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Thermal stability of Cu–K–V catalyst for diesel soot combustion

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This paper reports a study on the thermal stability of a Cu–K–V catalyst, which showed particular promise for low temperature combustion of diesel particulate. Prolonged treatments were performed at high temperatures (400–1000°C) for periods up to 15 days under different gaseous atmospheres. The effect of such treatments on the catalyst composition was investigated by means of weight-decrease measurements and composition analysis (atomic absorption, X-ray diffraction, etc.), whereas the catalyst activity towards soot combustion was determined via thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The apparent activation energy of the soot combustion process was calculated for a collection of catalyst samples, thermally treated according to several different representative conditions, by the Ozawa method on the basis of the DTA results. Some of the thermal treatments (especially those performed at high temperatures: 900–1000°C) resulted in a reduction of the catalyst activity as shown by the increase of both the activation energy and the soot ignition temperature, as a consequence of the volatilisation of at least some of the active compounds of the catalyst itself (KCl, $CuCl_2$, etc.). Any periodic thermal regeneration of a catalytically-activated trap for diesel emissions (leading to such high temperatures) performed to eliminate any accumulated soot, has thus to be avoided by designing a trap capable of burning out all the soot produced at the diesel exhaust temperatures (< 400°C).

Keywords: Cu–K–V catalyst; diesel soot; catalytic combustion; catalyst stability

1. Introduction

More and more severe standards, aimed at controlling autovehicle emissions, have been progressively adopted in recent years both in Europe and in the USA. In this context, particular concern has been addressed to diesel engine emissions. Compared to spark ignition engines, diesel engines enable lower emissions of CO and unburned hydrocarbons, as a counterpart of much higher NO_x and soot contents in the exhaust. Soot is constituted of small-size solid carbon particles which coalesce to form aggregates with dimensions ranging between 0.8 and 1.5 μm [1]. Unburned hydrocarbon molecules, several of which show a mutagenic or carcinogenic activity, condense on the surface of the soot particulate. As a consequence, diesel soot is a serious health hazard.

Ceramic traps were developed for the purpose of reducing the particulate content in diesel emissions. Such traps, characterised by either a honeycomb or a ceramic-foam or a fibrous structure, can actually filter the soot, but need periodical regeneration by burning the trapped particulate in order to avoid high engine backpressures. As diesel particulate burns at about 650°C, regeneration can be made by heating the traps up to this temperature using an external heating system (warming resistances, microwaves, etc.), but the ceramic filter can be damaged in the long term because the soot combustion causes localised overheating.

The application of a washcoat containing suitable oxidation catalysts (metal oxides, noble metals and other transition metals [2–7]) on the filter walls may lead to a marked reduction of the trap regeneration temperature. Considering that the exhaust temperature is generally lower than 400°C, the ultimate goal should be to catalytically promote diesel soot combustion at those temperatures. This would allow the combustion of the soot captured inside the trap during the autovehicle run, with no need of regeneration and acceptable backpressures.

Several investigations on catalysts for the oxidation of carbonaceous materials were performed in the past: at first with the aim of improving the carbon gasification process and, more recently, with the goal of decreasing the soot combustion temperature. For example, McKee tested routinely the transition metals and their oxides as catalysts for the oxidation of graphite, demonstrating that molybdenum, chromium, copper and vanadium oxides show an appreciable activity [2–4]. According to this author also some salts and oxides of alkaline metals have a catalytic effect in the gasification of carbon [5]. Unfortunately, in the case of diesel particulate combustion some of the most effective oxides of transition metals (for instance CuO and Cr_2O_3) do not guarantee a satisfactory activity, which remains generally lower than that of noble metals (e.g. Pt, Pd). This feature was attributed to the poisoning of the above metal oxides by the SO_2 contained in diesel emissions [6]. Conversely the activity of V_2O_5 was found to be even enhanced by

