

CATALYTIC OXIDATION OF SOOT FROM DIESEL EXHAUST GASES. 1. SCREENING OF METAL OXIDE CATALYSTS BY TG-DTG-DTA ANALYSIS *

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ABSTRACT

Thermal analysis was employed as a screening technique to evaluate the activity of catalysts for the oxidation of soot produced during combustion.

Oxidation took place over metal-oxide-based catalysts at temperatures much lower than in the absence of catalyst. Best results were displayed by a Cu/V/K-supported catalyst which is very active at about 330°C. In the absence of oxygen, 16% of soot was oxidised by the oxygen of the catalyst, suggesting that a redox mechanism is involved.

INTRODUCTION

Diesel-engine exhaust gases contain polluting quantities of SO_x, NO_x, unburned hydrocarbons and soot particles which are primarily composed of carbon and contain heavy metal inclusions as well as gases and liquids adsorbed on their surface [1,2]. Furthermore, soot is mostly composed (95% by mass) of solid (< 1 μm) particles [3] that carry noxious substances into the lungs. Diesel particulates are thus a health hazard and very severe standards for diesel engine emissions have been set by legislation in many countries [4]. Since these standards cannot be met by engine modifications alone, research has been directed to developing processes for the treatment of diesel exhaust gases.

Soot can be removed from the exhausts of stationary diesel engines used to cogenerate electrical and thermal power by treatment in a single fluidised bed acting as both filter-agglomerator and heat exchanger [5]. In the case of diesel engines on vehicles, this could be done by systems acting as filters and post-combustors. Ceramic filters [6] offer satisfactory soot filtration ef-

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iciency. However, the rapid increase in gas pressure drop due to soot accumulation requires frequent filter regeneration by particulate combustion. Thermal oxidation of deposited soot requires relatively high ignition temperatures and a long time for soot burnout. The process is thus too expensive and increases the probability that local temperatures, resulting in filter failure due to thermal stresses, will be reached [7]. Catalytic traps capable of lowering the combustion temperature of the particulates offer an alternative solution. Several studies of filter [8–10] or catalyst properties [11,12] have been undertaken for this purpose.

This paper describes the screening of 9 metal-oxide-based catalysts through their TG–DTG–DTA curves in order to select a suitable candidate for soot oxidation.

EXPERIMENTAL

Several catalysts were prepared by impregnation of γ -alumina (SNAM SP 200) particles (50 μm mean diameter) with aqueous solutions of metal salts (V, Cr, Mn, Ni, Cu, K) and subsequent calcination at 700 °C [13]. All the catalysts contained the same amount of metals (7.4 mmol per g of support). Table 1 reports the molar ratios of the metals.

Their activity was determined by simultaneous TG–DTG–DTA analysis with a Netzsch STA 409 analyser. Samples of soot–catalyst mixtures were loaded in the alumina crucible and heated in flowing air or nitrogen (200 $\text{cm}^3 \text{min}^{-1}$) from 25 to 700 °C. Soot–kaolin mixtures were loaded when performing comparative tests without catalyst. Heating rates were from 1 to 50 °C min^{-1} . High purity (> 99.99%) cylinder air and nitrogen were used without further treatment.

TABLE 1

Values of T_i , T_m and T'_m (see text for reference) from TG–DTG–DTA curves of soot–catalyst mixtures in flowing air

Catalyst	R^a	T_i (°C)	T_m (°C)	T'_m (°C)
Cu		445	560	525
V		320	510	480
Cu/V	1:1	325	500	444
Cu/Cr	1:1	420	545	482
Cu/Mn	1:1	420	540	480
Cu/Ni	1:1	418	530	469
Cu/Ni/Cr	1:1:1	470	545	510
Cu/V/K	2:1:2	230	410	360
Cu/Mn/K	2:1:2	360	460	435
No catalyst		490	655	628

^a R is the metal molar ratio in the multicomponent catalyst.

The soot used in the experiments was collected on a water-cooled flat surface immersed in a diffusion flame burning paraffin.

RESULTS AND DISCUSSION

Typical thermal curves (TG, DTG and DTA) in air flow for the soot-catalyst mixtures at 25–700 °C are presented in Fig. 1. The TG data are used to evaluate the temperature T_i at which the reaction starts and the conversion of soot, whereas the DTG curve gives the temperature T_m corresponding to the highest rate of reaction. The DTA curve also provides the temperature T'_m at which the exothermic signal due to the reaction displayed a maximum. Comparison of the T_i , T_m and T'_m values gives a qualitative indication of the temperature of ignition and of the rate of soot oxidation, and hence allows a preliminary screening of the catalysts.

