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Effect of support material on the catalytic combustion of diesel soot particulates

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Abstract

Several potential support materials were mixed with soot and subsequently the combustion temperature of the soot in 15% O₂ was determined. Al₂O₃ and SiO₂ showed no catalytic effect, TiO₂ and ZrO₂ lowered the soot combustion temperature with 80–90 K, whereas CeO₂, La₂O₂CO₃ and V₂O₅ (reference catalyst) showed a substantial activity for soot combustion. After poisoning with sulfur dioxide, the catalytic effect of CeO₂ was strongly inhibited, whereas La₂O₂CO₃ and V₂O₅ retained their high activity.

Keywords soot combustion, total oxidation

INTRODUCTION

Diesel engine powered vehicles are a major source for the emission of soot particulates in urban areas. Due to their small size, soot particulates can penetrate into the lung and they can form a serious health problem because of the presence of adsorbed (carcinogenic) hydrocarbons on their surfaces [1,2].

Soot emissions can be reduced by placing a filter in the exhaust pipe. To prevent pressure build-up, the accumulated soot particulates must be (periodically) removed from the filter. As the combustion temperature of the soot is much higher than the operational temperature found in the exhaust pipe, either the temperature in the exhaust pipe must be increased or the combustion temperature of the soot must be decreased.

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The combustion temperature of the soot particulates can be lowered by the addition of an oxidation catalyst in the form of fuel additives (organo-metal compounds) [3], by spraying a metal salt solution on the accumulated soot [4] or by impregnation of the filter walls with an oxidation catalyst [5]. For the last option, supported metal oxides are considered to be the most promising candidates. In general, the search for the "ideal" soot combustion catalyst is performed by mixing supported metal (oxides) with soot, followed by the measurement of soot combustion. Several studies of this type have been published, generally focussed on alumina-supported oxidation catalysts [5–8].

If we exclude ref. 7 and a recent patent concerning Pt/SiO₂ [9], the reported studies were performed in the absence of SO₂, although diesel fuels contain a considerable amount of sulfur. Since it is known that SO₂ can act as a poison for many catalysts, the objective of this study was to reinvestigate a series of different materials which might serve as a support for metal oxides or noble metals in order to classify their catalytic activity on the combustion of soot in the absence and in the presence of SO₂.

EXPERIMENTAL

Oxides/supports

Table 1 lists the materials applied (all potential supports), with their specific surface areas. Additionally, V₂O₅ is used as a reference material. Owing to its low melting point, it cannot be considered as a support but it was found to be one of the most active catalysts for the combustion of diesel soot [7].

TiO₂ and ZrO₂ were calcined in flowing air at 975 K for 2 h in order to remove any chlorine present. Lanthanum oxide was prepared by heating lanthanum citrate precursor in air at 773 K. The only phase detected by X-ray analysis

TABLE 1

Support materials with their specific surface areas

| Support material | Manufacturer | Specific surface area (m ² /g) |
|--|---------------------|---|
| Al ₂ O ₃ | Degussa Oxid C | 100 |
| SiO ₂ | Degussa Aerosil 130 | 130 |
| TiO ₂ | Degussa P25 | 50 |
| ZrO ₂ | Degussa 137 | 90 |
| CeO ₂ | Rhône-Poulenc | 5 |
| La ₂ O ₂ CO ₃ | IRC ^a | 20 |
| V ₂ O ₅ | IRC ^a | 34 |

^aPrepared at the IRC

after storage under ambient air is $\text{La}_2\text{O}_2\text{CO}_3 \cdot \text{V}_2\text{O}_5$ was prepared by decomposing N_2O_3 in air at 773 K

Soot

The soot was obtained from Renault-France. The particulates were produced by a diesel fuel burner and collected with a cordierite filter. They contained 1 wt.-% ash and the amount of adsorbed hydrocarbons was $\leq 1\%$. The composition of the inorganic material was determined by AAS (atomic absorption spectrometry) and ICP (inductively coupled plasma) analysis. The carbon, hydrogen, nitrogen, sulfur and oxygen contents were determined by elemental analysis. The results of these analyses are listed in Tables 2 and 3.