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sulphur dioxide [7]. Despite of this, as reported in literature [7] and also observed in our preliminary experiments, the rate of particulate combustion catalysed by V_2O_5 is not satisfactory at temperatures below 400°C. The synergistic effect of different substances (noble metals, transition metal oxides, alkaline metal salts) simultaneously present in some catalysts for the particulate combustion has been assessed [8–13]. Among the multicomponent catalysts a particularly promising one was recently patented by Ciambelli and co-workers [9]. According to these authors their catalyst, containing different compounds of Cu, K, V and referred to as 137AA, is effective below 400°C in the combustion of graphite, carbon black and diesel soot. Several studies about the activity of 137AA catalyst are reported in literature [10–13]. Other investigations [14], performed in order to assess the catalyst stability towards any eventual poisoning by some component of real diesel emissions, using a fixed-bed of catalyst particles connected to the exhaust pipe of a diesel engine, showed that the activity is not seriously affected by the presence of NO_x and SO_2 at normal working temperatures (around 350°C). On the contrary, the catalytic mechanism and the durability under extreme operating tempratures were not completely assessed.

Concerning this last point it has to be underlined how, if the catalyst is not active enough to burn out the soot produced by the diesel engine at any of its operating regimes, an accumulation of soot in the catalysed trap would occur, even if at a much lower rate than for uncatalysed traps. Periodic regeneration of the trap by temperature rising through electric resistances or similar devices would nonetheless be necessary, causing localised overheating (up to 800–1000°C) where trapped soot aggregates burn. Despite the above-underlined high activity of Cu–K–V catalyst compared with monocomponent catalysts, the avoidance of any periodic regeneration cycles still seems difficult to be envisaged. On the other hand, a complete soot combustion immediately after its deposition on the filter could be achieved with the aid of external heaters (e.g., warming resistances) which keep the catalysed trap at a temperature of about 400°C, at the price of a certain energy consumption.

This paper deals with the assessment of the thermal stability of catalyst Cu–K–V. The composition of such catalyst was tested by atomic absorption and X-ray diffraction techniques, after various thermal treatments, carried out at different temperatures, under different gaseous atmospheres (either inert or oxidizing) and for different periods of time. Thermogravimetric analysis and differential thermal analysis were performed on catalyst–soot mixtures for the assessment of the activity of the various catalyst samples toward soot combustion. The apparent activation energy for this last reaction was determined by the Ozawa method and used, together with the soot ignition temperature, as an index of the catalyst activity.

2. Experimental

2.1. Diesel particulate

The diesel particulate was collected by filtering the emission of a diesel engine (Lancia Thema 2500TD) on a cordierite honeycomb trap. The particulate was stored in a closed vessel in order to prevent the desorption of volatile hydrocarbons. Morphological observations by scanning electron microscope showed that the filtered particulate was constituted of large aggregates of small soot particles with a high porosity (fig. 1). A surface area of 126 m^2/g was measured by the nitrogen absorption BET method. The measurement of the particulate size distribution was carried out using a Malvern 2600/3600 Particle Sizer. The analysis was carried out on a particulate suspension in ethyl alcohol under stirring. The size distribution, detected immediately after the suspension so as to avoid progressive crushing of soot particles into smaller aggregates, was the following (wt% of particles in each dimensional band): > 30 μm: 9%; 20–30 μm: 24%; 20–10 μm: 41%; < 10 μm: 26%. The soluble organic fraction extracted by dichloromethane (soxhlet equipment) was of 11.7 wt%. The gaschromatographic analysis of the extracted fraction showed that it is chiefly composed of *n*-paraffins. The weight fraction of volatile compounds was determined by thermogravimetric analysis, under nitrogen atmosphere: the particulate progressively lost 15% of its weight during a run up to 1000°C, reached at a rate of 20°C/min.

2.2. The catalyst

The catalyst was prepared as described in literature [11,13] by impregnation of an α-Al_2O_3 powder with an aqueous solution of NH_4VO_3, $CuCl_2{\cdot}2H_2O$, KCl (atomic ratio of dissolved Cu, K and V: 2/2/1), drying at 120°C, calcination in air at 700°C, and rapid cooling in ambient air. As described later a calcination treatment at 700°C for 4 h allowed us to obtain a catalyst with the optimum activity. The weight percent content of the various elements in such catalyst was determined by atomic absorption spectrophotometry for copper, potassium and vanadium (Cu: 6.80%, K: 4.52%, V: 3.25%), and with a specific electrode after dissolution in distilled water for chlorine (Cl: 1.62%). Any thermal treatment, carried out to assess the catalyst stability, was performed employing this catalyst as the starting material (reference catalyst).

