Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 223 (2004) 114–121

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

# Diesel soot combustion on $Mo/Al_2O_3$ and $V/Al_2O_3$ catalysts: investigation of the active catalytic species

Isabela Caldeira Leite Leocadio,[a] Silvana Braun,[b] and Martin Schmal [a,*]

[a] NUCAT/PEQ/COPPE, Universidade Federal do Rio de Janeiro, Centro de Tecnologia bl.G, P.O. 68502, 21945-970, Rio de Janeiro, Brazil
[b] Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, R. Marquês de São Vicente, 225, 22453-900, Rio de Janeiro, Brazil

Received 23 October 2003; revised 7 January 2004; accepted 12 January 2004

## Abstract

We studied the reactivity of $Mo/Al_2O_3$ and $V/Al_2O_3$ catalysts for soot combustion, and the influence of their volatile ($MoO_3$ and $V_2O_5$) and superficial dispersed species. Differential exploratory calorimetry and temperature-programmed oxidation (TPO) experiments with catalyst and soot mixtures showed that lower combustion temperatures were obtained with increasing loading of Mo or V. TPO experiments performed on separate layers of soot and catalyst showed that both species were able to oxidize CO to $CO_2$, but the combustion temperature was lowered only when soot was in contact with the dispersed species. Infrared absorption spectroscopy analyses of CO adsorbed at several temperatures showed that all catalysts formed superficial carbonated species; however, on molybdenum catalysts, they were easily decomposed. Therefore, it is suggested that the reaction occurs by formation of carbonate species at the catalyst/soot interface yielding $CO_2$, and the better performance of molybdenum catalysts is due to the higher instability of carbonated species.

*Keywords:* Diesel particulate; Soot; $MoO_3/Al_2O_3$; $V_2O_5/Al_2O_3$; Molybdenum; Vanadium; Soot oxidation; Catalytic combustion

## 1. Introduction

Diesel engine vehicles are very popular due to the relatively higher efficiency of the fuel and to the longer durability of the engines when compared with gasoline engines. Diesel engines use oxidative mixtures with air/fuel ratios higher than 20, which result in relatively low-temperature combustion, so these engines produce low emissions of $CO_2$, $NO_x$, CO, and hydrocarbons; however, the emission of particulate matter is high [1–3].

The particulate matter consists basically of agglomerates of carbon nuclei, and of hydrocarbons, $SO_3$ or sulfuric acid, and water, adsorbed or condensed onto these carbon nuclei [1,4]. This particulate can be divided into two parts: the insoluble organic fraction (IOF), containing mainly carbon, and the soluble organic fraction, which contains the hydrocarbons derived from diesel and lube oil [5].

The negative effects of diesel particulate on health have stimulated the development of emission reduction technologies [2]. Despite the complex composition of diesel particulate, the principal challenge is the elimination of the insoluble organic fraction, also called *soot*. Despite of the efforts to improve fuel injector design in the last decade, it has not been possible to reduce soot emission to values lower than the limits of the legislation. A promising alternative is the development of a filter with a catalyst coverage that combines retention and oxidation of the emitted particulate matter [6], but it requires high performance at usually low temperatures of diesel exhaust. The technological key is to find a catalyst that decreases the combustion temperature of soot to near the diesel exhaust temperature and continuously oxidizes it [1].

Many attempts have been made to develop catalysts that promote soot combustion. Systematic investigations by Neeft et al. [6,7] have shown that some oxides such as $V_2O_5$ and $Co_3O_4$ exhibit high activity in tight contact with soot but very low activity in loose contact. Other oxides, such as $MoO_3$ and PbO, even less active than $V_2O_5$ and $Co_3O_4$ in tight contact, are still active in the loose mode. These authors reported that contact between soot and catalyst is a rate-limiting factor in oxidation of soot and that the contact under practical conditions is poor [7]. However, comparison of the results showed that some of those oxides, among them $MoO_3$, exhibit similar performance in both types of contact.

---

[*] Corresponding author.
*E-mail address:* schmal@peq.coppe.ufrj.br (M. Schmal).

0021-9517/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2004.01.011

According to these authors, for these oxides, catalytic activity may be related to the mobility of the active species in the reaction condition, or by surface migration or by melting of catalyst material and gas-phase transportation by a high partial pressure of the catalyst, so this mobility could improve the contact between soot and catalyst [6].

Although several catalytic systems based on transition metal oxides, single [6,8–12] or mixed [6,12–15], especially vanadium and molybdenum oxides, have been studied for diesel particulate oxidation, the idea of improving soot/catalyst contact has led many authors to test high-mobility catalysts based on eutectic mixtures [12–14], chloride-containing mixtures [13,15], and potassium-promoted oxides [15–17], which have lower melting points than single oxides. Thus, according to that idea, in a loose contact situation, migration of active component across the soot surface could play an important role in the reaction, as mobile catalysts could form a wet phase improving contact with soot by covering its surface and then catalytic reaction could occur. However, Van Setten et al. [14,18,19] have recently studied the activity of molten salts, especially $Cs_2MoO_4 \cdot V_2O_5$ and $CsSO_4 \cdot V_2O_5$, and have reported that, despite the promising activity of liquid catalysts, these coatings could not be applied to real systems because their thermal stability is low, so catalyst compounds could be emitted into the environment and the oxidation activity would drop dramatically [19]. These authors has also shown, by scanning electron microscopy analysis, that the liquid state of the catalysts does not seem to have decisive influence on their performance, not wetting the soot and having no affinity for it [19]. Consequently, although the creation of tight contact in the catalysts remains in theory the best option for continuous regeneration at very low temperatures, under practical conditions it does not seem feasible because a liquid catalyst does not work [19]. Therefore, loose catalyst/soot contact seems to be the only option. So it is important to investigate the mechanism of catalytic oxidation of soot in this type of contact.