The T_i , T_m and T'_m values for the nine catalysts are shown in Table 1, together with those in the absence of catalyst for comparison. Addition of a catalyst clearly leads to a marked reduction of those values, especially in the case of a Cu/V/K catalyst ($T'_m = 360^\circ\text{C}$ and $T_m = 410^\circ\text{C}$) [13]: this was therefore chosen as the candidate for further investigation.

Soot conversions as a function of temperature, as evaluated from TG analysis with and without catalyst, are compared in Fig. 2. Without catalyst,

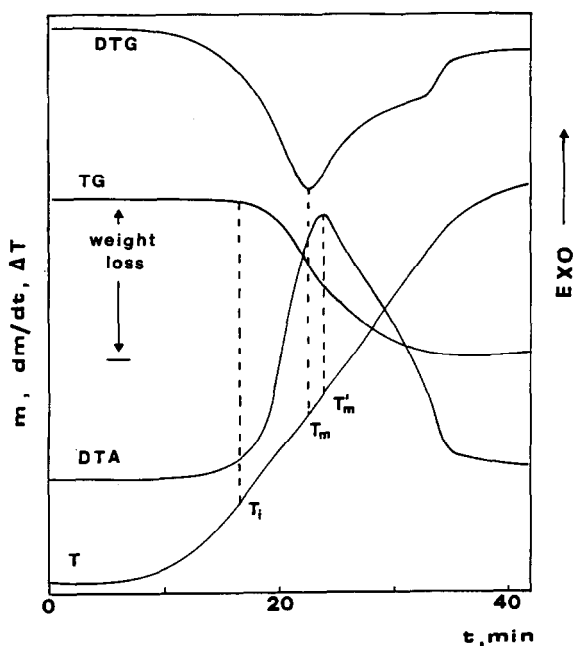


Fig. 1. Typical TG-DTG-DTA curves for soot-catalyst mixtures in flowing air.

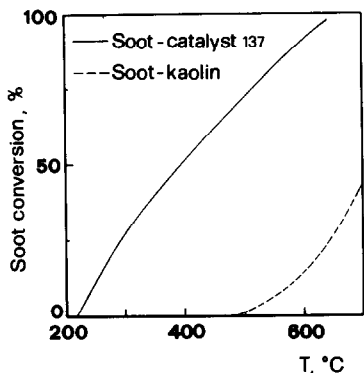


Fig. 2. Effect of the Cu/V/K catalyst on soot conversion as a function of the temperature.

conversion started at about 487°C, showed an exponential trend and reached only 22% at 640°C, whereas in the presence of catalyst the trend was quasi-linear and conversion reached 95% at the same temperature. Further comparison can be made from the DTA results. By performing DTA at different heating rates, β , and collecting T_m' data through the equation suggested by Kissinger [14]

$$\ln(\beta/T_m'^2) = -(E/R)(1/T_m') \quad (1)$$

the apparent activation energy of soot oxidation, E , can be evaluated. The value of E in the presence of catalyst was 56 kJ mol⁻¹, while for the soot alone it was 178 kJ mol⁻¹, as observed by other workers using different techniques [15,16].

The influence of oxygen content of the reacting gas was investigated by plotting TG curves for three oxygen concentrations (10, 15 and 20 vol.%). The soot conversion data are plotted as a function of sample temperature in Fig. 3. Conversion curves at 15 and 20% oxygen concentration showed relatively small differences in terms of both absolute values and slope,

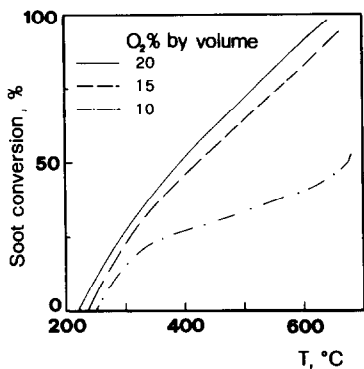


Fig. 3. Effect of O₂ concentration in the reacting gas on soot conversion on Cu/V/K catalyst as a function of the temperature.

