

THE EFFECT OF NO_x AND CO ON THE CATALYTIC SOOT OXIDATION ACTIVITY OF TRANSITION METAL OXIDES

G. Mul, F. Kapteijn and J.A. Moulijn

Delft University of Technology, Faculty of Chemical Engineering and Materials Science,
Department of Industrial Catalysis, Julianalaan 136, 2628 BL Delft

Introduction

Catalytic oxidation of soot by transition metal oxides has recently been investigated by several research groups 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 for the removal of soot from diesel exhaust [1]. Various metal oxides have been tested on their catalytic activity for the oxidation of soot in air [2]. However, the effects of NO_x and CO (other constituents of diesel exhaust gas), on the catalytic oxidation rate is usually not addressed. In this abstract the effect of these gases on the Co₃O₄-, Cr₂O₃- and CuO-catalyzed soot oxidation is described, as they represent catalysts that exhibit three different oxidation profiles [3]: Co₃O₄ shows an exponential decay-type profile, Cr₂O₃ a constant-type, and CuO a rising-type profile. The practical application of the NO_x/soot reaction for the removal of soot from diesel exhaust is also evaluated.

Experimental

Printex-U (a model soot, kindly provided by Degussa) was used to perform the oxidation studies. Unsupported transition metal oxides were prepared by decomposition of the corresponding nitrate at 875 K for 2 hours in an oven in static air [3]. The transition metal oxides and soot were either intensively mixed in a ball-mill in a catalyst to soot mass ratio of 2:1 (referred to as 'tight contact'), or simply mixed by using a spatula ('loose contact') [3]. The effects of NO_x and CO on the oxidation rate were determined in the so-called six-flow reactor setup [3]: 60 mg of a catalyst/soot mixture was reacted isothermally in 150 ml/min 10 vol% O₂ in Ar, either with or without 1000 ppm NO or 1000 ppm CO.

The concentration of the reactant and product gases was determined continuously with an ND-IR detector. Introduction of 1000 ppm NO into the 10% O₂/Ar stream, led to the formation of NO₂: a gas

composition of 650 ppm NO and 350 ppm NO₂ was obtained. The effect of CO and NO_x on the non catalytic soot oxidation rate was also determined.

Results and Discussion

An enhancement of the non catalytic soot oxidation rate was found after the addition of NO_x to the oxidizing medium, explained by reaction (1).



CO had no effect on the non catalytic soot oxidation rate. The effects of NO_x and CO on the oxidation profile of a CuO/soot physical mixture ('tight contact') are shown in figure 1. CuO shows a so-called rising-type oxidation profile at 675 K [3]. Addition of CO increases the oxidation rate over the entire conversion range and yields a more pronounced rising-type profile. In the presence of NO_x, initially a higher oxidation rate than in the presence of CO is observed.

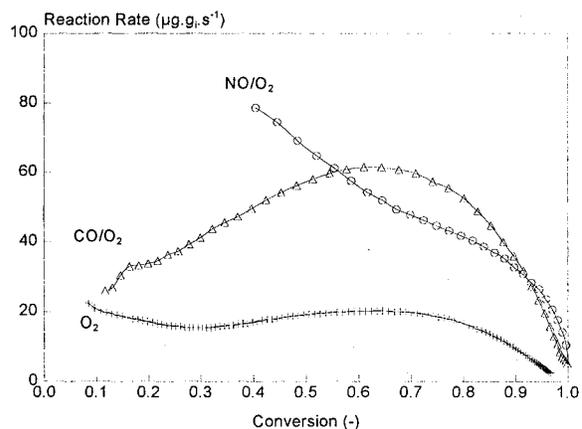
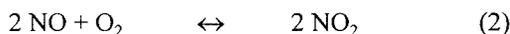


Figure 1. The oxidation rate of a 'tight contact' CuO/soot mixture at 675 K as a function of soot conversion for different gas compositions.

After evaluation of the numerous possibilities to explain these phenomena [4], the effect of CO on the CuO-catalyzed soot oxidation is tentatively explained

by the formation of a slightly reduced copper surface, which is created by reaction of CO with oxygen associated with the surface of CuO. This causes a higher effectivity in the activation of oxygen and a higher soot oxidation rate.

The effect of NO_x is explained by reactions 1 and 2:



CuO is catalytically effective for reaction (2) [4]. However, in view of a higher NO₂ conversion in the presence, than in the absence of CuO (not shown), the enhancement of the oxidation rate is not explained solely by an enhancement of NO₂ reformation, but also by a catalytic occurrence of reaction (1).