From Table 2, the main elements are Si, Al and Mg; they originate from cordierite particles. In addition the analysis shows considerably lower P, Ca and Zn contents than those reported in the literature [10,11]. This was due to the absence of oil consumption in the fuel burner. Since the soluble oil fraction (SOF) was quite low (ca. 1% by weight), the elemental composition of the organic part was not determined.

The BET surface area of the soot was $300 \text{ m}^2/\text{g}$, as measured by nitrogen adsorption.

TABLE 2

Chemical composition of the inorganic material in the soot AAS and ICP analysis

| Element | Ash (%) |
|---------------|----------------------|
| Al | 14.6 |
| Ca | 1.8 |
| Mg | 4.0 |
| V | 0.28 |
| Cr | 0.17 |
| Ti | 0.25 |
| Fe | 3.54 |
| K | 1.4 |
| Na | 1.2 |
| Co | 0.04 |
| Ni | 0.20 |
| Zn | 0.28 |
| Cu | 0.29 |
| Mn | 0.06 |
| Pb | 1.8 |
| Si | 23.4 (by difference) |
| S (inorganic) | 1.16 |
| P | 0.24 |

TABLE 3**Elemental composition of the soot**

| Element | wt -% |
|-----------|--------------------|
| C | 80.5 |
| H | 1.2 |
| N | <0.16 |
| S | <0.36 |
| O | 15.9 by difference |
| C/H ratio | 5.8 |

Mixing catalyst with soot

In a first series of experiments, it was observed that mechanical mixing of the soot and the catalyst in an agate mortar gave unreproducible results. Consequently we used the following method: 400 mg of catalyst and 100 mg of soot were placed in a 100-ml steel holder together with four small steel balls (8 mm I.D.), either under argon or air. Subsequently, the mixture was ball-milled for 30 or 60 min. Combustion tests proved that this procedure gave reproducible results.

Combustion measurements

The combustion of the soot was determined thermogravimetrically in a Setaram TGA-DTA-92 thermobalance coupled to a Balzers 420 QMG mass spectrometer. 25–35 mg of the support-soot mixture was placed in an alumina crucible suspended from one arm of the balance. All experiments were performed using a heating rate of 5 K/min in either 15% O₂ in N₂ or, for the combustion experiments of SO₂-poisoned samples, in 15% O₂/100 ppm SO₂ in Ar. Both the O₂ and SO₂ content represented realistic diesel exhaust-gas compositions. The combustion rates were obtained from the weight losses. The heat effects showed that the weight changes were due to soot combustion. The mass spectrometer (MS) was also used to check combustion by monitoring the gaseous reactant and any possible reaction products, namely O₂, CO, CO₂, H₂, H₂O, SO₂, SO₃, NO and NO₂. No quantitative MS data could be obtained. In particular, it was not possible to obtain a correct estimate of the relative proportions of CO and CO₂.

The CO/(CO+CO₂) ratio was determined separately by temperature-programmed oxidation (TPO) in air of identical soot-catalyst mixtures (total sample size: 100 mg) placed in a micro-reactor, with a heating rate of 0.8 K/min. The CO and CO₂ content of the product mixture was determined with a gas chromatograph equipped with a thermal conductivity detector.

SO₂ poisoning

Approximately 400 mg catalyst was placed in a U-shaped quartz reactor and heated to 625 or 925 K under a flow of 15% O₂/100 ppm SO₂ in N₂ (50 ml/min). After 6 or 20 h at the final temperature, the catalyst was cooled to room temperature, mixed with soot and subsequently the reactivity was measured with the thermobalance.

RESULTS

Mixing

In Table 4 the reaction rates at 625 and 730 K, expressed as mg soot combusted per minute, is given for (Al₂O₃ + soot) and (TiO₂ + soot) mixtures. The duration of the mixing procedure and the atmosphere was varied.

