A screening study on the activation energy of vanadate-based catalysts for diesel soot combustion

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The activation energy of carbon combustion catalysed by alkali vanadates or alkali vanadates/chlorides mixtures is assessed by the Ozawa method. The most active catalyst, $Cs_4V_2O_7$, entails more than 50% decrease of the activation energy compared to non-catalytic combustion (from 157 down to 75 kJ/mol). The catalyst performance is enhanced when the catalyst is dissolved in a eutectic liquid (e.g., AgCl + CsCl), which likely improves the catalyst/carbon contact conditions.

Keywords: Cs–K–V catalysts, diesel soot, catalytic combustion, activation energy, catalyst stability

1. Introduction

The use of a catalytic trap is one of the more promising passive methods proposed to date for the removal of particulate from diesel engine emissions. A catalytic trap consists of a ceramic substrate (e.g., foam, fibre mat, wall-flow monolith) suitable for soot filtration and of a catalyst deposited on its pore walls. This catalyst should be capable of lowering the soot ignition temperature down to 180–350 °C, a range typical of the exhaust gases from modern diesel oil-fueled cars at the silencer location. Only in this case, the soot particles will in fact burn as soon as they are intercepted by the filtering device, thus preventing significant soot accumulation inside the trap and undesired back pressure increase. This last occurrence would actually reduce the engine efficiency and entail a certain fuel penalty [1].

The non-catalytic ignition temperature of diesel particulates depends somehow on the content of adsorbed hydrocarbon (the so-called soluble organic fraction), but in any case generally exceeds 600 °C. A significant reduction in the ignition temperature is thus required through the development of suitable catalysts if the catalytic trap concept has to become practical. Several substances were proposed for this purpose: precious metals (Pt, Pd and Rd) [2]; metal oxides (of alkali metals, copper, vanadium, molybdenum, etc.) [3–6]; Cu–K–V–Cl and Cu–K–Mo–Cl systems [7–13] capable of providing mobile catalytic species (vapour or liquid) improving the catalyst-to-carbon contact. From these staring points, mobile catalysts based on alkali vanadates, but not containing copper (rather toxic and easily lost in the environment), were recently developed and described [14–16]. Some of these last catalysts, showing an appreciable activity already below 350 °C, are promising substances for catalytic trap development. However, in order to properly design catalytic filtering devices [17], the catalysed combustion reaction should be further investigated, with the aim of assessing the reaction kinetic law. This law should take into account several parameters: catalyst type, activation energy, oxygen concentration in the gaseous phase, contact sites among carbon, oxygen and catalyst, etc. Owing to the dynamic way of operation of the catalytic converters placed at the exhaust line of a car (e.g., frequent variations of flow rates and temperatures), the knowledge of the activation energy of the catalyst employed is of primary importance for the mentioned design purposes [18].

In this context, by analogy with a former study performed on a first generation of less active catalysts [19], the present paper deals with the assessment of the activation energy of the catalysts based on alkali vanadates in either fresh and, for the most promising ones, aged state.

2. Materials and methods

2.1. Catalyst preparation

Four different vanadates were prepared by solid state reaction and melting of suitable precursor powders according to the following reactions (where M = K or Cs):

$$M_2CO_3 + V_2O_5 \rightleftharpoons 2MVO_3 + CO_2$$
$$2M_2CO_3 + V_2O_5 \rightleftharpoons M_4V_2O_7 + 2CO_2$$

Each preparation involved the following steps:

- mixing of vanadium (penta)-oxide and alkali-metal carbonate powders in stoichiometric proportion;
- pressing of the blended powders to obtain tablets;
- tablets annealing for 1 h at 100 °C below the melting point of the vanadate that progressively forms (melting

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points: KVO_3 520 °C, $CsVO_3$ 641 °C, $K_4V_2O_7$ 675 °C, $Cs_4V_2O_7$ 870 °C, determined by hot microscopy);

- sample melting, performed in order to complete the reaction and achieve complete homogeneity;
- re-crystallisation at about 400 °C for 48 h.

The purity of each vanadate synthesised was tested by X-ray diffraction (XRD).

Binary and ternary catalysts were also prepared by mixing in a mortar, respectively, each *meta*-vanadate (KVO_3 or $CsVO_3$) with KCl (molar ratio 1 : 1) and each *pyro*-vanadate ($K_4V_2O_7$ or $Cs_4V_2O_7$) with an AgCl + CsCl mixture (molar ratio between the chloride mixture and the vanadate of 1 : 1). The mixture between AgCl and CsCl had the binary eutectic composition (molar ratio of 7 : 3). Also these two- and three-component catalysts were obtained by melting of the mixed precursor salts and slow cooling down to room temperature. The result of the preparation was checked by XRD analysis. The mentioned halides were added to pure vanadates in order to obtain eutectic mixtures that start melting at temperature ranges inside which each vanadate displays its specific combustion activity. The melting start of binary and ternary catalysts was investigated by using a heating microscope.

