

Investigation of diesel soot reactivity with a new TG-FTIR system for research with condensable and corrosive gases

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The very strict NO_x and particulate emission limits for diesel engines result in an increasing number of exhaust gas aftertreatment systems, which combine NO_x reduction and particulate filter functionalities.

At the Paul Scherrer Institute first investigations of a new exhaust gas aftertreatment system where urea is dosed in front of the particulate filter were done for Emitec® [1, 2]. The soot samples collected from a diesel engine were brought into a model diesel exhaust gas stream and the oxidation behaviour was monitored. Beside the soot oxidation an unexpected significant SCR effect was observed over the diesel soot sample due to the ammonia dosed as a model substance for urea.

Driven by these results the decision was made to use the opportunity to develop a new analytical apparatus for research in the field of exhaust gas aftertreatment in order to analyse the different processes and single reaction steps resulting from the combination of several aftertreatment functionalities and deeper investigate the observed SCR effect over soot as a first application example.

Since TG-FTIR (Thermogravimetry coupled with Fourier-Transform Infra-Red spectroscopy) systems are very efficient for the investigation of adsorption and desorption processes on catalyst and soot samples and the analysis of the gaseous reaction products, but have the disadvantage that experiments with condensable and corrosive gas components cannot be performed, we decided to redesign a standard TG-FTIR in order to make this powerful technique accessible to research in exhaust gas aftertreatment.

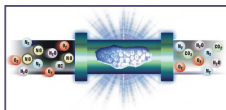
We coupled a TGA/DSC 1 from Mettler-Toledo with a Nicolet Antaris IGS FTIR spectrometer from Thermofisher. The gas inlet and outlet of the TG were redesigned for the usage of humid gases and all tubes upstream and downstream of the TG are heated up to 180°C. A new heated gas measuring cell was designed for the FTIR spectrometer by Thermofisher, which combines small inner volume and maximum beam intensity. The shape and volume of the gas cell are the best compromise between small flow rates in the system and short residence times in order to reach a high temporal resolution.

Further on, the instrument is equipped with a flexible gas supply system for the simulation of real diesel exhaust gases in a broad range of compositions. The standard gases dosed

are N_2 , NO, NO_2 , NH_3 , O_2 and H_2O plus SO_2 , CO and hydrocarbons for special investigations. Water is generated by hydrogen oxidation over a Pt-catalyst at $T > 250^\circ C$. Since we have almost finished the experimental setup and the modification of the standard apparatus we suppose to get first application results with the system until May 2009, which will be presented at the 13th ETH-Conference on Combustion Generated Nanoparticles.

References

- [1] O. Kröcher, M. Elsener, A method and a system for a treatment of a NO_x -containing exhaust gas, European patent application No. 2008P07268EP.
- [2] E. Jacob, R. Müller, A. Scheeder, P. Treiber, SCRi-Abgasnachbehandlungssystem zur gleichzeitigen PM- und NO_x -Verminderung bei On- und Non-road Applikationen, 05/2008, www.emitec.com.



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Motivation

The strict future emission limits for diesel engines will require the combination of SCR and DPF in the same vehicle, which forwards ideas to combine both functions in one aftertreatment device. According to this concept, DPF and SCR catalyst could be placed in the same housing, whereby the reducing agent is dosed upstream of the particulate filter. However, the combination of these processes result in increasingly complex technical solutions and a superposition of various physical and chemical processes. Therefore, adequate analytical techniques are required in order to separate the different processes and to analyse single chemical reaction steps.

The scope of this project is the development of a TGA-FTIR system (TGA: thermogravimetric analysis, FTIR: Fourier-Transform-Infrared spectroscopy) to be applied in R&D projects in the field of exhaust gas catalysis. This combination allows us to analyze mass changes of catalyst samples by oxidation, adsorption and desorption in parallel to the quantification of all infrared active gas components with high resolution and long-term stability.