The variation of the mixing conditions shows that the reactivity was strongly influenced by this procedure. Longer milling times resulted in higher reactivities. At high temperatures the combustion reactivity of a (Al₂O₃ + soot) mixture after mixing in argon was lower than after mixing in air. A standard mixing procedure was adopted in order to make a comparison between the different catalysts. All further combustion experiments were performed after 30 min ball-milling of the (support + soot) mixtures under a flow of argon.

Support and soot combustion

In Figs. 1–2, the derivatives of the weight loss curves [differential thermogravimetry (DTG) curves] of the combustion of (support + soot) mixtures are shown. The temperatures of the maxima of these curves and the CO/(CO + CO₂) ratios measured by TPO at this maximum are listed in Table 5.

These results show that the combustion temperature was substantially low-

TABLE 4

Combustion rate of soot as measured by TGA in the presence of different supports as a function of mixing time and atmosphere

| Support material | Atmosphere | Combustion rate at 625 K (mg/min) mixing time | | Combustion rate at 730 K (mg/min) mixing time | |
|--------------------------------|------------|---|--------|---|--------|
| | | 30 min | 60 min | 30 min | 60 min |
| | | Al ₂ O ₃ | Air | 0.014 | 0.033 |
| Al ₂ O ₃ | Argon | 0.013 | 0.035 | 0.080 | 0.129 |
| TiO ₂ | Air | 0.047 | 0.113 | 0.154 | 0.180 |

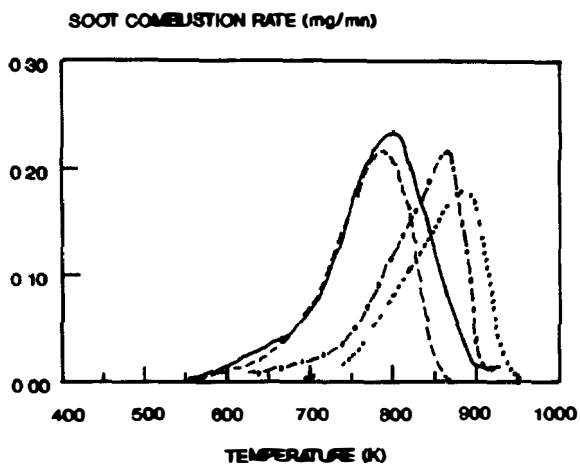


Fig 1 DTG curves of the combustion (15% O₂ in N₂) of soot (· · ·), in the presence of Al₂O₃ (- · - ·), in the presence of TiO₂ (- - -) and in the presence of ZrO₂ (—)

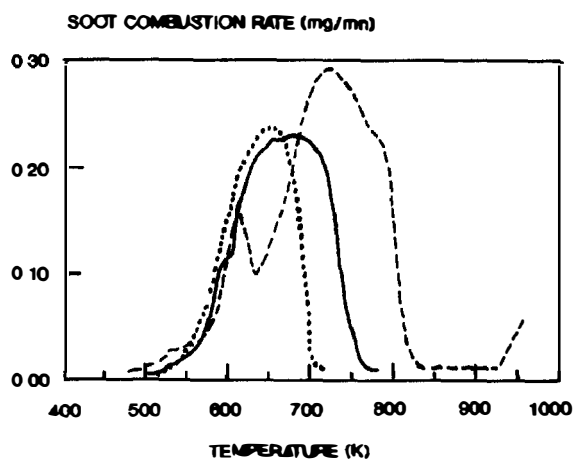


Fig 2 DTG curves of the combustion (15% O₂ in N₂) of soot in the presence of V₂O₅ (· · ·), in the presence of CeO₂ (—) and in the presence of La₂O₂CO₃ (- - -)

ered in the presence of V₂O₅ (- 220 K), CeO₂ (- 190 K) or La₂O₂CO₃ (- 150 K) TiO₂ and ZrO₂ addition resulted in a 80–90 K decrease in combustion temperature and the combustion temperature of the (Al₂O₃ + soot) and (SiO₂ + soot) mixtures (Fig 1) resembled that of pure soot