The X-ray diffraction analysis of the Al_2O_3-supported catalyst gave only indications about some of the phases formed during calcination because of their low content in the sample. The catalyst X-ray diffraction pattern (fig. 2) showed the presence of KCl deposited on α-Al_2O_3. On the basis of weaker diffraction peaks also the formation of CuO and of $CuCl_2{\cdot}3Cu(OH)_2$ can be inferred. This last phase is likely obtained by reaction of

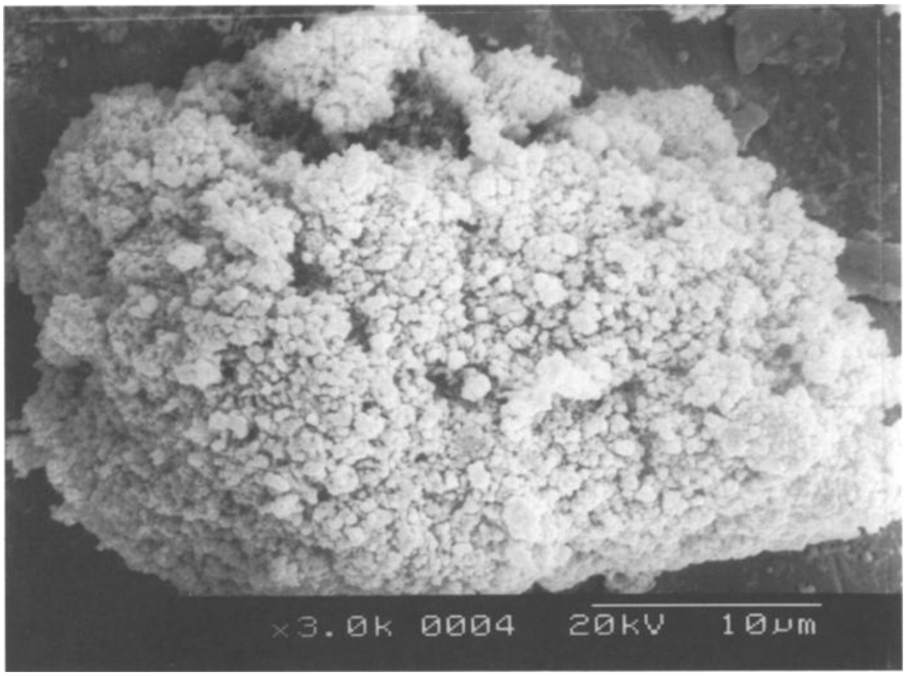

Fig. 1. SEM micrographe of a filtered soot aggregate.

a calcination product with the moisture of air. The formation of mixed vanadates probably occurs [11], but their identification through X-ray diffraction remains uncertain likely due to incomplete crystallisation of such phases. Further analyses are in progress so as to better understand the catalyst microstructure.

The surface area of the supported catalyst prepared (measured by the BET method) was about 1 m^2/g.

2.3. Thermal analysis

The activity of the catalyst was investigated by thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA), which are the most widely used experimental methods in the characterisation of the reactivity of the carbonaceous material [15]. The apparent activation energy was calculated from DTA data by using the Ozawa method [16–18].

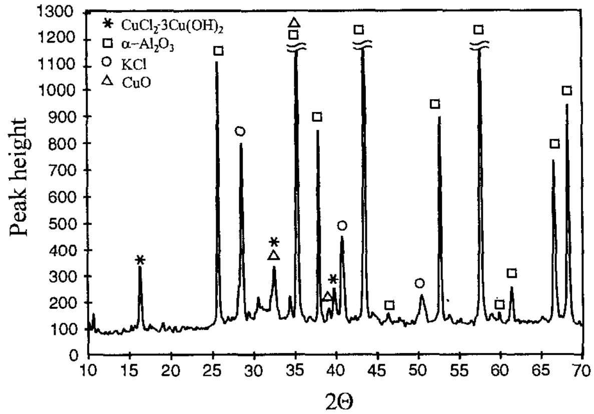

Fig. 2. X-ray diffraction pattern of the reference Cu–K–V catalyst.