Only a few studies have described catalytic reactions in detail, however. Proposed mechanisms basically involve a redox mechanism [8,16,20,21], consisting of carbon oxidation by lattice oxygen from the catalyst and reoxidation of the catalyst by oxygen from the gas phase, and oxygen spillover [8,22,23], which consists of dissociation of gas-phase oxygen over the catalyst followed by its transfer to the soot surface for reaction. A combination of both mechanisms occurring simultaneously was also proposed [8].

In previous work, we showed that the nature of the support could originate different molybdenum species in $Mo/SiO_2$ and $Mo/TiO_2$ catalysts, and that these different species presented performed differently in soot combustion reactions [24]. In another work, we showed that $MoO_3$ [25] and $V_2O_5$ [unpublished results] can spread over alumina by effect of thermal treatment originating dispersed molybdenum and vanadium species different from those obtained when $Mo/Al_2O_3$ and $V/Al_2O_3$ systems are prepared by an impregnation method. Because alumina is an important support for commercial catalysts, it is interesting to study the performance of this system in the diesel soot combustion reaction. Characterization of those $Mo/Al_2O_3$ and $V/Al_2O_3$ systems has shown that they have dispersed species and small crystals of $MoO_3$ and $V_2O_5$, respectively, which remain from the catalyst preparation procedure [25]. Considering that $MoO_3$ may sublimate [7] and $V_2O_5$ may melt and then volatilize [7] in the temperature range of the soot combustion reaction, it is possible that these oxides are also responsible for catalyst performance, because they could migrate to the soot.

So the aim of this work is to study comparatively the reactivity of $Mo/Al_2O_3$ and $V/Al_2O_3$ catalysts in the soot combustion reaction, intending to identify the Mo and V species really active and to understand the reaction pathway.

## 2. Experimental

### 2.1. Materials

$MoO_3$ (Aldrich), $V_2O_5$ (Vetec), and Alumina C-type (Degussa AG) were used to prepare $Mo/Al_2O_3$ and $V/Al_2O_3$ catalysts. The textural properties of alumina are: $100\ m^2\,g^{-1}$ specific area (BET surface area), average particle size 13 nm, and apparent density $50\ g\,dm^{-3}$ [26]. This support is nonporous and was chosen to obtain catalytic systems with textural properties similar to those of the soot. This material was heated in a muffle furnace at 773 K for 4 h, raising the temperature at $5\ K\,min^{-1}$, before catalyst preparation.

For reaction study, a model soot (Printex-V, Degussa AG) of $72\ m^2\,g^{-1}$ surface area (BET), 25-nm average particle size, and apparent density $160\ g\,dm^{-3}$ [27] was used.

### 2.2. Catalyst preparation

$Mo/Al_2O_3$ and $V/Al_2O_3$ catalysts were prepared by the thermal spreading method, which is appropriate for preparing catalysts using nonporous supports [25] and consists of submitting oxide mixtures to thermal treatment. Physical mixtures of $MoO_3 + Al_2O_3$ or $V_2O_5 + Al_2O_3$, with 5 and 14 wt% loadings of $MoO_3$ or $V_2O_5$, were prepared by hand-grinding these mixtures in a mortar for 10 min. Then, these mixed oxides were heated in a muffle furnace under air atmosphere at a heating rate of $10\ K\,min^{-1}$ up to 773 K for $MoO_3 + Al_2O_3$ and up to 873 K for $V_2O_5 + Al_2O_3$ and held constant for 24 h, respectively. These catalysts are referred to as 5Mo, 14Mo, 5V, and 14V.

### 2.3. Reactivity study

The soot combustion reaction was carried out by differential scanning calorimetry (DSC) and temperature-programmed oxidation (TPO). Each catalyst was mixed with soot at a 2:1 catalyst:soot (w:w) ratio by gently mixing this compounds with a spatula, which resulted in loose physical contact mixtures [8]. The alumina does not exhibit a catalytic effect [11], so it was used as a diluent to study a noncatalyzed reaction under conditions similar to those for catalyzed reactions with respect to heat and mass transfer.

DSC analyses were carried out with Rigaku TAS-100 equipment with a TG 8110 simultaneous TG-DSC analyzer, using 2 mg of the catalyst + soot mixture, 13% $O_2/N_2$ flow at 61 $\mathrm{mL\,min^{-1}}$, and heating rate of 10 $\mathrm{K\,min^{-1}}$. To compare with literature results, the performance of the catalysts was evaluated taking the temperature corresponding to the maximum of the peak, called combustion temperature ($T_c$), which represents the temperature of maximum soot combustion. The difference between the combustion temperature of the DSC curves of the soot and catalyst mixture and the soot and alumina mixture indicated the catalytic effect.

The enthalpy of the soot reaction in the presence of the catalysts or the alumina was calculated from the area under the DSC curve and was normalized taking into account the amount of sample.

The apparent activation energy of the combustion reaction for these catalysts was estimated by the Redhead method [16,28,29]. This method allows determination of the apparent activation energy if the temperature of maximum reaction rate and the reaction order are known. In most cases reported in the literature [16,29–31], the reaction order was estimated to be a unit or less (range 0.6–1.0) and to remain constant for the greater part of the reaction. For the present article we assumed the same considerations. Thus, from the equation

$$\ln\left(\frac{\beta}{T_c^2}\right) = -\frac{E}{R}\cdot\frac{1}{T_c} + \ln\left(\frac{AR}{E}\right), \tag{1}$$

where $T_c$ is combustion temperature [28], $R$ is the gas constant (8.314 $\mathrm{J\,K^{-1}\,mol^{-1}}$), and $A$ is the frequency factor, it is possible to determine the apparent activation energy ($E$) for the soot combustion reaction regardless of the reaction order by taking differential thermal analysis at several heating rates.

Therefore, two other DSC analyses were carried out using heating rates ($\beta$) of 15 and 20 $\mathrm{K\,min^{-1}}$.