The vanadate that displayed the best catalytic activity (namely $Cs_4V_2O_7$, see section 3.2) was also supported on α-Al_2O_3 powders (alumina particle size ranging between 100 and 200 μm). The supported catalyst (50 wt% of alumina), used for stability tests described in the subsequent paragraphs, was prepared by impregnation of alumina powders with a water solution of $Cs_4V_2O_7$, drying at 120 °C and annealing for 30 min at 400 °C. Alumina was selected as a catalyst carrier for its low catalytic activity and high chemical inertness in the temperature range of interest (it does not appreciably catalyse carbon oxidation react significantly with the catalyst itself [13,15]) and because, once toughened with ZrO_2 [20], it can be used as a constituting material for diesel particulate foam traps.

2.2. Screening of catalysts by TGA and TPO activity evaluation

These catalytic activity tests were performed by using a mixture of each unsupported catalyst (made of one, two or three components) and amorphous carbon (particle size 45 nm, ashes 0.34 wt%, moisture 12.2 wt%). Catalyst/carbon mixtures (2 : 1 weight ratio) were carefully prepared, in order to guarantee reproducible homogeneity and contact conditions, according to the following steps:

- catalyst grinding in a ball mill, drying and weighing;
- mixing of catalyst and carbon in a mortar, which allows for achieving tight contact conditions (working with loose contact conditions, obtained, e.g., by simple shaking in a vessel, entails much lower reproducibility);
- further homogenisation of this mixture in a jar-mill for 1 h;
- storage of the sample under dry atmosphere (guarantee by the presence of silica gel).

A reference sample, without catalyst, was also prepared by mixing inert α-Al_2O_3 and carbon powder (weight ratio 2 : 1).

The samples were then submitted to thermal gravimetric analysis (TGA) using a Perkin–Elmer 7 equipment under air flow gliding over the sample holder. The TGA measurements were carried out under an air flow (30 ml/min) with temperature scanning rates of 5, 10, 20 and 50 °C/min. Both the weight loss curves and their derivatives (DTGA) were recorded. The apparent activation energy for the combustion reaction was calculated starting from the TGA results according to the Ozawa method (briefly discussed in the section 2.3).

The activity hierarchy, derived for the pure vanadates by TGA experiments, was also confirmed by using thermal-programmed oxidation (TPO) technique.

TPO tests allow one to check the performance of the catalysts: a fixed bed containing both catalyst and carbon is permeated by an air stream. However, since TPO experiments require much more time than TGA ones, they were not systematically used during the first investigation step of catalyst screening. Conversely, this method was regarded as more convenient for the subsequent investigation of both activity and stability of supported $Cs_4V_2O_7$ catalysts, the most active one, as described later on (see section 3.1.4).

The fixed bed for the TPO experiments was prepared by using catalyst/carbon mixtures with a catalyst/carbon weight ratio of 2 : 1 or 4 : 1, for unsupported or supported catalyst, respectively. 40 mg of these samples were mixed with 150 mg of silica pellets (0.3–0.7 mm in size) and kept inside the microreactor between two layers of quartz wool. An air flow was delivered through the fixed bed at the constant rate of 100 ml/min, while the temperature was raised up to 700 °C with a constant rate of 5 °C/min. The combined measurements of sample temperature and CO_2 outlet concentration allowed one to evaluate the peak temperature, corresponding to the maximum conversion rate of carbon to CO_2. The fraction of carbon converted to CO_2 was also calculated as the ratio between the integral amount of CO_2 produced and that expected in case all the carbon present in the initial sample were converted to carbon dioxide. More details about the TPO apparatus were reported in a previous paper [14].

Some TPO runs were carried out also on aged catalysts. A catalyst used for the reduction of soot concentration in the diesel emissions may loose its activity due to several reasons: temporary temperature rise up to unusual values (>600 °C, due to, e.g., the sudden burning of large soot aggregates), poisoning effect caused by some components of diesel exhausts (e.g., SO_2, H_2O), prolonged working time. In order to consider separately (when possible) the effect of each of these factors, ageing treatments were performed on the alumina-supported $Cs_4V_2O_7$ catalyst in the particular experimental conditions listed below:

- thermal ageing in dry air at 380 and 600 °C for 96 and 24 h, respectively;
- thermal ageing at the same temperature and time values above and under wet air, containing 12 vol% of moisture (which is characteristic of diesel emissions);
- thermal ageing at the same temperature and time values above and under dry air containing 200 ppmv of SO_2 (a concentration about ten times higher than those obtained from the combustion of modern gas oils for automotive application).

All these treatments were carried out in a tubular furnace with a gaseous flow of 50 ml/min. In addition, the possible loss of catalytic activity due to prolonged catalyst operation was checked. For this purpose the catalyst was mixed with carbon (weight ratio 9 : 1) and kept at 450 °C for 2 h to achieve the complete carbon combustion. This treatment was repeated by using the same catalyst sample so as to carry out up to eight combustion cycles. After each ageing treatment the catalyst was characterised by XRD and its catalytic activity tested by TPO.