For TGA measurements a Perkin Elmer Series 7 equipment was used; temperature scans with a rate of 20°C/min were performed keeping the sample in static air. The derivatives curves (DTGA) were also computed. DTA measurements (Netzsch calorimeter mod. 404) were carried out in air (flow rate of 500 ml/min) with scanning rates of 10, 20, 30 and 40°C/min. In each analysis a sample of 1 mg of a catalyst–soot mixture and 1 mg of α-Al_2O_3 as a reference were used. The samples were prepared by mixing in an agate mortar the diesel particulate with the catalyst at a 1/1 ratio. On the other hand α-Al_2O_3, instead of the catalyst, was mixed with the soot for studying the uncatalysed reaction. The conditions reported above for the air delivery in the calorimetric cells of both DTA and TGA equipment were chosen so as to operate in large excess of oxygen.

A peculiar characteristic of the Ozawa method is that the activation energy, which can be calculated on the basis of thermal analysis data, is only apparent. In fact, when a process involves several different phenomena (see below), the calculated activation energy is an average value which is not merely related to any of these single phenomena.

Previous investigations [16–20] on the combustion kinetics of bituminous coals containing a volatile fraction showed that several parallel processes occur:

(a) volatilisation of compounds, and combustion of volatiles in the gas phase;

(b) combustion of volatiles directly on the coal surface;

(c) combustion of the solid carbon.

Furthermore, kinetic studies on coal combustion processes put into evidence that different activation energy values correspond to subsequent combustion steps [19,20]. These values change with the fraction of converted coal following a trend which depends on the coal characteristics [20]. However, in order to compare the reactivity of coals a weighted-mean activation energy was used [18,19]. As diesel particulate should behave like high volatile coals, the Ozawa method, which gives an average value of activation energy, seems suitable to investigate the combustion kinetic of soot.

According to the Ozawa method the following kinetic law is proposed for the transformation investigated:

$$\frac{d\alpha}{dt} = K(T) f(1-\alpha)\,, \qquad (1)$$

where α is the fraction of reacted material; $K(T) = K_0 \exp(-E/RT)$ is the reaction constant; E the activation energy; and $f(1-\alpha)$ is a whatever function of the fraction of unconverted material.

The major advantage of this method is that the function $f(1-\alpha)$ must not be expressed. Starting from the above expression, Ozawa obtained the following equation which relates the scanning rate Φ with the absolute temperature (T) at which, during the temperature scan, a fixed fraction of material is reacted away:

$$\log \Phi = A - 0.4567\, E/RT\,, \qquad (2)$$

where A is constant.

For a fixed fraction of burned soot (α_i) the slope of the semilogarithmic plot of the scanning rates versus the $1/T$ corresponding to α_i (the DTA peak area is assumed to be proportional to the heat of combustion and to the amount of diesel particulate employed) gives the apparent activation energy. Ozawa plots were obtained processing the DTA results for uncatalysed and catalysed combustion of soot particulate. These plots were attained for fractions of converted material corresponding to 25, 50 and 75% of the overall heat of combustion.

2.4. Catalyst stability

The salts of Cu, K and V used for the impregnation of the α-Al_2O_3 undergo chemical reactions during calcination and, starting from about 450°C, form a liquid phase. This last property might be useful during catalyst preparation since it can guarantee a good lining of the support with the catalytic material. However, the melt material can lose some components by evaporation; for this reason the activity of the catalyst appreciably depends on the calcination time and temperature as discussed in the next section. Catalyst samples were isothermally treated at 700, 800, 900 and 1000°C with the final goal of a better understanding of the change in composition which happens when the catalyst is kept at high temperature under static air. After treatment periods fixed in advance, part of each sample was analysed in order to evaluate the weight loss and the residual content of Cu, K, V and Cl. The activation energy for the catalysed particulate combustion was determined by the Ozawa method before and after submitting the catalyst to isothermal treatments. These last thermal treatments were carried out in a few representative different conditions scheduled on the basis of both the results of the above described experiments and the normal and extreme working conditions expected for the catalysed trap:

(1) Catalyst samples were isothermally treated in air at 400, 800 and 1000°C for 15 days, 8 days and 3 h respectively.