The TPO experiments were performed in a test unit using a fixed-bed quartz reactor coupled to a mass spectrometer Balzers/Prisma-QMS200 quadrupole. For quantification of reactants and products ($O_2$, CO, $CO_2$) the area under the curves was related to the areas from curves of known volume pulses of these compounds. Quantification of CO ($m/e = 28$) was performed discounting the amount of CO from $CO_2$ ($m/e = 44$) fragmentation. The soot and catalyst mixtures and the soot and alumina mixture were prepared as described, using about $0.0100 \pm 0.0005$ g of soot. These samples were pretreated under helium flow at 60 $\mathrm{mL\,min^{-1}}$, at 473 K for 1 h, and a heating rate of 10 $\mathrm{K\,min^{-1}}$. Then, the reaction was carried out under a descendent flow of 5% $O_2$/He at 60 $\mathrm{mL\,min^{-1}}$, at 10 $\mathrm{K\,min^{-1}}$ from 298 to 923 K, and kept at 923 K until complete oxidation, i.e., until CO and $CO_2$ were no longe detected. The temperature of maximum oxygen consumption ($T_c$) was taken for comparison of catalyst performance.

To investigate the contribution of both species in catalyst 14Mo (dispersed Mo species and small crystallites of $MoO_3$) [25], soot combustion was performed in two other TPO experiments, using separated beds for catalyst 14Mo and the mixture of soot and alumina: (a) by placing the soot + alumina mixture under the catalyst sample (referred to as 14Mo/soot); and (b) by placing the catalyst sample in the reactor, and then the soot + alumina mixture above (referred to as sample soot/14Mo). The beds were separated by quartz wool, and the catalyst:soot ratio was 2:1 (w/w) for comparison with the other TPO analyses. Similarly, two other TPO analyses were performed with catalyst 14V:samples 14V/soot and soot/14V.

Infrared spectroscopic analyses of the catalysts were carried out after carbon monoxide adsorption, using a Perkin–Elmer 2000 infrared spectrometer operating with a spectral resolution of 4 $\mathrm{cm^{-1}}$. Catalyst samples of about 25 mg were pressed into self-supporting wafers, and then pretreated at 773 K under an oxygen flow of 50 $\mathrm{mL\,min^{-1}}$ for 1 h at a heating rate of 10 $\mathrm{K\,min^{-1}}$, followed by vacuum at $10^{-5}$ Torr for 1 h. After the system cooled to room temperature, carbon monoxide was added at 30 Torr for about 15 min until pressure stabilization; then the first IR spectrum was taken. With the system kept closed, without evacuation, it was heated at 10 $\mathrm{K\,min^{-1}}$ to 373 K for 15 min, and the second IR spectrum was taken after waiting for the system to cool at room temperature. This procedure was repeated twice, by heating the system to 573 and 773 K, and two other IR spectra were taken.

## 3. Results and discussion

DSC profiles of soot combustion in the presence of alumina and catalysts 5Mo, 14Mo, 5V, and 14V are shown in Fig. 1, whereas Table 1 lists the combustion temperatures ($T_c$), enthalpies ($\Delta H$), and activation energies ($E$).

The soot combustion temperature in the presence of alumina is 897 K (called “soot” in Table 1). However, this temperature decreases in the presence of the catalysts, being 869, 826, and 889 K for 5Mo, 14Mo, and 14V, respectively. For catalyst 5V the combustion temperature is 904 K, which is very close to that of alumina. However, it can be observed that $T_c$ decreases as Mo and V contents increase. The best performance was displayed by catalyst 14Mo, which lowered the combustion temperature from 897 to 826 K, i.e., a reduction of about 70 K. These results agree with those reported in the literature [6,11,15], considering simple catalytic systems without promoters. In addition, comparison with other works should be made with caution because of the specificities of the reaction conditions, such as heating rate, gas phase composition, soot/catalyst contact type, and soot/catalyst ratio.

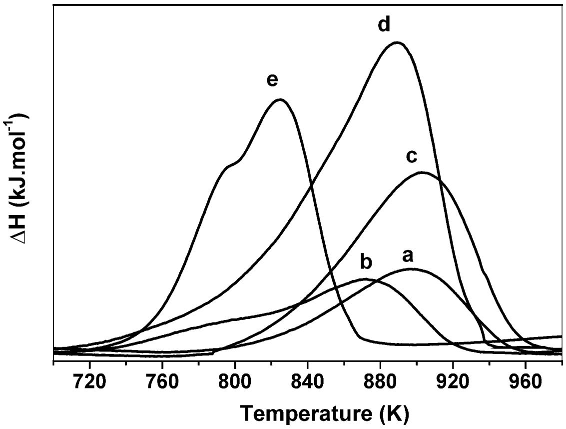

Fig. 1. DSC curves of combustion of soot mixed with alumina (a) and with the catalysts 5Mo (b), 5V (c), 14V (d), and 14Mo (e).

Table 1
Combustion temperature ($T_c$), reaction enthalpy, and activation energy, resulting from DSC analysis, for soot reaction with alumina (named soot) and the catalysts 5Mo, 14Mo, 5V, and 14V

| Sample | $T_c$ (K) | $\Delta H$ (kJ mol$^{-1}$) | $E_{at}$[a] (kJ mol$^{-1}$) |
|---|---|---|---|
| Soot | 897 | −87 | 180 |
| 5Mo | 869 | −108 | 100 |
| 14Mo | 826 | −189 | 97 |
| 5V | 904 | −180 | 120 |
| 14V | 889 | −312 | 110 |

[a] Estimated according to Eq. (1) [28,29].

The apparent activation energy for noncatalytic soot combustion is 180 kJ mol$^{-1}$ (Table 1). This value was expected considering the values reported in the literature, such as 168 kJ mol$^{-1}$ for Printex-U (Degussa) [30], 158 kJ mol$^{-1}$ for real soot [29], and 130 kJ mol$^{-1}$ for amorphous carbon black [16]; and the variation in these values may be attributed to surface heterogeneity and structural properties of different types of carbon. Despite that, it is generally agreed that activation energy increases if the structure of the carbon becomes more ordered [30].