The catalytic activity and the activation energy of the sample which underwent the most severe ageing conditions (i.e., 600 °C under a SO_2-rich atmosphere) was also tested by TGA method. This last analysis was performed with the method previously described; however, the initial weight ratio between the alumina-supported catalyst and carbon was kept equal to 4 : 1, in order to keep unchanged the vanadate/carbon ratio with respect to the other TGA tests.

2.3. Calculation of activation energy by Ozawa method

The kinetics of carbon combustion may be studied by using the Ozawa method, which allows one to calculate the apparent activation energy of carbon combustion [19,21–23]. As for the catalytic combustion of carbon, the reaction rate depends on several factors: the intrinsic activation energy; the degree of contact among carbon, catalyst and oxygen, which also depends on the catalyst and carbon particle size, as well as on the way these two counterparts are mixed; the oxygen concentration in the gaseous atmosphere, etc. Furthermore, some of these conditions (the size of carbon particles, the contact degree between carbon and the catalyst, the composition of the gaseous atmosphere and the oxygen concentration in the gaseous phase) may change during a combustion test. However, most of these parameters can be kept constant during an experiment, or at least during the first steps of combustion. In order to achieve this condition, for instance, the combustion can be carried out with a great excess of oxygen, and the starting dimensions of both carbon and catalyst particles as well as the carbon/catalyst mixing method have to be strictly controlled. Notwithstanding the care put in the standardisation of the experimental conditions, the activation energy thereby obtained should still be regarded as "apparent", because the combustion rate depends on both the particular reaction investigated and the transport phenomena, which become more and more important and hard to predict as long as the catalyst melts and the catalyst mobility increases.

Anyway, under the controlled conditions described above, the following kinetic law may be proposed:

$$\mathrm{d}\alpha/\mathrm{d}t = A\exp(-E/RT)f(1-\alpha), \qquad (1)$$

where α is a fraction of burned carbon, $\mathrm{d}\alpha/\mathrm{d}t$ is a carbon fraction which burns in the unit of time (reaction rate), A is a constant value (a function of contact conditions), E is an activation energy, and $f(1-\alpha)$ is a whatever function of the fraction of unburned carbon.

During the TGA experiment, since air is fed to the reactor in large excess with respect to the oxygen stoichiometric requirement, the oxygen concentration can be considered constant as well as its effect on the reaction rate. Such effect, among others, is accounted for in the constant A.

Ozawa demonstrated that, when the kinetic law assumes the form of equation (1), the activation energy can be calculated even though the $f(1-\alpha)$ function is unknown, provided that several non-isothermal experiments are performed at different heating rates. During each of these experiments, the temperature T_α corresponding to the transformation of a pre-fixed fraction α of the key reactant (for instance, the temperature at which 50 wt% of carbon is burned) is measured. Ozawa obtained the following equation which links the heating rate (ϕ) to T_α:

$$\ln\phi = B - 0.4567(E/RT_\alpha), \qquad (2)$$

where B is a constant value depending on the chemical reaction.

If the logarithm of each ϕ value is plotted against the corresponding value of $1/T_\alpha$ (Ozawa plot), a linear dependence is obtained. The activation energy is calculated from the slope of the best-fit straight line in the Ozawa plot. Pair of values of ϕ_i and $T_{\alpha i}$ (where i refers to a particular heating rate) can be rather easily obtained by means of TGA experiments.

The Ozawa method can be considered a self-consistent calculation method, because the experimental points well fit a straight line only if the reaction kinetics agree with equation (1). In contrast, when the rate of the investigated process is ruled by a kinetic law different from equation (1), the experimental points in the Ozawa plot match with a curved line, which entails that the method is not appropriate.

For this reason, the correlation factor (resulting from linear regression calculation) for each plot was checked to be reasonably close to one.

3. Results and discussion

3.1. XRD and melting point characterisation

The systems $KVO_3 + KCl$ and $CsVO_3 + KCl$ promote liquid at 485 and 389 °C, respectively, that is well below

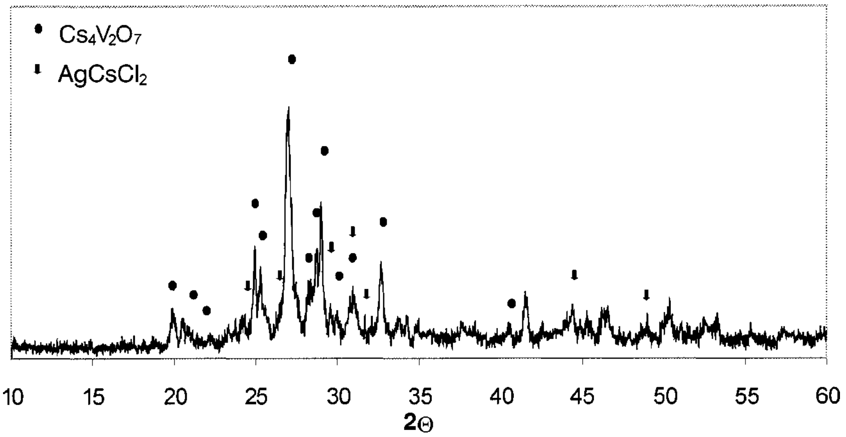

Figure 1. XRD diffraction pattern of the $Cs_4V_2O_7 + AgCl + CsCl$ catalyst.

