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Low temperature diesel soots combustion using copper based catalysts modified by niobium and potassium promoters

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Abstract

Gravimetric temperature programmed oxidation was used to study the combustion of a diesel soot mixed with copper catalysts supported on La_2O_3 or $La_2O_2CO_3$. In a first step, different systems associating copper oxide with an other metal oxide were prepared and tested in presence of SO_2. The association of copper and niobium was found the most active. The influence of alkali on the activity was also studied. It results that potassium is the most effective in lowering the combustion temperature domain in agreement with literature. Finally, Cu-Nb-K catalysts deposited on lanthanum oxide have an improved catalytic activity at low temperatures compared to Cu-V-K or Cu-Mo-K/TiO_2, reported in literature. For this catalyst, the maximum oxidation rate was observed at ca. 300°C with the combustion starting at about 250°C. A similar behaviour is obtained when replacing Nb by Ta or the support La_2O_3 by either $La_2O_2CO_3$ or TiO_2.

Keywords: Cu catalysts; Gravimetric temperature programmed oxidation; Diesel soot; Niobium promoter

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1. Introduction

Restrictions on emissions from diesel engines are being tightened both in the US and in Europe. In particular, new EU standards concerning the particulate emissions in the diesel vehicles exhausts will be effective in 1996. A particulate limit of 0.08 g km^{-1} will be imposed. Moreover, a growing recognition of the influence of the particulates on the health problems may lead to more stringent limitations. Although significant progresses have been made in the design and technology of the diesel engines, the use of exhaust aftertreatment catalytic device seems indispensable to meet the new standards to come. A literature survey indicates that the most active oxides in the carbon oxidation or soot combustion are those able to undergo redox cycles during the oxidation processes. Among them, the most often cited are V_2O_5, CuO, MoO_3, MnO_2, Fe_2O_3, WO_3 or CeO_2 [1-5]. Mixed oxides are generally more active than a single one. In most of the patents, copper is the base element and synergetic effects are obtained by addition of several elements. In fact, the usual diesel exhaust catalysts

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have multiple active constituents. Among the various formulations cited in the literature, Cu + V + K and Cu + Mo + K systems appear the best up to date [4,6,7]. However, V_2O_5 has a low melting point (690°C) and loss of MoO_3 by sublimation could eventually occur, which is detrimental for the stability of the catalyst. The objective of this paper is to find systems able to burn at low temperatures the soots present in the diesel emissions. We have tried to find synergetic effects between copper and transition metal oxides, particularly the possibility of substituting, for V or Mo, other more stable metal oxides, like niobium or tantalum oxides which have melting points of respectively 1512 and 1785°C. Although neither Nb_2O_5 nor Ta_2O_5 showed any catalytic activity in the oxidation of graphite [3], their chemistry close to that of V_2O_5 allowed to consider a good activity for oxidation.

2. Experimental

The support $La_2O_2CO_3$ and La_2O_3 were prepared by calcination of a citrate precursor at 500°C under air for 15 h. To synthesize La_2O_3, it was necessary to pretreat the citrate at 80°C under vacuum instead of air for the dioxomonocarbonate. Their specific surface areas were 16 and 20 $m^2\ g^{-1}$, respectively for the oxide and the carbonate. TiO_2 was a Degussa P25 support with 50 $m^2\ g^{-1}$.

The supported catalysts were prepared by successive incipient wetness impregnation and calcination at 800°C for 2 h in air. The starting salts were either nitrates or chlorides. For Nb and Ta only the chlorides were used. In the following, the catalysts are referenced with numbers between parentheses indicating the nominal quantity (mmol of each element per g of support). To simulate the poisoning due to the presence of sulfur in the diesel fuel, the samples were treated before each combustion test for 6 h at 350°C in a flux of air containing 100 ppm SO_2. Then, they were mixed with soot (20 wt.-% of the final mixture) according to a well reproducible procedure [5].

The soot was collected from a diesel fuel burner. Its surface area was 300 $m^2\ g^{-1}$, as determined by the BET method after desorption at 250°C. Its chemical composition was previously detailed [5]. The ash content was 1.0 wt.-% and the C/H ratio was around 6. This value is higher than that usually found in the literature, which can be related to a low reactivity of the soot. The percentage of volatile materials (18 wt.-%) was obtained from a thermodesorption under argon up to 800°C. After a small desorption peak at 65°C due to water loss (2 wt.-%), the main peak started at 400°C with a maximum at 650°C. Because of the elevated temperature, this high-temperature weight loss is probably caused by pyrolysis of (part of) the soot and not by a desorption of volatile materials which could affect the combustion of soot.

The combustion of the soot was followed by thermogravimetry in a TGA–DTA 92 Setaram apparatus coupled with a Balzers 420 QMG mass spectrometer. The TPO was performed with a heating rate of 5°C min^{-1}. The gas mixture included 15% O_2 + 100 ppm SO_2 in N_2. Some experiments were also done in a microreactor in order to measure the selectivity in carbon monoxide.