For catalytic soot combustion, apparent activation energies are rarely reported. Dernaika et al. [29] studied soot combustion with oxides, such as $Al_2O_3$, $CeO_2$, $La_2O_3$, $SiO_2$, $TiO_2$, and $ZrO_2$, and reported that activation energy was lowered by about 7 kJ mol$^{-1}$ with respect to noncatalytic oxidation, which demonstrates the small influence of these oxides on soot combustion. In addition, they also performed the reaction with these oxides impregnated with Pt, and the results showed that the catalyst 1% Pt/$La_2O_3$ produced the best result, decreasing the activation energy by only 17 kJ mol$^{-1}$, although the combustion temperature had decreased 85 K. Other authors [32,33] reported a decrease in activation energy of almost 45% for promoted catalysts. In the present work, for catalysts 5Mo, 5V, and 14V, the apparent activation energy values are similar, being 100, 120, and 110 kJ mol$^{-1}$, respectively, and are almost half the value for the noncatalyzed reaction. The lowest value was obtained with catalyst 14Mo: 97 kJ mol$^{-1}$. Therefore, although the apparent activation energies of noncatalytic and catalytic soot combustion are not comparable, because they are referred to substantially different sets of reactions, they do predict the influence on soot combustion.

The enthalpy change accompanying the reaction is −87 kJ mol$^{-1}$ with alumina (Table 1), while for molybdenum catalysts the enthalpy is higher, increasing with Mo content, being −108 kJ mol$^{-1}$ for 5Mo and −189 kJ mol$^{-1}$ for 14Mo. Similarly, reaction enthalpy is higher in the presence of vanadium catalysts than in the presence of alumina, and catalyst 14V exhibited the highest enthalpy: −312 kJ mol$^{-1}$. These different values may be related to the formation of different products.

The standard enthalpies of CO and $CO_2$ formation and of CO oxidation, at 298 K, are related as follows:

$$C_{(s,\ graphite)} + O_{2(g)} \rightarrow CO_{2(g)}, \qquad \Delta H^{\theta} = -394\ \mathrm{kJ\,mol^{-1}}, \tag{2}$$

$$C_{(s,\ graphite)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)}, \qquad \Delta H^{\theta} = -111\ \mathrm{kJ\,mol^{-1}}, \tag{3}$$

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}, \qquad \Delta H^{\theta} = -283\ \mathrm{kJ\,mol^{-1}}. \tag{4}$$

These values may be related to the calculated enthalpies of the soot reaction in the presence of the catalysts, even though the conditions for DSC analyses differ from standard conditions. So the larger the amount of $CO_2$ formed, the higher the enthalpy of the reaction.

Fig. 1 shows that the temperature at the onset of soot combustion in the presence of alumina and catalyst 5V is around 790 K. Catalyst 14V exhibits the lowest onset temperature, about 700 K, and for both molybdenum catalysts this temperature is almost the same: 725 K. Even though the heat effect accompanying a reaction depends on the heat diffusion into the system, it can be observed that the temperature at which the heat effect ends is about 870 K for catalyst 14Mo, whereas it is 940 K for catalyst 14V. So catalyst 14Mo does change the heat effect, resulting in soot combustion at lower temperatures.

The DSC curves of soot combustion with vanadium catalysts and alumina show similar patterns, which look like Gaussian curves. The molybdenum catalysts also show similar patterns of curves, although they are different from those of vanadium catalysts: a shoulder can be observed before combustion temperature, with maxima at 823 and 809 K for catalysts 5Mo and 14Mo, respectively. This observation clearly indicates that different thermal phenomena are occurring in the Mo system, which may be related to distinct reaction processes.

Table 2 displays the temperature of maximum consumption of oxygen ($T_c$), and the percentages of CO and $CO_2$ obtained from TPO analyses for noncatalyzed soot combustion (in the presence of alumina, called "soot"), for the reactions with catalysts 5Mo, 14Mo, 5V, and 14V. Fig. 2 displays the consumption of oxygen (curve a) and the formation of carbon monoxide (b) and carbon dioxide (c) from TPO analyses

Table 2
Combustion temperature ($T_c$) and CO and $CO_2$ selectivity, resulting from TPO analysis, for noncatalyzed soot combustion (named soot), for combustion of soot mixed with the catalysts 5Mo, 14Mo, 5V, and 14V, and for the samples 14Mo/soot, soot/14Mo, 14V/soot, and soot/14V, where the catalysts and soot are separated in two beds

| Sample | $T_c$ (K) | CO (%) | $CO_2$ (%) |
|---|---|---|---|
| Soot | 917 | 71 | 29 |
| 5Mo | ~ 923 | 67 | 33 |
| 14Mo | 859 | 25 | 75 |
| 5V | 923 | 63 | 37 |
| 14V | 891 | 43 | 57 |
| 14Mo/soot | 919 | 57 | 43 |
| Soot/14Mo | 913 | 61 | 39 |
| 14V/soot | 912 | 59 | 41 |
| Soot/14V | > 923 | 62 | 38 |

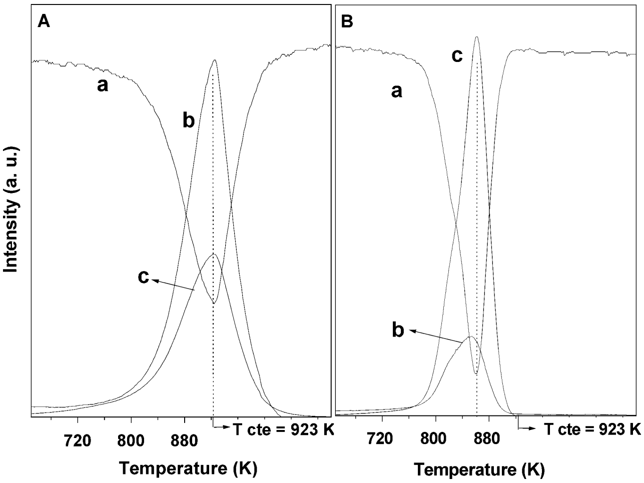

Fig. 2. Curves of oxygen consumption (a) and CO (b) and $CO_2$ formation (c) versus temperature from TPO analysis for combustion reaction of soot mixed with the catalysts 5Mo (A) and 14Mo (B).

for the reaction with molybdenum catalysts: 5Mo (Fig. 2A) and 14Mo (Fig. 2B). Because all the TPO profiles are similar, the others are not shown.