The DTG curve of La₂O₂CO₃ during combustion of the soot shows a three-peak pattern (Fig 2) The low-temperature weight loss (640–645 K) is accompanied by water production, as determined by on-line mass spectrometric analysis

The second weight loss peak is situated at 715–730 K, followed by a high-

TABLE 5

Characteristics of the soot combustion in the presence of supports

| Support | Temp of max (K) (TGA) | CO/(CO + CO ₂) (TPO) | Temp. of max (K) after SO ₂ treatment (TGA) ^a |
|--|-----------------------------|-------------------------------------|---|
| None | 865-880 | 0.30 | - |
| Al ₂ O ₃ | 845-865 | 0.31 | 840-860 |
| SiO ₂ | 865-875 | 0.29 | - |
| TiO ₂ | 775-790 | 0.16 | 805-825 |
| ZrO ₂ | 785-795 | 0.17 | 815-835 |
| CeO ₂ | 670-690 | 0.04 | 765-775 |
| La ₂ O ₂ CO ₃ | 715-730 | 0.08 | 725-735 |
| V ₂ O ₅ | 645-655 | 0.12 | 675-685 |

^aFor samples pretreated with SO₂, combustions were performed in the presence of O₂ (15%) + Ar + 100 ppm SO₂

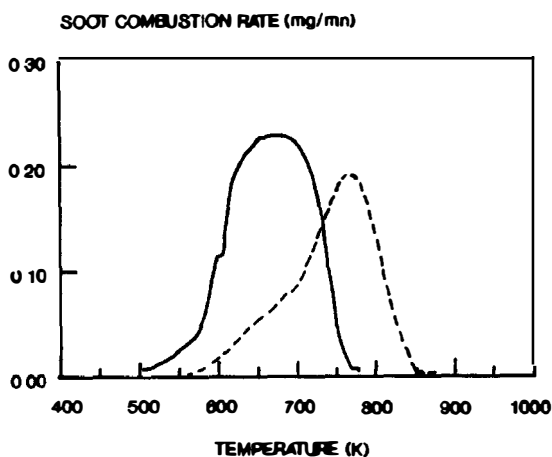


Fig 3 DTG curves of the combustion of soot in the presence of CeO₂ (15% O₂ in N₂) (—) and in the presence of SO₂-treated CeO₂ (100 ppm SO₂, 15% O₂ in Ar) (- - -)

temperature weight loss, which starts at 935 K. Both weight losses were accompanied by CO₂ production as evidenced by MS. In order to determine the DTG curve of La₂O₂CO₃ itself, a sample without soot was submitted to similar experimental conditions. A low-temperature (605 K) weight loss accompanied by water production and a high-temperature peak (975 K) accompanied by CO₂ production accounted for two of the weight losses found during soot combustion in the presence of La₂O₂CO₃.

Apart from La₂O₂CO₃, all (support + soot) mixtures show a single combustion peak, as confirmed by DTA and MS.

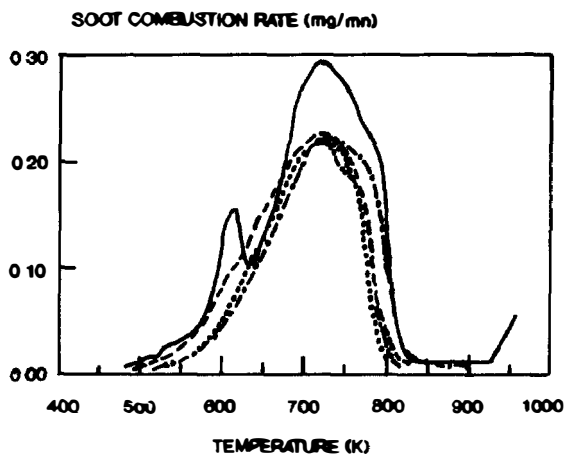


Fig 4 DTG curves of the combustion of soot in the presence of $\text{La}_2\text{O}_2\text{CO}_3$ 15% O_2 in N_2 (—) 100 ppm SO_2 , 15% O_2 in Ar, after SO_2 pretreatment (6 h at 625 K) (· · ·) 100 ppm SO_2 , 15% O_2 in Ar, after SO_2 pretreatment (6 h at 925 K) (- - -) 100 ppm SO_2 , 15% O_2 in Ar, after SO_2 pretreatment (20 h at 925 K) (- -) 100 ppm SO_2 , 15% O_2 in Ar, after SO_2 pretreatment (6 h at 925 K after heat treatment at 975 K) (- · -)

