

SOOT OXIDATION CATALYZED BY A CU/K/MO/CL CATALYST: EVALUATION OF THE CHEMISTRY AND PERFORMANCE OF THE CATALYST

*Guido Mul, John P.A. Neeft, Freek Kapteijn, Michiel Makkee, Jacob A. Moulijn
Delft University of Technology, Section Industrial Catalysis, Julianalaan 136, 2628 BL Delft.*

Introduction

Because of the introduction of three way catalysts for otto motors, diesel engines have become more important contributors to air pollution. The amount of NO_x and soot emitted by diesel engines is much larger than that emitted by otto engines equipped with catalytic converters.

Soot emission from diesel engines can be reduced in various ways [1]. The best option is filtration and simultaneous oxidation of diesel soot at diesel exhaust temperatures (560-670 K), using a ceramic filter loaded with a catalyst.

The most active soot oxidation catalyst reported in the literature contains Cu, K and Mo oxides on a TiO_2 carrier [2] and is able to oxidize soot at 600 K. This catalyst is prepared from a solution containing KCl, CuCl_2 , and $(\text{NH}_4)_2\text{Mo}_7\text{O}_{22}$. A similar catalyst is described by Ciambelli et al. [3] based on KCl, CuCl_2 , and NH_3VO_3 .

XRD- and XRF-analyses of the Cu/K/Mo/Cl catalyst revealed that several potassium- and copper molybdates are present in the catalytic mixture after preparation. Moreover, KCl is still present in a considerable amount. Little is known, however, about the active component in this catalytic system and the reasons why three metals are needed. Here we give a description of the chemistry and nature of the active component within the Cu/K/Mo/Cl catalyst. The practical applicability of this system is also evaluated.

Experimental

Materials

The molybdates present in the Cu/K/Mo/Cl catalyst after calcination, were synthesized individually by solid state reactions. KCl (Baker), CuCl_2 , CuCl_2 /alumina and CuCl (Aldrich) were used as received. Cu_2OCl_2 was prepared by reaction of CuO (Merck) with CuCl_2 .

Several mixtures of KCl and CuMoO_4 were prepared by milling the two compounds (2:1 by weight) in a mortar and calcining for different periods of time at 673 K. XRD analysis of the powdered samples was performed with Cu-K α radiation [4].

Activity determination

The activities of the investigated molybdates in soot oxidation were determined in an STA 1500H thermobalance by measurement of the weight loss (TG) and the heat flow (DSC) [4]. Activities were determined in two ways. (i) Before a TG/DSC experiment the oxidic catalysts (molybdates) were milled with soot in a ratio of 2:1 (by weight) for one hour in a ball mill. These samples are referred to as being in "tight contact". (ii) The oxidation temperatures of several chlorides were determined by mixing the catalyst and soot in a ratio of 2:1 by weight with a spatula (i.e. "loose contact") [4].

Results and Discussion

The activities of the several molybdates in "tight contact" are given in figure 1. Apparently none of the individual oxidic compounds in the mixture of the Cu/K/Mo/(Cl) catalyst is as active as the mixture itself.

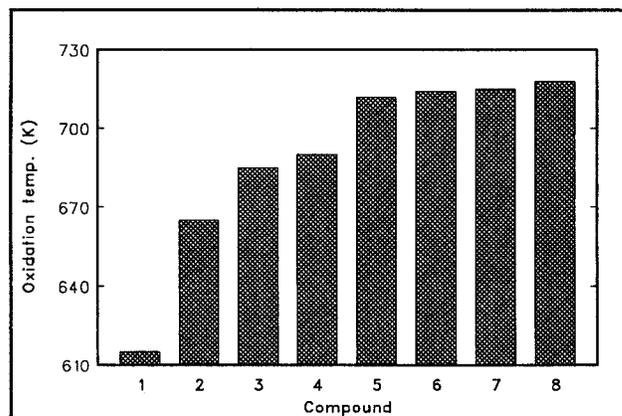
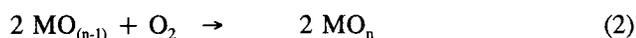


Figure 1. Soot oxidation temperatures as determined by DSC for the molybdates present in the Cu/K/Mo/Cl catalyst in tight contact. 1. Cu/K/Mo/Cl 2. $\text{K}_2\text{Cu}_2(\text{MoO}_4)_3$, 3. K_2MoO_4 , 4. $\text{K}_2\text{Mo}_2\text{O}_7$, 5. $\text{K}_2\text{Mo}_3\text{O}_{10}$, 6. $\text{K}_2\text{Mo}_4\text{O}_{13}$, 7. CuMoO_4 , 8. $\text{Cu}_3\text{Mo}_2\text{O}_9$.