For noncatalyzed soot combustion, the temperature of the maximum consumption of oxygen ($T_c$) is 917 K (Table 2) and is almost the same as the temperature of maximum formation of CO and $CO_2$. In the presence of catalyst 5Mo, maximum consumption of $O_2$ occurs around 923 K, whereas for 14Mo, it occurs at 859 K (Table 2). As observed for the noncatalyzed reaction, in soot combustion with 5Mo (Fig. 2A), maximum consumption of oxygen and maximum formation of CO and $CO_2$ occur at the same temperature. However, with catalyst 14Mo (Fig. 2B), maximum formation of CO occurs at a temperature 14 K lower than that at which maximum consumption of oxygen and $CO_2$ formation takes place. For vanadium catalysts, maximum consumption of oxygen and maximum formation of CO and $CO_2$ occur almost at the same temperature: at 923 and 891 K for 5V and 14V, respectively. So, catalyst 14Mo exhibits the best catalytic performance, lowering the soot combustion temperature from 917 to 858 K, which is a reduction of about 59 K. DSC results for this catalyst show a reduction of about 70 K. However, the differences observed in combustion temperature obtained between DSC and TPO analyses may be related to differences in experimental conditions [34]. Nonetheless, these results are in agreement.

The TPO results show that $O_2$ consumption is lower for the noncatalyzed reaction than for the catalyzed reaction, and higher for the 14Mo catalyst than for the other catalysts. During the pretreatment with He flow before TPO analyses, it is possible that Mo and V species may be partially reduced and thus regenerated during the TPO analyses, increasing $O_2$ consumption. Although it cannot be disregarded, these results are related mainly to the amount of $CO_2$ formation.

$CO_2$ selectivity is 29% for the noncatalyzed reaction (Table 2). However, with molybdenum catalysts, it is 33% for 5Mo and 75% for 14Mo, whereas for vanadium catalysts, it is 37% for 5V and 57% for 14V. These results indicate that the catalysts favor the complete combustion of soot. In addition, $CO_2$ selectivity is higher for catalysts with higher loadings, i.e., for catalysts 14Mo and 14V.

Considering the enthalpy of the reaction and $CO_2$ selectivity, it can be seen that the enthalpy with catalyst 5V ($-180$ kJ mol$^{-1}$) is about 1.7 times higher than that with 5Mo ($-108$ kJ mol$^{-1}$), even though the $CO_2$ selectivities of the two catalysts are very close (37 and 33%, respectively). Similarly, the results show that the enthalpy of the reaction with catalyst 14V ($-312$ kJ mol$^{-1}$) is about 1.7 times higher than that with 14Mo ($-189$ kJ mol$^{-1}$), despite the lower $CO_2$ selectivity for 14V (57% vs 75%, with 14Mo). Therefore, it may be inferred that formation of $CO_2$ in the presence of vanadium and molybdenum catalysts occurs by different reaction processes, which may involve adsorption and desorption steps and probably can affect the enthalpy values.

Fig. 3 displays the percentage of soot conversion versus temperature obtained from TPO results for the noncatalyzed reaction and for reactions in the presence of 5Mo, 14Mo,

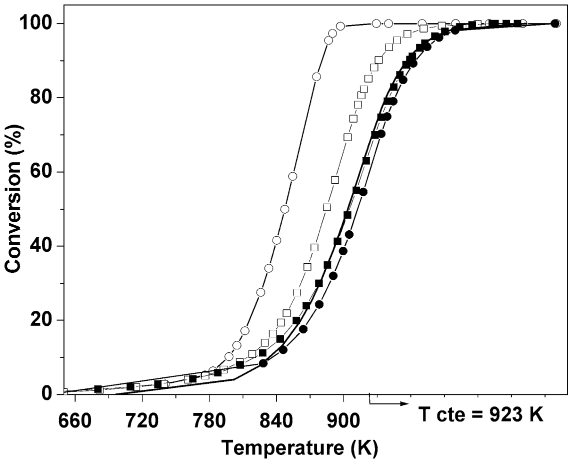

Fig. 3. Percentage of soot conversion versus temperature from TPO results for the noncatalyzed soot combustion reaction (—) and for the reaction of soot mixed with the catalysts 5Mo (●), 14Mo (○), 5V (■), and 14V (□).

5V, and 14V. The conversion curves for alumina and catalysts 5Mo, 5V, and 14V are similar. However, for catalyst 14Mo, the curve is shifted to lower temperatures and exhibits a different shape, with a higher slope, suggesting that catalyst 14Mo increased the reaction rate of soot combustion, reaching 100% conversion very fast.

Considering that the catalysts with higher loading of molybdenum and vanadium exhibit the best performance, TPO analyses in two beds were performed only with 14Mo and 14V. Table 2 lists the combustion temperature ($T_c$) and percentages of CO and $CO_2$ resulting from these analyses for samples 14Mo/soot and 14V/soot (where the gas flows first through the catalyst) and soot/14Mo and soot/14V (where the gas flows first through the mixture of soot and alumina).