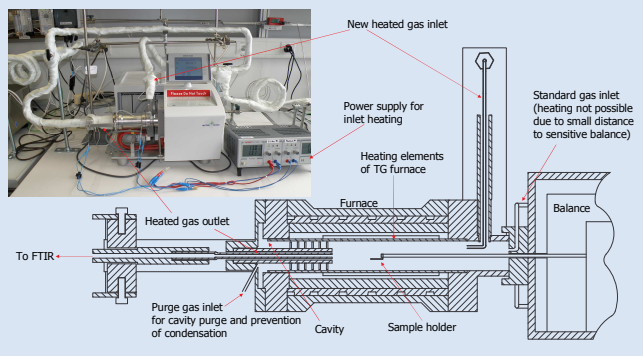
TGA-FTIR setup



TGA by Mettler-Toledo

- FTIR spectrometer by Thermofisher
- 8 MFC by Brooks, driven by a LabView program written in house
- Pt-catalyst for the generation of water by controlled hydrogen oxidation → pulsation-free dosage
- Computer for controlling TGA, FTIR spectrometer and MFCs
- Heating system for the gas supply system and the transfer line to prevent condensation

TGA unit



Fourier-Transform-Infrared Spectrometer

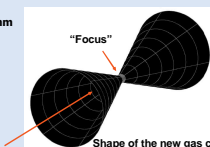
Redesign of the FTIR:

Standard cell is too large in volume in comparison to the total flow.

→ A cell which is a compromise between small flow rates and an adequate residence time had to be designed.

Shape of the new FTIR cell:

The shape of the new cell corresponds with the envelope of the not collimated IR beam and therefore looks like two cones lying with their tips in opposite to each other. Volume = 38,69 mL. Path length = 178 mm



Preliminary performance tests: Soot oxidation in presence of water and NO₂

Sample: diesel soot collected on a metal fleece from the exhaust gas of a state-of-the-art diesel engine ($d_{\text{sample}}=15 \text{ mm}$; soot loading 0.46 mg/cm^2 ; model gas flow: 100 mL/min)

Soot oxidation with O₂ in the presence of water (Figure 1 a & b):

- Reactive gas composition: O₂ (10%), H₂O (5%) in N₂.
- The onset temperature of the soot oxidation lies above 550°C.
- At temperatures around 490°C CO₂ evolution can be observed in the FTIR signal.
- The sharp peaks at the beginning of the experiment are due to the start of water dosage at 100°C, since condensation has to be avoided.
- The increase in mass above 650°C was due to oxidation of the metal fleece (Figure 1a).
- CO evolution is not shown since the spectrometer is not yet calibrated for all gas components which may occur.

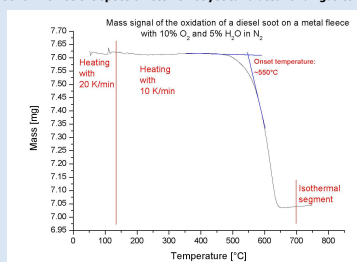


Figure 1 a

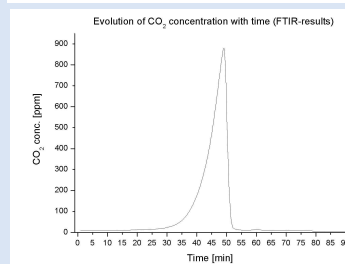


Figure 1 b

Soot oxidation with O₂ and NO₂ in the presence of water (Figure 2):

- Reactive gas composition: O₂ (5%), NO₂ (0.1%), H₂O (5%) in N₂.
- The mass loss of the soot sample and the evolution of CO₂ (not shown here) were observed already at about 100°C, which was likely caused by the decomposition of surface functionalities and above 200°C by the oxidation with NO₂. Therefore an estimation of an onset temperature of the soot oxidation due to O₂ was not possible.
- The sharp peaks at the beginning of the experiment are again due to the start of water and NO₂ dosage, since condensation has to be avoided here as well.
- The increase in mass above 650°C was again due to oxidation of the metal fleece.

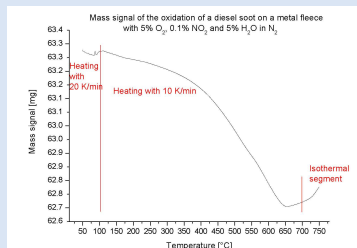


Figure 2

Conclusion

This first performance test proves that the system works properly and that all gases can be dosed without corrosion and condensation in the system.