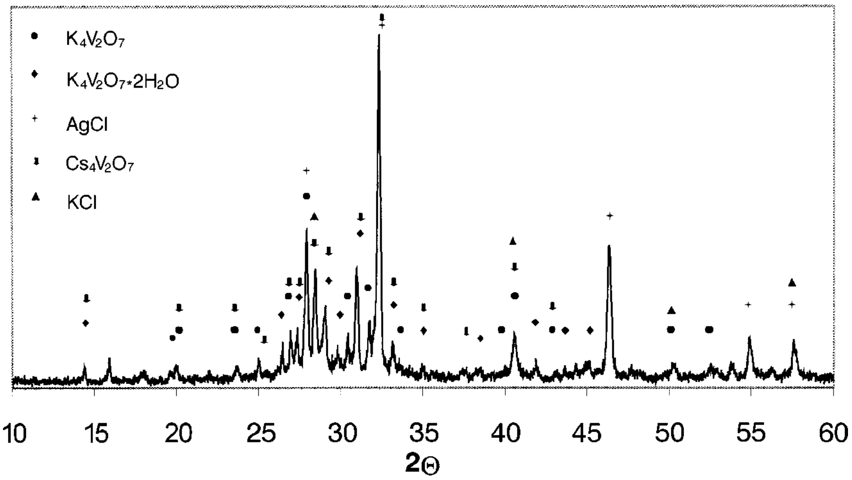

Figure 2. XRD diffraction pattern of the $K_4V_2O_7 + AgCl + CsCl$ catalyst.

the melting points of pure vanadates. The two ternary catalysts ($M_4V_2O_7$ + AgCl + KCl) give a very small amount of eutectic liquid (just detectable through the heating microscope) already at about 280 °C.

Diffraction patterns of prepared *meta*-vanadates contained the reflexes pertaining to these compounds only (matching JCPDS cards 33-382 and 33-1052), showing that the synthesis method gives well crystallised substances of good purity. The diffraction spectra of *pyro*-vanadates were more complex and difficult to be interpreted. Actually, the XRD $Cs_4V_2O_7$ spectrum reported in literature, which refers only to a limited range of diffraction angles (JCPDS card 37-393), well matches with that experimentally obtained for the prepared $Cs_4V_2O_7$; however, additional diffraction peaks lying out from this range could not be attributed.

Potassium *pyro*-vanadate gives three crystalline forms (anhydrous $K_4V_2O_7$, monohydrated $K_4V_2O_7 \cdot H_2O$ and bihydrated $K_4V_2O_7 \cdot 2H_2O$) whose XRD patterns are known (JCPDS cards 22-869, 22-871 and 22-872). Due to the high hygroscopicity of this compound, the XRD pattern of the prepared *pyro*-vanadate sample showed the simultaneous presence of peaks pertaining either to anhydrous and hydrated $K_4V_2O_7$; these last becoming progressively more relevant after exposition of the sample to the humidity of ambient air [15].

No significant reaction occurred between *meta*-vanadates and KCl during the binary catalyst preparation; only the diffraction peaks of the two catalyst components were in fact detected in the corresponding diffraction patterns.

In contrast, the spectrum of the $Cs_4V_2O_7 + AgCl + CsCl$ ternary catalyst (figure 1) shows that the two halides react during catalyst preparation to give the mixed chloride $AgCsCl_2$ (JCPDS card 37-875). This reaction did not occur during the preparation of $K_4V_2O_7 + AgCl + CsCl$ ternary catalyst because CsCl preferentially reacted with $K_4V_2O_7$ giving some $Cs_4V_2O_7$ and, likely, KCl (figure 2).

3.2. Catalytic activity

The temperatures corresponding to the combustion of half of the carbon contained in the sample (indicated as T_{50} in the following) were measured by TGA experiments, performed with different rates of temperature increase (table 1).

The results listed in table 1 show that both the catalytic and the non-catalytic combustion of carbon occur at tem-

Table 1

T_{50} (°C) measured for different catalysts and temperature scanning rates ϕ (°C/min).