For the molybdenum catalyst, the temperature of maximum consumption of $O_2$ ($T_c$), where gas flows first through catalyst 14Mo (sample 14Mo/soot), is 919 K and the $CO_2$ selectivity is 43%. When the beds are inverted, i.e., the gas flows first through the mixture of soot and alumina (sample soot/14Mo), $T_c$ is 913 K and $CO_2$ selectivity is 39% (Table 2). On the other hand, for the vanadium catalyst, the maximum consumption of $O_2$ ($T_c$) occurs at 912 K and $CO_2$ selectivity is 41% for sample 14V/soot. When the bed configurations are inverted (sample soot/14V), the combustion temperature is reached after the isothermal treatment at 923 K, and $CO_2$ selectivity is 38%. Therefore, catalysts 14Mo and 14V in both configurations exhibit similar behavior.

Comparing these results with those for the noncatalytic reaction (Table 2), it can be noted that the presence of catalysts 14Mo or 14V, in both configurations, slightly increases $CO_2$ selectivity (almost 10% points), but basically does not affect combustion temperature. This suggests that the vanadium and molybdenum active species involved in both configurations are related to the oxidation of CO from the gaseous phase. In this way, when gas flows first through the catalytic bed, the volatile species from $MoO_3$ and $V_2O_5$ crystallites, which are the only species involved in this configuration, may be transferred to the soot bed, promoting the increase in $CO_2$ selectivity. However, when gas flows first through the soot–alumina mixture, it may be inferred that the CO formed by the noncatalyzed soot reaction may be oxidized to $CO_2$ when passing through the catalytic bed. Therefore, both volatile and dispersed species of these catalysts are probably involved.

Similarly, comparing the results of combustion for separated beds, catalyst above and soot below (samples 14Mo/soot and 14V/soot) with the combustion of the mixed bed catalyst and soot (Table 2), $CO_2$ selectivity was markedly enhanced and combustion temperature was significantly lowered for the last case. When catalyst and soot are in separated beds, the only species involved are the volatile ones; then it may be inferred that these species are not responsible for catalytic performance. Similar behavior was observed for the opposite layer position: catalyst 14Mo or 14V under the soot bed (samples soot/14Mo and soot/14V). Again, the mixed catalyst and soot bed layer (Table 2) showed enhanced $CO_2$ selectivity and lower combustion temperature. This confirms our suggestion that the Mo and V dispersed species in contact with soot play an important role in catalytic soot combustion.

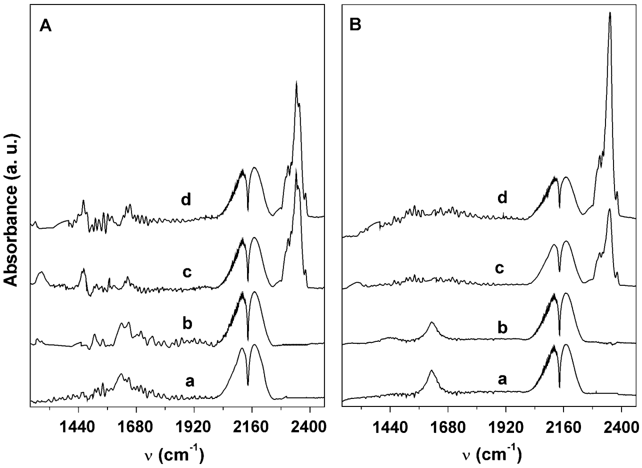

Fig. 4. IR spectra of the catalysts 5Mo (A) and 14Mo (B), with CO adsorbed at 273 K (a), 373 K (b), 573 K (c), and 773 K (d).

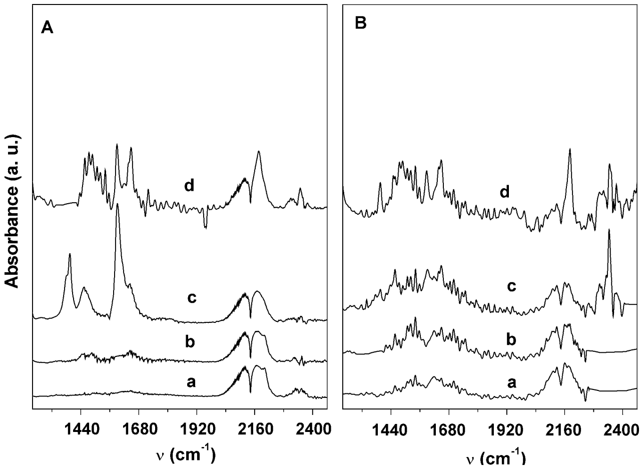

Fig. 5. IR spectra of the catalysts 5V (A) and 14V (B), with CO adsorbed at 273 K (a), 373 K (b), 573 K (c), and 773 K (d).

Figs. 4A and 4B are the IR spectra of molybdenum catalysts 5Mo and 14Mo, respectively, with CO adsorbed at 298 K (spectrum a), 373 K (b), 573 K (c), and 773 K (d). Similarly, the IR spectra of vanadium catalysts 5V and 14V, under a CO atmosphere, are in Figs. 5A and 5B, respectively.

It can be observed that spectrum a of 5Mo (Fig. 4A) clearly shows a doublet band at 2120 and 2180 $cm^{-1}$, which should be assigned to CO physically adsorbed and CO from the gas phase [35], which would be removed after evacuation. Other bands, less intense, are seen at 1460 and 1620–1610 $cm^{-1}$, and are assigned to mono- and bidentate carbonated species [35,36], respectively. Spectrum b shows these same bands, with almost the same intensity. However, spectrum c shows a more intense band at 1460 $cm^{-1}$, while the intensity of the band at 1610 $cm^{-1}$ decreased; it is important to note the very intense band at 2350 $cm^{-1}$, which is associated with $CO_2$ molecules slightly disturbed [35]. Spectrum d also shows the band at 2350 $cm^{-1}$, but with higher intensity. These results suggest the formation of carbonated species at the surface of the 5Mo catalyst at all temperatures. However, the $CO_2$ physisorbed band appears only after heating at 573 and at 773 K, exhibiting higher intensity when the temperature increases.