A constant-type oxidation profile is obtained in 10% O₂/Ar for Cr₂O₃, which is not affected by the presence of 1000 ppm CO. NO₂ significantly increases the oxidation rate. A monotonically decreasing reaction rate, is obtained [4].

Cr₂O₃ is a very effective catalyst for reaction (2), explaining a high 'loose contact' activity in NO_x/O₂. However, as in the case of CuO, an increase in the intimacy of contact between the catalyst and soot considerably enhanced the soot oxidation rate in NO_x, indicating a catalytic activity for reaction (1).

The activity profile of a 'tight contact' Co₃O₄/soot mixture is presented in figure 2. A rapidly decreasing reaction rate is obtained up to a soot conversion level of 0.5. In the final stage of the reaction, Co₃O₄ hardly affects the soot oxidation rate.

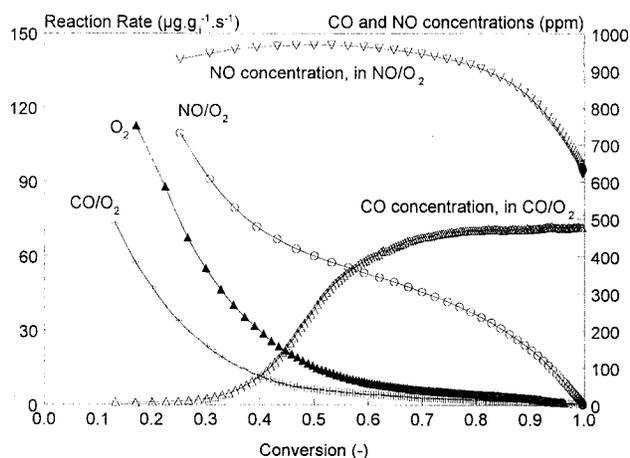


Figure 2. The oxidation rate of a 'tight contact' Co₃O₄/soot mixture at 675 K as a function of soot conversion for different gas compositions.

CO decreases the soot oxidation rate, and the CO concentration is shown to increase strongly in the soot conversion range of 0.3 to 0.6. Although these

observations are not yet entirely understood, CO is likely to reduce the Co₃O₄ surface slightly. Apparently, contrary to the CuO catalyzed soot oxidation, this results in a lower soot oxidation activity than the activity of Co₃O₄ without CO in the gas phase. The peculiar decrease of the CO conversion as a function of soot conversion, might be related to sintering of the catalyst, but this needs to be further investigated.

NO_x positively affects the activity of Co₃O₄ over the entire soot conversion range. The observed NO concentration amounted to about 1000 ppm, indicating that the (catalytic) NO₂/soot reaction occurred.

Evaluation

In general, the NO/transition metal oxide combination provides a bifunctional catalyst, where the role of NO is to improve the efficiency of the transition metal oxide by transporting activated oxygen. The highest NO_x/soot reaction rates can be obtained if the catalyst and soot are intimately mixed. The application of the NO_x/soot reaction reaction seems to be promising as a practical solution for the removal of soot from diesel exhaust. The effect of CO on the NO oxidation activity, and the possible formation of SO₃ need to be further investigated.

Conclusions

- Addition of NO_x to the oxidizing medium (10% O₂ in Ar) enhances the rates of Cr₂O₃, Co₃O₄ and CuO catalyzed soot oxidation. The rate enhancement is explained by the catalyzed formation of NO₂ and the catalyzed and uncatalyzed reaction of soot with NO₂.
- Addition of CO enhances the soot oxidation rate in the presence of CuO, whereas it inhibits the Co₃O₄ catalyzed soot oxidation and hardly affects Cr₂O₃ catalysis.

References

- [1] Lox, E.X., Engler, B.H., Koberstein, E. *in proc. of Catalysis and Automotive Pollution Control*, Amsterdam, 1991, p. 291.
- [2] Neeft, J.P.A., Makkee, M., Moulijn, J.A., *Appl. Catal. B: Env.* 8 (1996) 57.
- [3] Neeft, J.P.A., 'Catalytic oxidation of soot-Potential for the reduction of diesel particulate emissions', PhD thesis TU Delft, (1995).
- [4] Mul, G., 'Catalytic Diesel exhaust Purification- A DRIFT spectroscopic and mechanistic study of soot oxidation', PhD thesis TU Delft, (1997).