Catalyst	T_{50} (°C)			
	$\phi = 5$ °C/min	$\phi = 10$ °C/min	$\phi = 20$ °C/min	$\phi = 50$ °C/min
None	650	671	714	755
KVO_3	470	494	513	560
$KVO_3 + KCl$	461	490	507	555
$CsVO_3$	445	465	480	540
$CsVO_3 + KCl$	380	411	439	470
$K_4V_2O_7$	425	450	475	520
$K_4V_2O_7 + AgCl + CsCl$	350	395	412	445
$Cs_4V_2O_7$	340	375	395	450
$Cs_4V_2O_7 + AgCl + CsCl$	338	370	395	450

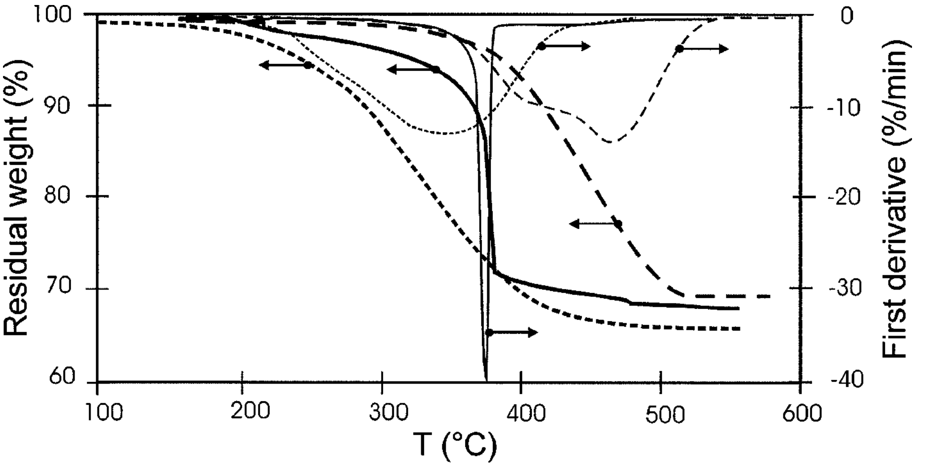

Figure 3. TGA and DTGA plots for the catalytic combustion of carbon over: $CsVO_3$ (dashed lines), $CsVO_3+KCl$ (full lines) and $Cs_4V_2O_7$–AgCl–CsCl (dotted lines).

perature ranges progressively increasing with the enhancement of the heating rate. All the vanadate-based catalysts show an appreciable catalytic activity since they significantly lower down the temperature range for carbon combustion.

The activity of *pyro*-vanadates is generally higher than that of the twin *meta*-vanadates. Both the *pyro*- and *meta*-vanadates of cesium are more active than the corresponding potassium vanadates. The addition to the catalyst of proper salts (KCl or AgCl+CsCl in the case of *meta*-vanadates and *pyro*-vanadates, respectively) enhances the catalytic activity through the formation of eutectic liquid which enables a certain catalyst mobility [12,13]. This effect is more remarkable when the eutectic melts well below the temperature at which the pure vanadate displays its activity; furthermore, this catalytic mechanism becomes significant only if an appreciable quantity of vanadate is incorporated into the liquid.

In particular, in the case of $CsVO_3 + KCl$ catalysts the eutectic melting at 389 °C shifted the T_{50} temperature (measured with heating rate of 5 °C/min) from 445 °C (characteristic of pure $CsVO_3$) to 380 °C only. Also the addition of AgCl + CsCl to $K_4V_2O_7$ caused a similar favourable effect, which may be only partially attributed to the eutectic liquid, because during the ternary catalyst preparation the formation of some $Cs_4V_2O_7$ (showing a higher intrinsic activity) occurred.

The formation of eutectic liquid was not so useful in the case of both KVO_3 (because the eutectic KVO_3–KCl melts at the rather high temperature of 485 °C) and $Cs_4V_2O_7$ catalyst (because only a small amount of $Cs_4V_2O_7$–AgCl–CsCl liquid forms at about 280 °C). In any case, the catalyst mobility increase, achieved through liquid formation, reduced the width of the combustion temperature range (see figure 3 for the systems $CsVO_3$ and $CsVO_3 + KCl$). From the same figure, it can be seen that, owing to the small amount of liquid formed, the $Cs_4V_2O_7$–AgCl–CsCl plots are more similar to those of the non-mobile $CsVO_3$ rather than to those of the mobile $CsVO_3$ + CsCl catalyst.

TPO experiments also confirmed that an activity hierarchy exists between the different vanadates: $Cs_4V_2O_7 > K_4V_2O_7 > CsVO_3 > KVO_3$. In table 2 for pure vanadates the T_{50} values obtained by TGA (with a temperature increase of 5 °C/min) are compared with the peak temperatures measured by TPO.