Similarly, all spectra of the 14Mo catalyst (Fig. 4B) show the doublet band at 2120–2180 $cm^{-1}$, referring to reversible CO adsorption and molecular CO. The band at 1620–1610 $cm^{-1}$, which is assigned to carbonate species [35,36], is evident in spectra a and b, while the band at 2350 $cm^{-1}$, related to physisorbed $CO_2$, appears after heating at 573 and 773 K.

Comparing the spectra of catalysts 5Mo and 14Mo, one notes that both catalysts exhibit the same bands when compared under the same conditions; in addition, these bands are more intense for the 14Mo catalyst. This suggests that CO molecules may adsorb onto molybdenum catalysts surface at low temperatures (298 and 373 K), yielding carbonate species, which than decompose by heating, forming $CO_2$ at higher temperatures (573 K). The higher intensity of these bands for the 14Mo catalyst may indicate its higher ability to adsorb CO and desorb $CO_2$.

For the vanadium catalysts, all spectra of catalyst 5V (Fig. 5A) show the bands at 2120 and 2170 $cm^{-1}$, which are assigned to reversible CO adsorption. Spectrum b shows slight bands in the range 1300–1700 $cm^{-1}$, which are related to carboxylate $CO_2$ and carbonate species (mono- and bidentate) [35,36]. However, when the system is heated at 573 K (spectrum c), it clearly exhibits highly intense bands in the range 1300–1700 $cm^{-1}$, which are at 1400, 1460, and 1590 $cm^{-1}$. After heating at 773 K (spectrum d), the band at 1400 $cm^{-1}$ disappears; the band at 1590 $cm^{-1}$ is less intense than in spectrum c, while the intensity of bands at 1460 and 2170 $cm^{-1}$ increase. In addition, a new, slight band appears at 2350 $cm^{-1}$, and is assigned to physisorbed $CO_2$.

IR spectra of catalyst 14V (Fig. 5B) at room temperature (spectrum a) and after heating at 373 K (spectrum b) show bands at 2120 and 2170 $cm^{-1}$, which are assigned to reversible CO adsorption and to mono- and bidentate carbonate species (1440–1700 $cm^{-1}$), as already observed for catalyst 5V. After heating at 573 K (spectrum c), the bands referred to carboxylate–carbonate species (1300–1700 $cm^{-1}$) remain, with the appearance of the band 2350 $cm^{-1}$, assigned to physisorbed $CO_2$. After the system is heated to 773 K (spectrum d), the intensity of the band related to adsorbed CO (2170 $cm^{-1}$) increases, while the intensity of the band related to physisorbed $CO_2$ (2350 $cm^{-1}$) decreases. The noisy spectrum is probably due to higher vanadium loading, which turns the sample darker.

Therefore, these results also indicate that vanadium catalysts may adsorb CO, mainly at high temperatures, yielding carbonate species, but, contrarily, the Mo catalysts are hardly desorbed. Moreover, carbonate species on catalyst 14V seem to be more easily desorbed as $CO_2$ than those formed on 5V.

For molybdenum and vanadium catalysts, formation of $CO_2$ after CO adsorption clearly shows the role of the oxygen lattice of these catalysts. In addition, considering that carbonate species are formed on molybdenum catalysts at low temperatures (298, 373 K), and then disappear at high temperatures (573, 773 K), while for vanadium catalysts these species are formed mainly at 573 K and remain at 773 K, the carbonate species formed on vanadium samples seem to be more stable thermally than those formed on molybdenum catalysts.

Some authors [37–39] have studied the interaction of $CO_2$ with active catalysts for soot combustion, and observed that the most active catalysts were that having stronger interaction with $CO_2$. According to them, surface carbonates were formed on catalyst, suggesting that these compounds could act as reaction intermediates during soot combustion. In our work, considering that the molybdenum catalysts exhibited better performance for soot combustion, and that under a CO atmosphere, carbonate species are more unstable than on vanadium catalysts, it may be suggested that the thermal stability of carbonate species formed on these catalysts is inversely related to catalytic performance.

From the results presented here, we suggest a reaction pathway for catalyzed soot combustion: when in contact with the catalyst, soot interacts with the superficial oxygen of the molybdenum and vanadium dispersed species, yielding those carbonated species at the interface, i.e., at the contact boundary between these solids; then, these carbonate species may be released to the gaseous phase as CO or $CO_2$.

This reaction pathway may be related to the redox mechanism in which lattice oxygen from the surface dispersed species promotes the oxidation of soot by formation of carbonate species, followed by decomposition to CO or $CO_2$; then the Mo and V dispersed species are reoxidized by $O_2$ supplied from the gas phase. Oxygen spillover may also be involved and cannot be disregarded.

The proposed pathway would also explain why the contact between soot and Mo and V dispersed species is so important. Moreover, it would clarify that the different performances exhibited by Mo and V dispersed species, i.e., the combustion temperature and the $CO_2$ selectivity, are related to their distinct reactivity for the formation and desorption of the carbonate species. In addition, the stronger interaction of the carbonated species formed on vanadium catalysts than on molybdenum catalysts would explain the higher enthalpy changes accompanying the combustion reaction when the soot is in contact with vanadium catalysts, as these carbonate species would need higher energy to desorb as $CO_2$.

Noteworthy is that the true active sites for diesel soot combustion on $Mo/Al_2O_3$ and $V/Al_2O_3$ catalysts are the Mo and V dispersed species at the surface and not the $MoO_3$ and $V_2O_5$ crystallites. As reported in the literature these crystallites are not stable at high temperature, mainly in the presence of water vapor. However, recent results have shown that the performance of these catalysts is stable after three consecutive soot combustion experiments, and after analysis the dispersed species are still present, which is strong evidence of stabilization of the dispersed species during the combustion reaction. Although these catalysts are not yet recommended for practical solutions, because the soot combustion temperature is still too high compared with the exhaust diesel engines, it seems that with the understanding of the reaction surface and the molybdenum and vanadium dispersed species on alumina-supported catalysts as active surface species of diesel soot combustion, it would be possible to suggest a way to develop real catalysts for soot combustion.

