

Potential of NO_x storage/release materials for high temperature diesel soot oxidation

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Introduction

Particulate matter (soot) and NO_x are the main pollutants in diesel engine emissions and represent health and environmental problems. In Euro V emission standards for cars and light trucks, which are expected to be implemented in 2009, level of soot in exhaust should be decreased almost five times in comparison with Euro IV regulations¹. Normally soot can be oxidised by oxygen to CO+CO₂ around 600°C. During most of the diesel engine operations the exhaust gas temperature is below 300°C which is too low to initiate continuous uncatalysed soot oxidation. Soot is, therefore, collected on a filter and further can be oxidised at high temperatures to regenerate the filter. To improve fuel economy the duration of the regeneration interval should be as short as possible and it should at the same time ensure complete trap regeneration.

Since NO₂ is a more powerful oxidant than oxygen, a possible strategy is to use a combination of a NO_x storage material which will store the NO_x at temperatures below 300°C as nitrates and release it at the temperature of regeneration^{2,3}. An oxidation catalyst will oxidize NO into NO₂ and subsequently the NO₂ will convert soot selectively into CO₂ and back to NO as schematically shown in the Figure 1. As NO_x storage materials, alkali, alkali-earth and rare-earth oxides have clearly potential, since they can store NO_x in form of nitrates and nitrites at low temperatures and release it as NO, NO₂, and active oxygen upon heating.

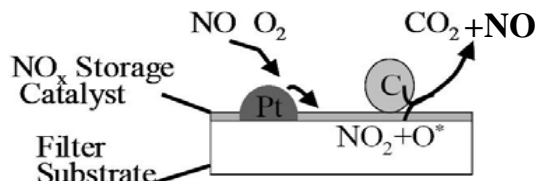


Figure 1: Soot oxidation on the filter combining NO_x storage material and oxidation catalyst.

Experimental

A large variety of mono and bimetallic NO_x storage/release systems supported on Al₂O₃, ZrO₂ and CeO₂ have been prepared. In most cases Pt was added to oxidize NO into NO₂. Textural properties of resulting catalysts were studied using N₂ adsorption measurements, XRD, and TGA. NO_x storage/release behavior was analyzed as a function of temperature by FTIR and by temperature programmed desorption (TPD) both coupled with a MS. Soot oxidation was studied both in isothermal and temperature-programmed conditions.

Results and Discussion

For alkali-earth and rare-earth based systems NO_x storage capacity was found to be significantly lower than theoretical calculated assuming 100% nitrate formation for storage component. For alkali-earth based systems the NO_x storage capacity increases on going from Ba via Sr and Ca to Mg while the stability of formed nitrates decreases. The pretreatment conditions and temperature of NO_x storage also have a significant effect on the storage capacity. The presence of soot decreases the temperature of NO_x release. The main product of nitrates decomposition in the presence of soot is nitrogen monoxide and NO has a significantly smaller effect on soot oxidation than NO₂. Therefore, the presence of oxidation catalyst is beneficial. It is found that even above 450°C, where NO conversion to NO₂ is thermodynamically unfavorable, the presence of small amounts of NO₂ has a very strong positive effect on soot oxidation due to high recycle efficiency of NO into NO₂. In this case soot is oxidized through two parallel paths: oxidation with NO₂ and oxidation with oxygen. Heat produced during soot oxidation by NO₂ can be utilized to initiate soot oxidation with oxygen. The presence of stored NO_x does not influence soot oxidation selectivity, while the presence of oxidation catalyst increases selectivity to CO₂ significantly. These trends are illustrated here on the example of Sr-based system and the main results are summarized in Table 1.

Table 1. Soot oxidation with air in the presence of NO_x storage/release system.

System	T _{max1} , °C*	T _{max2} , °C**	S ₁ , %***	T _{20%} , °C	S _{CO2} , %
20%Sr(NO ₃) ₂ /Al ₂ O ₃	552	-	-	-	-
soot+Al ₂ O ₃ (1:20)	-	633	0	584	88
soot+1%Pt/Al ₂ O ₃ (1:20)	-	613	0	565	93
soot+20%Sr(NO ₃) ₂ /Al ₂ O ₃	507	643	5.2	539	85
soot+20%Sr(NO ₃) ₂ /Al ₂ O ₃	503	610	9.1	509	86
soot+1%Pt-20%Sr(NO ₃) ₂ /Al ₂ O ₃	467	591	34.9	484	97

* temperature of the maximum for NO_x assisted soot oxidation (correlate with temperature of NO_x release)

** temperature of the maximum for soot oxidation with oxygen

*** share of NO_x assisted soot oxidation in overall soot conversion

Conclusions

It is shown that the combination of NO_x storage/release component and oxidation catalyst enables to decrease time and the temperature of the diesel soot oxidation significantly which would result in lower fuel penalty for the soot filter regeneration.

References

1. <http://www.dieselnet.com/standards/>
2. A. Setiabudi, M. Makkee, J.A. Moulijn, Appl. Catal. B, 50 (2004) 185.
3. K. Krishna, M. Makkee, Catal. Today, 114 (2006) 48.