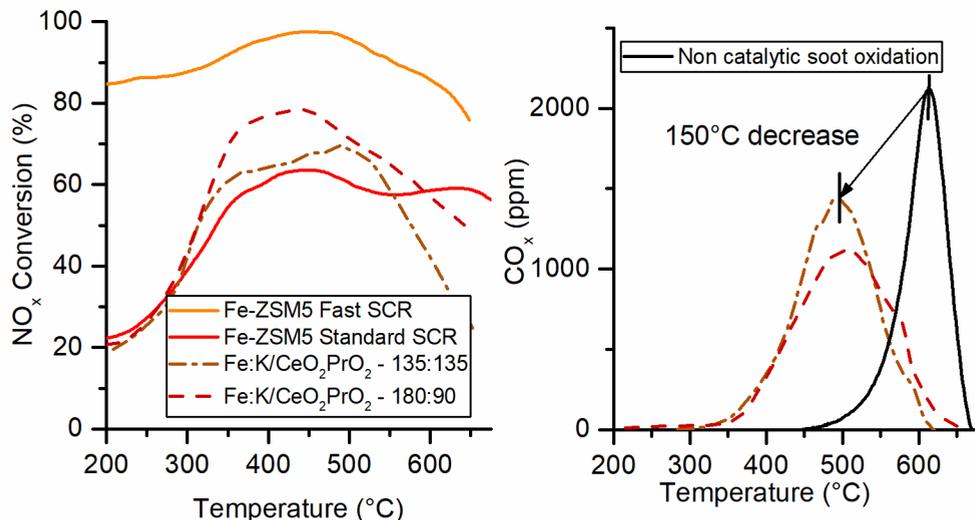


Figure 4. Integrated NO_x SCR and soot oxidation over Fe-ZSM5 and K/CeO₂-PrO₂ mixtures. Reaction conditions same as in Figure 3.

4. Conclusions

The integration of NO_x SCR and improved soot oxidation was achieved by combining a commercial catalyst (Cu and Fe zeolite) with a tailor-made soot oxidation catalyst. It was demonstrated that the soot oxidation temperature can be reduced by more than 150 °C while simultaneously improving NO_x conversion. This enables milder regeneration conditions and lower fuel penalty. The soot oxidation catalyst used for the improved SCR_oF, in general, has to have the following characteristics:

1. The oxidation of the reductant (in this case ammonia) must be avoided as it would have detrimental effect on the SCR of NO_x. The inhibition of ammonia adsorption was achieved by selectively poisoning the acid sites with potassium
2. The reaction rate of NO₂ consumption during the NO_x SCR is orders of magnitude higher than its reaction rate with soot. The main oxidant available in the SCR_oF is O₂, hence the catalyst should be highly active for O₂-soot reaction
3. It is preferable that the soot oxidation catalyst is also active for the NO to NO₂ oxidation. On SCR_oF higher NO₂/NO_x ratios are preferred as it

- improves both the NO_x conversion and soot oxidation
4. The contact between soot and the soot oxidation catalyst has to be maximized as the soot not in contact with the soot oxidation catalyst can be deactivated.

References

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