## 4. Conclusions

The superficial dispersed species of both molybdenum and vanadium catalysts are responsible for lowering soot combustion temperature when in contact with soot.

The reaction pathway when the soot is in contact with the catalysts may be explained by the interaction of the soot with the superficial oxygen from the molybdenum and vanadium dispersed species to form carbonated species at the interface, i.e., at the contact boundary between these solids. This reaction pathway may be related to a redox mechanism in which lattice oxygen from the surface dispersed species promotes oxidation of the soot by the formation of carbonate species, followed by decomposition to CO or $CO_2$. Therefore, the better performance of molybdenum catalysts is related to the higher facility of decomposition of those carbonated species on Mo superficial dispersed species.

## Acknowledgments

We acknowledge Degussa for providing us with alumina and soot, and PRONEX/CNPq FINEP for financial support. I.C.L. Leocadio is grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the Master Fellowship.

## References

[1] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Fuel Process. Technol. 47 (1996) 1.
[2] P. Degobert, Automobiles and Pollution, SAE, Warrendale, PA, 1995.
[3] R.J. Farrauto, J. Adomaitis, J. Tiethof, J. Mooney, Autom. Eng. 100 (1992) 19.
[4] J. Lahaye, F. Ehrburger-Dolle, Carbon 32 (1994) 1319.
[5] P. Zelenka, W. Carterllieri, P. Herzog, Appl. Catal. B 10 (1996) 3.
[6] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Appl. Catal. B 8 (1996) 57.
[7] J.P.A. Neeft, O.P. van Pruissen, M. Makkee, J.A. Moulijn, Appl. Catal. B 12 (1997) 21.
[8] G. Mul, F. Kapteijn, C. Doornkamp, J.A. Moulijn, J. Catal. 179 (1998) 258.
[9] U. Hoffmann, J. MA Chem. Eng. Technol. 13 (1990) 251.
[10] A.F. Ahlstrom, C.U.I. Odenbrand, Appl. Catal. 60 (1990) 157.
[11] J. van Doorn, J. Varloud, P. Mériaudeau, V. Perrichon, M. Chevrier, C. Gauthier, Appl. Catal. B 1 (1992) 117.
[12] S. Liu, A. Obuchi, J. Uchisawa, T. Nanba, S. Kushiyama, Appl. Catal. B 37 (2002) 309.
[13] G. Saracco, C. Badini, N. Russo, V. Specchia, Appl. Catal. B 21 (1999) 233.
[14] B.A.A.L. van Setten, C. van Gulijk, M. Makkee, J.A. Moulijn, Top. Catal. 16/17 (2001) 275.
[15] G. Mul, J.P.A. Neeft, F. Kapteijn, M. Makkee, J.A. Moulijn, Appl. Catal. B 6 (1995) 339.
[16] V. Serra, G. Saracco, C. Badini, V. Specchia, Appl. Catal. B 11 (1997) 329.
[17] Y. Teraoka, K. Kanada, S. Kagawa, Appl. Catal. B 34 (2001) 73.
[18] B.A.A.L. van Setten, J.M. Schouten, M. Makkee, J.A. Moulijn, Appl. Catal. B 28 (2000) 253.
[19] B.A.A.L. van Setten, Development of a Liquid Catalyst for Diesel Soot Oxidation, D.Sc. dissertation, Technische Universiteit Delft, 2001.
[20] D.W. Makee, J. Catal. 108 (1987) 480.
[21] P. Ciambelli, M. d'Amore, V. Palma, S. Vaccaro, Combust. Flame 99 (1994) 413.
[22] G. Neri, L. Bonaorsi, A. Donato, C. Milone, M.G. Musolino, A.M. Visco, Appl. Catal. B 11 (1997) 217.
[23] R.T.K. Baker, J.J. Chludzinsky, Carbon 19 (1981) 75.
[24] S. Braun, L.G. Appel, M. Schmal, Appl. Surf. Sci. 201 (2002) 227.
[25] S. Braun, L.G. Appel, V.L. Camorim, M. Schmal, J. Phys. Chem. B 104 (2000) 6584.
[26] Degussa AG, Technical Bulletin Pigments, High Dispersed Metallic Oxides Produced by the Aerosil® Process, sixth ed., No. 56, Germany, March 1993.
[27] Degussa AG, Technical Bulletin Pigments, Method of Analysis for Pigment Blacks, second ed., No. 14, Germany, March 1992.
[28] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[29] B. Dernaika, D. Uner, Appl. Catal. B 40 (2003) 219.
[30] J.P.A. Neeft, T.X. Nijhuis, E. Smakman, M. Makkee, J.A. Moulijn, Fuel 76 (1997) 1129.
[31] Z. Du, A.F. Sarofim, J.P. Longwell, Energy Fuels 5 (1991) 214.
[32] P. Ciambelli, V. Palma, P. Russo, S. Vaccaro, J. Mol. Catal. A 204–205 (2003) 673.
[33] D. Fino, N. Russo, G. Saracco, V. Specchia, J. Catal. 217 (2003) 367.
[34] B. Stanmore, P. Gilot, G. Prado, Thermochim. Acta 240 (1994) 79.
[35] A.A. Davydov, C.H. Rochester (Eds.), Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides, Wiley, Chichester, 1990, p. 37.
[36] G. Mul, F. Kapteijn, J.A. Moulijn, Carbon 37 (1999) 401.
[37] E.E. Miró, F. Ravelli, M.A. Ulla, L.M. Cornaglia, C.A. Querini, Catal. Today 53 (1999) 631.
[38] V.G. Milt, C.A. Querini, E.E. Miró, Thermochim. Acta 404 (2003) 177.
[39] M.L. Pisarello, V. Milt, M.A. Peralta, C.A. Querini, E.E. Miró, Catal. Today 75 (2002) 465.