The combustion temperatures obtained with different experimental methods employed are not exactly the same. Actually, the T_{50} temperature generally does not correspond intrinsically to the temperature of maximum combustion speed (T_p of TPO measurements). Furthermore, carbon

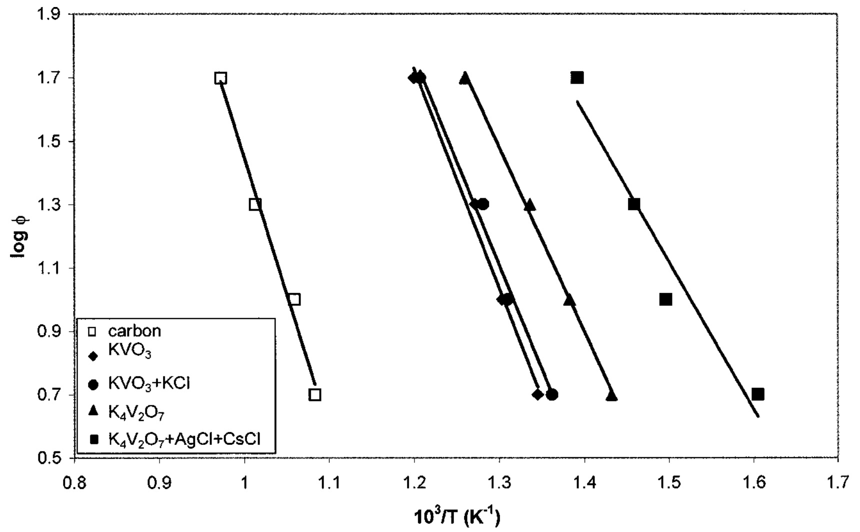

Figure 4. Ozawa plots for the catalysts based on potassium vanadates.

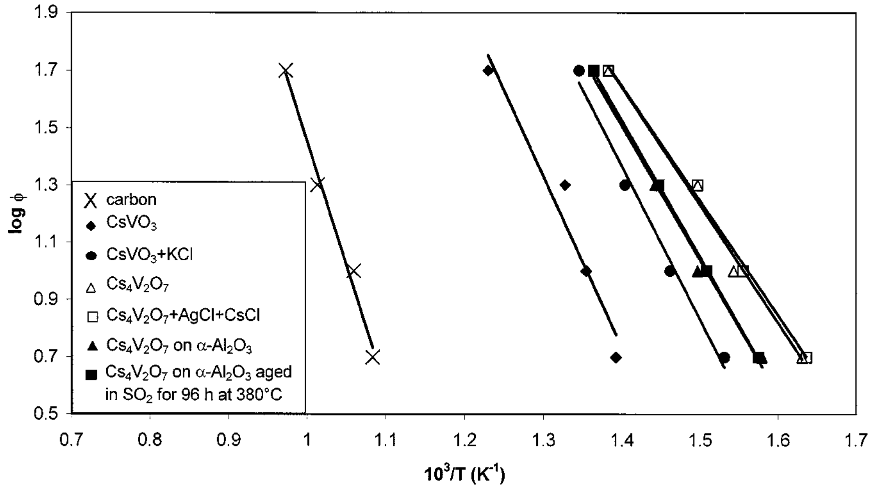

Figure 5. Ozawa plots for the catalysts based on cesium vanadates.

Table 2

Comparison of T_{50} and peak temperature for CO_2 formation, measured by TGA and TPO, respectively (scanning rate 5 °C/min).

Catalyst	T_{50} (°C)	T_p (°C)
KVO_3	470	451
$CsVO_3$	445	422
$K_4V_2O_7$	425	377
$Cs_4V_2O_7$	340	311

Table 3

Activation energy and correlation factor resulting from linear regression of the conversion data obtained with the investigated catalysts.

Catalyst	Activation energy (kJ/mol)	Correlation factor
None	157	0.989
KVO_3	126	0.988
$KVO_3 + KCl$	120	0.989
$CsVO_3$	109	0.950
$CsVO_3 + KCl$	97	0.989
$K_4V_2O_7$	106	0.998
$K_4V_2O_7 + AgCl + CsCl$	85	0.947
$Cs_4V_2O_7$	75	0.988
$Cs_4V_2O_7 + AgCl + CsCl$	73	0.995

combustion occurred more easily in the TPO equipment than in the TGA one because in the former the air flow permeates the fixed bed, whereas in the latter the air was gliding on the sample surface only, thus eventually enabling some oxygen transfer limitation.

3.3. Activation energy calculation

The Ozawa plots, based on the data listed in table 1, are shown in figures 4 and 5. The activation energy values and correlation factors, resulting from the linear regression calculation performed are listed in table 3. The correlation factor values show that the experimental results always well fitted a straight line in the Ozawa plots (as shown in figures 4 and 5).