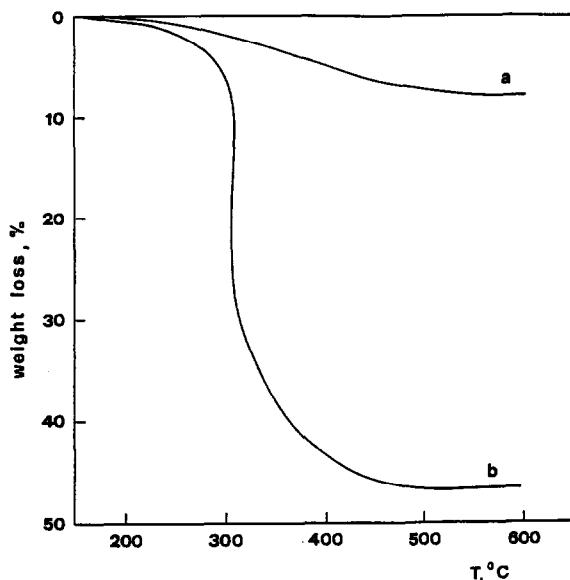


Fig. 4. Sample weight-loss percent with respect to the mass of soot as evaluated from TG curves in flowing N_2 : a, without catalyst; b, with Cu/V/K catalyst.

whereas greater differences were found on comparing the curve for 10% oxygen. At $680^\circ C$, about 100% conversion was reached in the presence of 20 and 15% oxygen, whereas only 50% conversion was reached with 10% oxygen.

Oxygen concentration should play a substantial role in the oxidation of soot with Cu/V/K catalyst, as these transition metals act as catalysts through a redox mechanism. As a preliminary check of the reducibility of the catalyst, we carried out reaction tests through thermal analysis in the absence of oxygen. A typical result is reported in Fig. 4. It shows that the

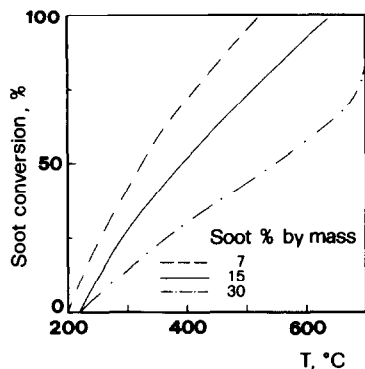


Fig. 5. Effect of the soot concentration in a soot-catalyst mixture on soot conversion on Cu/V/K catalyst as a function of the temperature.

catalyst oxidises the soot at the expense of framework oxygen. Indeed, in the absence of catalyst the sample weight-loss with respect to the mass of the soot was about 8%, whereas in the presence of catalyst it increased to about 48% (Fig. 4). The former value was due to volatile compounds present on the soot surface, while the latter indicates that about 16% of the soot was converted. The conversion was evaluated by making the correction for the loss of volatiles and taking into account the fact that the soot was oxidised to carbon monoxide by the framework oxygen. Spot analytical tests showed that this assumption was correct [17].

The effect of soot concentration in a soot-catalyst mixture on the extent of the reaction was investigated by operating at 20% oxygen concentration and changing the soot weight percentage from 7 to 30 with respect to the catalyst. Conversion curves obtained through thermal analysis are reported in Fig. 5. The lower the soot content in the sample, the higher was the soot conversion. This suggests that the ratio of catalyst surface and soot surface have a noticeable influence on the reaction rate.

CONCLUSIONS

The oxidation of soot particles formed during combustion requires rather high temperatures (600–750 °C), but it can be accomplished at relatively low temperatures (300–400 °C) in the presence of metal oxide catalysts. In particular, an alumina-supported catalyst containing V, Cu and K displayed high activity at about 330 °C, lowering the activation energy from 178 to 56 kJ mol⁻¹.

Preliminary TG-DTA investigations showed that the catalytic oxidation of soot appears to be controlled by the gaseous oxygen concentration and the soot/catalyst weight ratio.

Thermal analysis in the absence of gaseous oxygen also indicated that the catalyst works through a redox mechanism. The catalyst framework oxygen, in fact, seems to be able to oxidise the soot, and the gaseous oxygen may be assumed to reoxidise the reduced catalyst.

Our study has made clear that simultaneous thermogravimetric and differential thermal analysis can be usefully employed as a fast technique for the screening of catalytic activity in the oxidation of soot particles.

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