3. Results and discussion

3.1. Study of the systems oxide + oxide / support

As illustrated in Fig. 1, the derivative curve of the weight loss during the TPO exhibits a major oxidation step with a marked minimum. Using the position of this minimum which corresponds to the maximum rate of combustion, it is possible to compare the activity of the different catalysts.

The initial soot is difficult to oxidize. In air, it starts to burn at 420°C and the maximum oxidation rate is obtained at T_{max} of about 600°C [5]. We have shown in a previous study, that

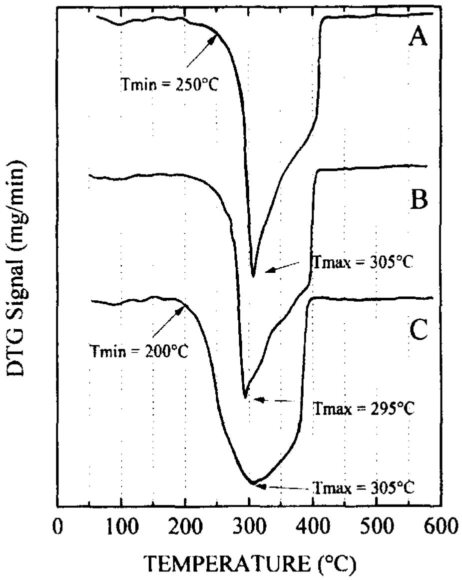

Fig. 1. Activity in soot combustion measured by thermogravimetry (DTG signal) during a TPO treatment: 5°C min^{-1}, 15% O_2 + 100 ppm SO_2 in N_2, soot/catalyst = 1/4. The three curves are related to Cu(2)-Mo(2)-K(2)/TiO_2 (curve A), Cu(2)-V(2)-K(2)/TiO_2 (curve B) and Cu(2)-Nb(2)-K(2)/La_2O_3 (curve C).

Table 2
Influence of the content of the active elements in the system Cu-Nb/$La_2O_2CO_3$ on the temperature T_{max} (°C) at the maximum oxidation rate of the soot

Catalyst [a]	Cu(1)-Nb(1)	Cu(1)-Nb(2)	Cu(2)-Nb(1)	Cu(2)-Nb(2)
T_{max}	405	390	380	370

[a] The numbers between parentheses correspond to the amount of mmol of each element per g of support.

$La_2O_2CO_3$ intimately mixed with soot, could decrease this temperature to 460°C and that the activity of this support was unaffected by SO_2 poisoning [5]. In the case of La_2O_3 and TiO_2, we obtained 430 and 530°C, respectively.

In this preliminary study, $La_2O_2CO_3$ was impregnated with salts of V, Cu and Mo, since, as outlined in the introduction, these elements catalyse oxidation reactions. Cerium oxide was eliminated as being poisoned by sulfates adsorption [5]. As mentioned before, niobium was also studied, since niobium oxide is able to behave as V_2O_5 but with a better thermal stability than vanadium or molybdenum oxides. Bimetallic systems were prepared, based on copper or Nb. Table 1 gives for each system the values of T_{max}, the temperature for which the oxidation rate is maximum.

There is no significant change in activity when copper is deposited on the support which is itself already active. Among the bimetallic systems, the couple Cu–Nb is the most active for oxidation with a T_{max} of 405°C. Its activity is higher than that observed for the system Cu + V, although Ahlström and Odenbrand found it promising [8,9]. The same comparison for solids based on niobium indicates also that the association between Cu and Nb is the best of the series.

As shown in Table 2, the combustion activity is improved when the amount of active phase is doubled. The order of activity is as follows: Cu(2)–Nb(2) > Cu(2)–Nb(1) > Cu(1)–Nb(2) > Cu(1)–Nb(1). Both elements are important in the activity increase, but copper seems to have the largest influence. For the Cu(2)–Nb(2)/$La_2O_2CO_3$ catalyst, T_{max} = 370°C. At this temperature, the selectivity for CO is 8%, whereas it is 30% in absence of catalyst.

Table 1
Temperature T_{max} (°C) at the maximum oxidation rate of the soot as determined by DTG

Catalyst [a]	Support alone	Cu(1)	Cu(1)-V(1)	Cu(1)-Nb(1)	Cu(1)-Mo(1)
T_{max}	460	450	440	405	440
Catalyst [a]			Nb(1)-V(1)	Nb(1)-Cu(1)	Nb(1)-Mo(1)
T_{max}			510	405	525

[a] $La_2O_2CO_3$ as support.

