

DRIFT ANALYSIS OF CARBON-OXYGEN SPECIES ON PRINTEX-U AFTER CATALYTIC OXIDATION BY METAL OXIDES IN AIR, NITROUS OXIDE AND OZONE

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Introduction

This study has been performed as part of the project "Removal of Soot from Diesel Exhaust Gases". One is interested in a catalyst for the oxidation of soot particulates because: (i) diesel engines can no longer meet the requirements of the particulate (soot) emission standards, and (ii) collection of soot in a monolithic filter and simultaneous oxidation at diesel exhaust gas temperatures (600 K) is considered to be the best option to abate the emission of soot.

Several metal oxides appear to be rather active soot oxidation catalysts, once contact between the catalyst and soot has been established mechanically [1]. Several authors report on the formation of Surface Oxygen Complexes (SOC) on carbonaceous materials after non catalytic oxidation in air (e.g. Zhuang *et al.* [2]). SOC are thought to be important intermediates in the formation of CO and CO₂ [3]. Little is known, however, about the chemical processes occurring between the catalyst, soot and oxygen upon catalytic oxidation. Here we report on the formation of SOC in the presence of a catalyst in air, in nitrous oxide or in ozone.

Experimental

Printex-U (a model soot purchased from Degussa) and a metal oxide were mixed in a ratio of 1:1 by weight in a ball mill for one hour in order to establish "tight contact". These samples were treated *ex situ* in an STA 1500H balance. Soot conversion levels of approximately 30% were reached by heating the catalyst

and soot in air for 15-30 minutes at 620-700 K (depending on the activity of the catalyst).

Soot and Fe₂O₃ as well as soot and CuO mixtures were also treated in 5% N₂O in He at 773 K until about 40% of the soot had been converted.

"Ozonized" soot was obtained by treatment of the soot (with catalyst) in a flow of approximately 5% ozone in air at 350 K for 30 minutes.

Diffuse Reflectance Infrared Fourier Transformed (DRIFT) spectra were recorded on a Nicolet Magna 550 spectrometer equipped with a DTGS detector and a Spectratech DRIFT accessory. KBr was used as a diluent. Spectra are displayed in 8 cm⁻¹ resolution in absorbance reflectance mode against a soot in KBr background.

Results and Discussion

DRIFT spectra after catalytic oxidation of soot in air are shown in figure 1. Generally three types of SOC can be identified with DRIFT after (partial) oxidation of soot in air (i) ethers (1250 cm⁻¹), (ii) quinones (1605 cm⁻¹), and (iii) lactones (1735 cm⁻¹). The lactone species are the least stable ones and decompose *non-catalytically* releasing CO and CO₂ at 750 K [2]. CuO, Cr₂O₃, and MoO₃ clearly cause an enhancement in the amount of SOC, compared with non catalytic oxidation under similar conditions. The spectra shown for Fe₂O₃ and Co₃O₄ are similar to the one obtained after non-catalytic oxidation. Results for several catalysts are summarized in table 1.

TABLE 1. Experimental data for the treatment of several soot/catalyst mixtures in air.

Catalyst	Temperature (K)	Time (min)	Conversion (%)	Complexes
MoO ₃	675	15	35	++
Cr ₂ O ₃	685	35	30	+
CuO	695	20	25	++
Fe ₂ O ₃	700	15	40	--
Co ₃ O ₄	635	25	45	--

The reasons for the different behaviour of metal oxides with respect to the formation of SOC in air, are not yet understood. Two explanations suggest themselves: (i) after the milling procedure catalysts, which can increase the amount of SOC, are activating soot in such a way, that SOC are formed by direct reaction of soot with air or (ii) catalysts, increasing the rate of formation of SOC, are activating oxygen in such a way that SOC is being formed by some kind of spill-over mechanism.

After catalytic soot conversion in N_2O with CuO , Fe_2O_3 or Co_3O_4 , SOC are not observed. For CuO this is rather surprising. The underlying reason might be that CuO is reduced in an N_2O atmosphere into Cu_2O . A possible explanation is therefore that O_2 formed by N_2O decomposition over Cu_2O cannot spill-over to the soot surface.

As can be seen in figure 2, the formation of SOC at low temperatures in ozone is also influenced by the presence of a catalyst. In the absence of a catalyst several SOC can be identified. An extra peak at 1780 cm^{-1} can be observed in the DRIFT spectrum of ozonized soot in comparison with air, probably due to oxygen complexes which are only stable at low temperatures. With Fe_2O_3 and Co_3O_4 , soot oxidation in ozone hardly results in the formation of SOC, while in the presence of some other catalysts (CuO , Cr_2O_3 and MoO_3) SOC can be observed. Generally, catalysts which cause the formation of SOC in air also enhance the amount of SOC at low temperatures in ozone. Considering this, proposition (ii) to explain the formation of SOC in air (and ozone) seems to be plausible. However more research is needed to obtain information on this spill-over mechanism in the catalytic formation of SOC on soot and the role of these complexes in the catalytic oxidation. Also the oxidation mechanism of catalysts like Fe_2O_3 or Co_3O_4 which do not give rise to

SOC formation (but do enhance the oxidation rate) has to be studied in more detail.

Conclusions

- DRIFT is an excellent technique to study the formation of SOC on soot surfaces.
- Some catalysts (MoO_3 , CuO , Cr_2O_3) cause the formation of SOC in air, while others (Fe_2O_3 and Co_3O_4) do not.
- CuO , Fe_2O_3 and Co_3O_4 do not catalyze the formation of SOC in N_2O .
- Catalysts which cause the formation of SOC in air also enhance the amount of SOC at low temperatures in ozone.
- Tentatively it is proposed that SOC are formed by a spill-over mechanism.

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References

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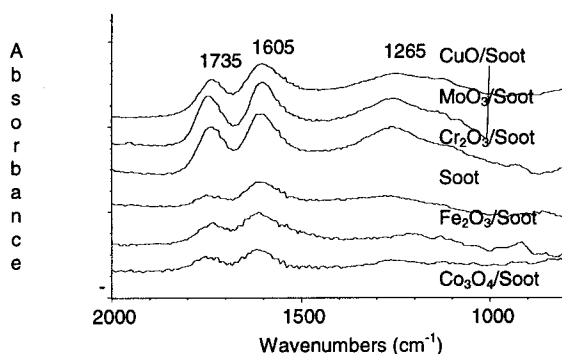


Figure 1. DRIFT spectra of soot after catalytic oxidation in air with several catalysts. For conditions see Table 1.

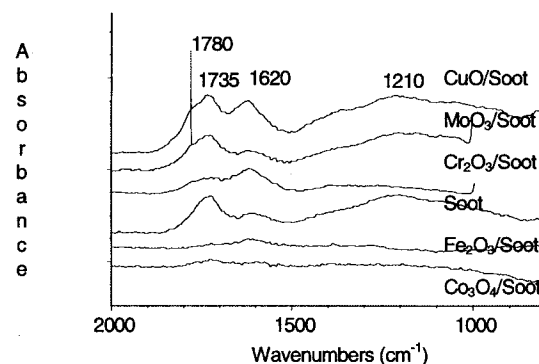


Figure 2. DRIFT spectra of soot after catalytic oxidation in ozone at 350 K.