CO oxidation

The $\text{CO}/(\text{CO} + \text{CO}_2)$ ratios in Table 5 indicate that TiO_2 , ZrO_2 and even V_2O_5 are moderate CO oxidation catalysts, whereas CeO_2 and $\text{La}_2\text{O}_2\text{CO}_3$ are relatively good catalysts for this reaction. None of the used supports is capable of complete CO conversion.

Sulfur dioxide poisoning of the supports

An important parameter for testing the applicability of catalysts for the combustion of soot is resistance towards SO_2 poisoning.

Preliminary experiments showed that adding 100 ppm SO_2 to the reaction mixture caused only a minor increase in the combustion temperature of (support + soot) mixtures, suggesting that a more severe poisoning procedure should be used. Therefore, the solids, prior to mixing with soot, were treated for 6 h at 625 K in a flow of 100 ppm $\text{SO}_2/15\% \text{O}_2/\text{N}_2$. After such a treatment, the catalyst was mixed with soot following the procedure described previously, and subsequently the reactivity was determined gravimetrically in 15% $\text{O}_2/100$ ppm SO_2 in balance Ar with this poisoning pretreatment. The sulfate formation was promoted. However, the absence of deactivation after the reactivity test was not a guarantee that a support would remain active under more realistic conditions. In fact our poisoning procedure acted as a negative test. The results are reported in Table 5.

A slight increase of the combustion temperature (10–30 K) was observed

for all the active supports, except CeO_2 for which the combustion curve was shifted by about 100 K (Fig. 3). $\text{La}_2\text{O}_2\text{CO}_3$ being the less affected by the poisoning procedure at 625 K, was further tested by submitting the solid to a 6- or 20-h SO_2 pretreatment at 925 K. Furthermore, a $\text{La}_2\text{O}_2\text{CO}_3$ sample was heated in air to 975 K in order to decompose the carbonate groups, followed by SO_2 poisoning at 925 K for 6 h. As shown in Fig. 4, in all cases, the catalytic activity was slightly lowered after exposure to SO_2 , but remained at the high level obtained for the unpoisoned sample.

DISCUSSION

As can be seen in Table 4, increased mixing times result in higher combustion rates. This effect was found for all the catalysts studied and was largest for the most active catalyst. Furthermore, the combustion rate was somewhat higher, when the (catalyst + soot) mixture was mixed in air. The soot combustion is a reaction of a solid (soot) with oxygen, catalyzed by a solid catalyst. If one accepts that the rate of the soot combustion is dependent on the contact zones between the soot and the catalyst, it is obvious that the method used to mix the two solids influenced the rate of soot combustion. The increased reactivity with increased mixing time can be explained by a more intimate contact and also by a structural modification of the soot, especially in the presence of air. According to Barthe et al. [12], the reactivity of demineralized coke increased after 24 h grinding time due to the formation of carboxylic surface groups during ball-milling and subsequent exposure to air.

Although this mixing procedure does not reflect the actual soot-catalyst contact on a soot filter it answers to the desired purposes for this study which is to establish a reactivity scale for the different oxides; it allows a reproducible mechanical mixing of catalysts with soot and, as is shown, the mixing efficiency is high enough to show differences in catalytic activity for different catalysts. Based on these results, a standard mixing procedure (30 min under argon atmosphere in order to minimize structural modifications of the soot [12]) is used throughout this study.