3.2. Influence of alkali and earth-alkali additives

In the literature, it has been shown that alkali can promote the activity in graphite or soot combustion [4,10]. For this reason, we prepared several three-metallic systems by adding 2 mmol of alkali (Na, K, Rb, Cs) to the Cu(2)–Nb(2) couple. In this case, the support was lanthanum oxide La_2O_3 instead of dioxomonocarbonate. The corresponding T_{max} was found to be 355°C instead of 370°C for the $La_2O_2CO_3$ support. Two other catalysts were also tested with earth alkali additives (Ca, Ba) which are also effective in graphite oxidation [11]. The results are given in Table 3.

A significant improvement of the combustion activity was obtained with potassium addition, whereas sodium or calcium has no significant influence and Rb, Cs or Ba have a negative effect. The best system corresponding to the catalyst Cu(2)–Nb(2)–K(2)/La_2O_3 had T_{max} 305°C. A similar behaviour was found when replacing the lanthanum support by titania [12]. With the initial $La_2O_2CO_3$ support, T_{max} is 320°C. For these catalysts, the CO selectivity is not changed by alkali addition (8%).

3.3. Comparison of the catalysts X(2)–Nb(2)–K(2)/La_2O_3 and Cu(2)–X(2)–K(2)/La_2O_3

The results presented above put in evidence a large effect of the association of copper, niobium and potassium on the soot combustion. In order to precise if this synergy is due mainly to copper or to niobium and also if other systems could be better potential catalysts for soot oxidation, we have compared the activity of different solids based either on niobium or copper, i.e., the systems X(2)–Nb(2)–K(2)/La_2O_3 and Cu(2)–X(2)–K(2)/La_2O_3. The transition metal oxides were chosen according to their ability to have several oxidation numbers and to undergo redox cycles. The concentrations of each element were 2 mmol g^{-1} support. The results are given in Table 4.

Table 3
Influence of the nature of alkali additive on the temperature of the maximum combustion rate. The base system is Cu(2)–Nb(2)/La_2O_3

Alkali	Without	Na(2)	K(2)	Rb(2)	Cs(2)	Ca(2)	Ba(2)
T_{max} (°C)	355	350	305	390	410	350	380

Table 4
Temperature T_{max} (°C) at the maximum oxidation rate for catalysts with three components

VB	VI B	VII B	VIII	I B	II B
X(2)–Nb(2)–K(2)/La_2O_3					
V		Mn	Fe	Cu	Zn
420		380	425	305	375
Cu(2)– X(2)–K(2)/La_2O_3					
V		Mn	Fe	Cu	Zn
295		360	370		350
Nb	Mo				
305	305				
Ta	W	Re			
310	350	395			

In the series X(2)–Nb(2)–K(2)/La_2O_3, copper appears to be a better element than Mn or V, which confirms the results obtained in absence of potassium (Section 3.1). In the second series, the best activity patterns were obtained when copper and potassium are associated with V, Nb, Ta or Mo. It seems logical to obtain similar behaviours for V, Nb and Ta since they all are Vb elements with the same type of chemistry. Molybdenum is a VIb element and possesses also a large number of potentially available oxygen. However, tungsten, which is also a VIb element, does not really improve the oxidation activity.

From these data, it results that the best catalysts of this study are Cu(2)–Nb(2)–K(2)/La_2O_3, Cu(2)–V(2)–K(2)/La_2O_3 and Cu(2)–Mo(2)–K(2)/La_2O_3. In the literature, similar formulations were proposed. Watabe et al. [4] have prepared catalysts containing $CuCl_2$–KCl–NH_4VO_3 or $CuCl_2$–KCl–$(NH_4)_6Mo_7O_{24}$ supported on titanium oxide. The combustion temperature were lowered to 320–370°C. Similar formulations Cu–V–K supported on alumina were also proposed by Ciambelli et al. [6,7] and were found active in the combustion of soots and various carbon based materials [13–15]. For a better comparison of these different systems, we prepared two of these catalysts and tested them in our conditions.

Fig. 1 gives the DTG curves for the three solids. The catalysts based on vanadium and molybdenum present a narrow domain of combustion with a rather sharp maximum at 295 and 305°C, respectively. On the opposite, the temperature domain for the sample based on niobium is broader with the maximum also at 305°C, but is more efficient at lower temperature. Indeed, we observe the beginning of the combustion at ca. 200°C instead of 250°C for the solids based on vanadium or molybdenum. Finally, we noted that, for all samples, the combustion is total at about 380°C. We can conclude that niobium can serve advantageously as a substitute for vanadium or molybdenum.

4. Conclusion

Compared to the previous systems, Cu–V–K/TiO_2 and Cu–Mo–K/TiO_2, it has been shown that Cu–Nb–K/La_2O_3 catalysts can be a better catalyst in the combustion of Diesel soots. If the maximum oxidation rates occur at almost the same temperature (ca. 300°C, simulated Diesel soots), it is clear, from the TPO–DTG curves, that in the case of the Cu–Nb–K system, the beginning of the combustion starts at almost 200°C, e.g., at a temperature lower than 250°C which is required with the other systems.

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