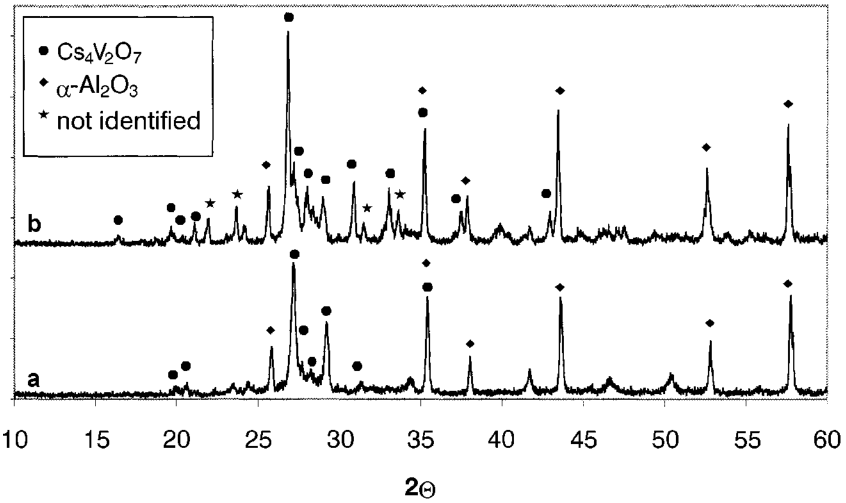

Figure 6. XRD diffraction pattern of the $Cs_4V_2O_7$ + AgCl + CsCl catalyst before (a) and after (b) under SO_2-rich atmosphere.

The activation energy for the uncatalysed reaction is rather high (157 kJ/mol) because amorphous carbon without any adsorbed liquid hydrocarbon was used in this investigation. This value is in good agreement with literature data concerning pure carbon [24]. The more active catalysts ($K_4V_2O_7$ + AgCl + CsCl, $Cs_4V_2O_7$ and $Cs_4V_2O_7$ + AgCl + CsCl) roughly halve the above activation energy value. As the catalyst prepared by using $K_4V_2O_7$, AgCl and CsCl contains a significant amount of $Cs_4V_2O_7$, which forms during the catalyst processing through a reaction between $K_4V_2O_7$ and CsCl (see XRD in figure 2), $Cs_4V_2O_7$ has to be considered the best catalytic species among all the tested vanadates. In addition, potassium *pyro*-vanadate showed a high degree of hygroscopicity (much higher than $Cs_4V_2O_7$) which makes difficult the production and the handling of the catalysts based on this compound.

The values of activation energy calculated are very likely different from those typical for diesel-soot combustion, because soot contains not only solid carbon but also a certain fraction of adsorbed hydrocarbon, mainly depending on the engine operating regime. Soot combustion is a complex process that involves several chemical reactions; as a consequence, an apparent activation energy, which averages the activation energies for each soot component, should be considered in order to state the effectiveness of combustion catalysts. However, as adsorbed hydrocarbons are believed to burn easier than pure carbon [24], the catalyst activities assessed in this investigation are thus to be regarded as conservatively under-estimated.

3.4. Catalytic activity and stability of $Cs_4V_2O_7$ supported catalyst

The comparison among the different investigated catalysts, carried out in the first part of this paper on the basis of TPO, TGA and activation energy calculations, showed that cesium *pyro*-vanadate displays the best catalytic activity towards carbon combustion. The addition of halides suitable for the formation of eutectic liquid at low temperature and, as a consequence, capable of enabling a certain degree of mobility to the catalyst, did not result in an appreciable improvement of catalyst performance. For these reasons, further ageing experiments were performed by using pure $Cs_4V_2O_7$.

However, the manufacturing of a catalytic trap requires the deposition of the *pyro*-vanadate on a ceramic filtering device. Chemical compatibility between ceramic support and vanadate is requested as well as great catalyst stability in the real working conditions (temperatures and gaseous environment characteristic of diesel emissions). In order to asses that $Cs_4V_2O_7$ fulfils these last requirements, the vanadate was supported on alpha-alumina powders and the behaviour of this catalyst was compared before and after thermochemical ageing treatments.

All the ageing treatments carried out at 380 or 600 °C in dry and wet air and the repeated use of this catalyst in combustion cycles (according to the experimental conditions described in section 2.2) did not cause changes in the corresponding XRD patterns.

In contrast, isothermal treatments under an atmosphere containing SO_2 (200 ppm) resulted in the growth of new diffraction peaks in the XRD spectrum, which can be attributed to the formation of reaction products, which, unfortunately, could not be identified (figure 6). However, the formation of these new catalyst components did not cause significant loss of catalytic activity, as TPO experiments showed. The TPO results of aged samples are compared with that of the as-prepared supported catalyst in table 4.

The peak temperature for CO_2 formation was found to slightly increase or decrease after thermal ageing, but the variations observed with respect to the untreated sample were always lower than 20 °C. More significant changes were shown by the measured values of selectivity towards CO_2. The measurement of this last parameter suffers of certain experimental errors because of the low mass of carbon (less than 10 mg) contained in the TPO samples. In fact, a less-than-perfect sample homogeneity or a small error in sample weighing might result in large errors in the selectivity calculation. Anyway, the selectivity values obtained show that the carbon may be considered almost completely converted to CO_2 during the TPO experiments.