Although little is known about the exact nature of the chemical processes occurring when soot (or carbon) is catalytically oxidized by metal oxides, the reaction is often thought to proceed through a reduction/oxidation mechanism ($n \geq 1$):



Also Ciambelli *et al.* explain the activity of their Cu/K/V catalyst in soot oxidation in terms of reducibility [3]. However, because of the low activity of the molybdates, an explanation of the high activity of the Cu/K/Mo catalyst based on a simple reduction/reoxidation cycle of the metal oxides, is doubtful.

From an XRD study it was concluded that the following reactions occur upon heating of a mixture of KCl and CuMoO₄ [4]:

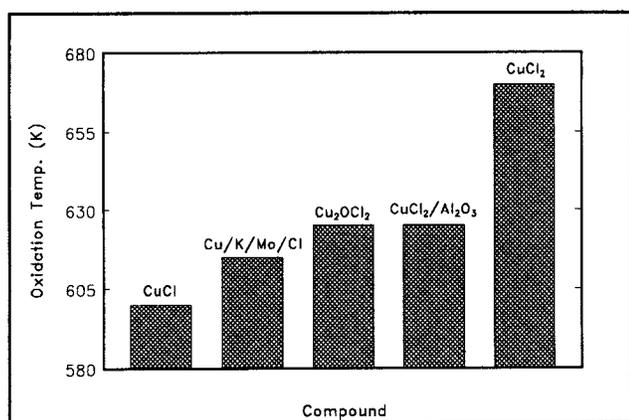
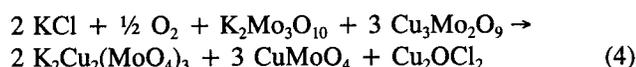
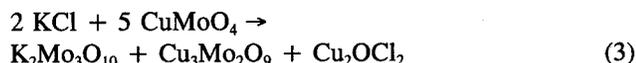


Figure 2. Soot oxidation temperatures for the chlorides present in the Cu/K/Mo/Cl catalyst. Temperatures were determined in loose contact.

As can be seen from figure 2, Cu₂OCl₂ is about as active as the Cu/K/Mo/Cl catalyst in "loose contact" and is therefore thought to be the active component. The high activity of copper chlorides, compared to molybdates in "loose contact" can at least partially be explained by the fact that these compounds have very low melting points. Therefore (re)distribution of the catalyst over the soot surface occurs, and tight contact between the catalyst and soot is established *in situ*. This (re)distribution of the catalyst can occur *via* a so-called "wetting" process or *via* gas phase transport. Probably both modes of transport occur simultaneously. The activity of copper chlorides is even higher than CuO in "tight contact". This can be explained in two ways: (i) the milling procedure results in less intimate contact than

"wetting" or condensation, or (ii) the presence of chlorine results in better reduction and reoxidation properties of CuO, needed for high activity. Both possibilities are currently being investigated.

A major problem of the application of a soot oxidation catalyst based on copper (oxy) chloride will be deactivation by evaporation and/or decomposition of the active compound [4].

Another important aspect of the copper (oxy) chloride catalyzed soot oxidation worthwhile mentioning is the possibility that carbon-chlorine bonds are being formed. Luijk *et al.* [5] have demonstrated that during combustion of an activated carbon catalyzed by CuCl₂, the carbon structure can be chlorinated. A relatively small burn-off of the chlorinated carbon surface can eventually lead to the formation of polychlorinated dibenzo-*p*-dioxines at carbon surfaces in the temperature region of interest. In this respect copper and chlorine containing soot oxidation catalysts can be considered to be less attractive for practical applications.

Evaluating the presented data, we conclude that the activity of catalysts prepared by Ciambelli [3] and Watabe [2] are very likely based on the high soot oxidation activity of copper oxy chlorides formed according to reactions (3) and (4). The practical application of these systems is doubtful because of deactivation and the potential formation of chlorinated compounds.

Acknowledgement

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