The combustion experiments of the (support + soot) mixtures clearly show that some supports can act as a catalyst for the combustion of soot and simultaneously for CO oxidation. The results permit a division of the supports into three groups. (1) Little or no catalytic effect: Al_2O_3 and SiO_2 . (2) Moderate activity: TiO_2 and ZrO_2 . (3) High activity: CeO_2 and $\text{La}_2\text{O}_2\text{CO}_3$.

The lack of activity of Al_2O_3 and SiO_2 is in agreement with the results of McKee [13], who measured the effect on the oxidation of graphite. The combustion temperature of the (Al_2O_3 + soot) and (SiO_2 + soot) mixtures are similar to those of pure soot.

The order of reactivity found in this study corroborates the results for graphite oxidation reported by Heintz and Parker [14]. The catalyzed oxidation of

graphite at 975 K in their study followed the order: $V \sim Ce > La \gg Zr > Ti$. The relatively high activity of $La_2O_2CO_3$ is slightly unexpected since it was reported earlier that La_2O_3 is a poor oxidation catalyst [15]: this discrepancy could be due to the use in ref. 15 of a La_2O_3 material having a low specific area.

The low- and high-temperature peaks in the three peak pattern of the weight loss curve of $(La_2O_2CO_3 + soot)$ are also present when the support is heated under similar conditions in the absence of soot. The low-temperature peak is accompanied by water production as evidenced by MS and can be ascribed to the decomposition of $-OH$ groups [16]. This peak is very intense when $La(OH)_3$ is submitted to a temperature program. The high-temperature maximum is due to the decomposition of the carbonate group of $La_2O_2CO_3$ resulting in La_2O_3 and CO_2 [16,17]. It is known that, even at room temperature, the reverse reaction can take place. Therefore, under diesel exhaust conditions, lanthanum oxide will probably be in the carbonated form.

The poisoning of the CeO_2 with SO_2 results in a substantially higher combustion temperature. The deactivation of CeO_2 upon exposure to SO_2 was also found by Sultanov et al [18], who studied the effect of SO_2 on CO oxidation activity. The temperature at which 50% CO conversion was reached increased from 600 to 1020 K after exposure to SO_2 . Only after heating the deactivated CeO_2 to 1175 K could the initial CO oxidation activity be restored [18].

V_2O_5 is more stable than CeO_2 towards SO_2 . However, a deactivation is observed, in disagreement with ref. 7. It is probable that under test conditions vanadium sulfate is formed. Nevertheless, after the poisoning procedure, V_2O_5 remains the most active oxide of the series.

In contrast with CeO_2 and V_2O_5 , soot combustion in the presence of $La_2O_2CO_3$ remained virtually unchanged after SO_2 poisoning. Also after prolonged poisoning (20 h) and at a higher poisoning temperature ($T = 925$ K) the combustion temperature hardly changed. Thus, lanthanum oxide exhibited an higher activity than TiO_2 and could be used as a support. Apparently, $La_2O_2CO_3$ and La_2O_3 are stable towards SO_2 under the applied poisoning conditions. Even after decomposition of the carbonate groups and subsequent SO_2 exposure the high soot combustion activity is retained.

CONCLUSIONS

The mixing procedure and mixing conditions are important parameters, which influence the combustion characteristics of the catalysts. The applied mixing procedure is a reproducible method, which enables us to discriminate between the catalytic effect of different catalysts on the combustion of soot particulates.

In the absence of SO_2 , the studied supports can be divided into three groups, based on their catalytic effect on soot combustion and CO oxidation. (1) Not

active: SiO_2 and Al_2O_3 . (2) Moderately active: TiO_2 and ZrO_2 (3) Active: $\text{La}_2\text{O}_2\text{CO}_3$ and CeO_2 .

From the active supports, only $\text{La}_2\text{O}_2\text{CO}_3$ is unaffected by SO_2 poisoning and can be regarded as a promising support for oxidative diesel soot catalysts. V_2O_5 is slightly affected by SO_2 poisoning but still remains the most active oxide of our test. CeO_2 is easily deactivated by the SO_2 treatment, probably by the formation of sulfates.

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