Both XRD and TPO analyses indicate that the more significant changes in the catalyst were obtained after ageing in SO_2-rich environments. For this reason, the as-prepared supported catalyst and the aged one in presence of SO_2 (24 h at 600 °C) were studied by TGA in order to calculate the corresponding activation energy. The results of TGA tests are reported in table 5.

An increase of $Cs_4V_2O_7$ activation energy (of about 10 kJ/mol) resulted from the deposition of this vanadate on alumina powder. Very probably, this is caused by the diluting effect of the support; *pyro*-vanadate and alumina were mixed in a 1 : 1 weight ratio, thus, due to the high molecular weight of $Cs_4V_2O_7$, the surface of the alumina particles might not have been completely covered by the catalyst. The contact between carbon particles and zones of alumina surface not coated by $Cs_4V_2O_7$ should make the combustion reaction more difficult and governed by an activation energy higher than that typical of cesium pyrovanadate.

This feature, which probably also occurs when the vanadate is deposited on ceramic filtering devices, enlightens the importance of conferring to the catalyst a certain degree of mobility by means of eutectic liquid formation. Further investigations on this topic will be necessary, because the twin of chlorides AgCl+CsCl used in this study do not give a sufficient amount of molten eutectic in the temperature range characteristic for the carbon combustion catalysed by $Cs_4V_2O_7$.

However, the Ozawa plot for the supported catalyst (figure 5) shows that the deposition on alumina does not change the kinetic law for the combustion reaction: the experimental points are in fact fitted very well by a straight line (the correlation factor is very close to unity). Figure 5 also shows that the activation energy value is practically unchanged by a thermal treatment performed under a SO_2-rich gaseous atmosphere, even though following this treatment slight changes in the catalyst composition occurred, as shown in the XRD pattern of the aged sample. This is quite useful to preserve the performance of a catalytic trap in the long term under real operating conditions.

Table 4
Effect of ageing treatments on TPO peak temperature (T_p) and selectivity toward CO_2 (η) of supported $Cs_4V_2O_7$ catalyst.

Ageing treatment	T_p (°C)	η (%)
None	311	99
96 h at 380 °C in dry air	309	91
24 h at 600 °C in dry air	304	91
96 h at 380 °C in wet air	309	100
24 h at 600 °C in wet air	293	100
96 h at 380 °C in air + SO_2	315	100
24 h at 600 °C in air + SO_2	315	100
Eight repeated combustion cycles at 450 °C	308	90

4. Conclusions

The Ozawa method was successfully used for calculating the activation energy of carbon combustion catalysed by alkali vanadates or alkali vanadates/chlorides mixtures. The activation energy evaluation permits a correct comparison among different catalysts, because this parameter is characteristic of each catalyst and it is not affected by the experimental conditions adopted for carbon burning.

The activation energy values obtained by this method allow for drawing the following major conclusions:

- catalysts based on vanadates are suitable for greatly reducing the activation energy for carbon combustion;
- catalysts based on cesium vanadates are always more effective than those containing the corresponding potassium vanadate;
- *pyro*-vanadates show higher activity than *meta*-vanadates, likely owing to their higher O/V ratio;
- the most active catalyst, $Cs_4V_2O_7$, causes an activation energy decrease greater than 50% (from 157 down to 75 kJ/mol);
- the catalyst performance may be enhanced providing that the catalyst becomes “mobile” at its working temperature through the formation of an eutectic liquid, which improves the catalyst/carbon contact by wetting the carbon particles;
- this mechanism (achieved by mixing vanadates with suitable metal chlorides) is really powerful only if the eutectic melts at low temperature incorporating a sufficient amount of the active vanadate.

The deposition on α-Al_2O_3 of the more active $Cs_4V_2O_7$ catalyst only slightly decreases its activity, due to the diluting effect of the support itself. A complete compatibility of this catalyst and alumina was assessed. This supported

Table 5
Values of T_{50} temperature and activation energy evaluated by TGA tests for the supported catalyst before and after thermal treatment under SO_2.

Catalyst	T_{50} (°C) at various scanning rates				Activation energy	Correlation
	5 °C/min	10 °C/min	20 °C/min	50 °C/min	(kJ/mol)	factor
$Cs_4V_2O_7 + Al_2O_3$	360	395	420	460	85	0.997
Aged $Cs_4V_2O_7 + Al_2O_3$	362	390	418	460	86	0.998

catalyst shows great thermal and chemical stability at temperatures (380–600 °C) and under gaseous environments (containing oxygen, water vapour and SO_2) which simulate those characteristic of diesel emissions. Current efforts are focused on finding out new stable eutectic mixtures capable of dissolving a more and more significant amount of $Cs_4V_2O_7$ at lower and lower temperatures.

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