(2) Other samples were inserted in silica tubes, which were then sealed under vacuum and treated at 400 and 800°C as above.

(3) A specimen was heated at 1000°C under inert gas flow (argon).

The ageing test at 400°C was carried out because, as discussed earlier, probably a particulate trap activated with the Cu–K–V catalyst could provide efficient combustion of diesel particulate working at this temperature with the aid of external heaters. Furthermore, temperatures of 800 and 1000°C are the peak temperatures which can be reached during the particulate burning after soot accumulation in the trap. Figs. 3a and 3b show respectively the temperatures reached inside a particulate diesel trap during regeneration after a middle and a high level of particulate deposition (courtesy of Centro Ricerche Fiat, Orbassano, Turin).

The runs with sealed samples were performed so as to assess whether losses in the catalyst activity can be attributed merely to catalyst evaporation or also to some changes in its composition. In particular, from the comparison between the results obtained after treatment in air and in sealed vessel, it is possible to see the effect of evaporation, whereas the comparison between the runs in air and in inert gas puts into evidence the effect of oxygen partial pressure in conditioning the chemical nature and activity of the catalyst.

Further, the run under inert gas atmosphere was carried out to simulate those conditions in which large soot aggregates burn locally enhancing the temperature and depleting the oxygen concentration.

3. Results and discussion

Preliminary tests performed with the aim to optimize the catalyst preparation method, showed that the efficiency of this catalyst is affected by both calcination temperature or time. Samples of catalyst were calcined at different temperatures for 4 h. The activity towards particulate combustion was assessed for each of these samples by TGA experiments. In table 1 the temperatures of

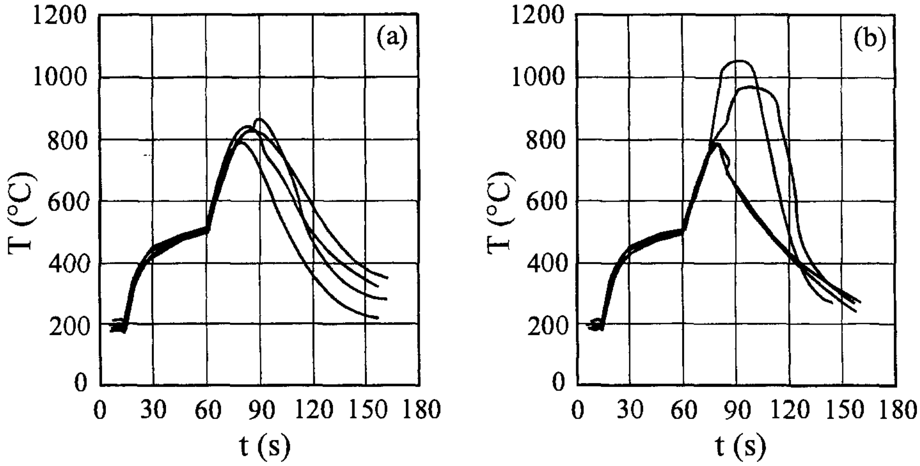

Fig. 3. Temperature evolution in several axial points of an uncatalysed honeycomb particulate trap during thermal regeneration: (a) low soot load; (b) high soot load. (Courtesy of Centro Ricerche FIAT, Orbassano, Italy).

maximum rate of weight loss (i.e. the peak temperature in the derivative curves of TGA) are reported. Since the peak in DTGA curves for uncatalysed particulate combustion was 669°C (with a scanning rate of 20°C/min), it can be concluded that the catalyst greatly increases the soot reactivity. Table 1 shows that calcination at temperatures higher than 700°C decreases the catalyst activity. The X-ray diffraction patterns of the different catalyst specimens show only slight differences in the relative intensities of the peaks attributed to copper oxychloride and potassium chloride. As a result, the observed decrease of activity can be attributed to a small variation in the ratio between the phases formed during calcination, likely due to partial evaporation of some components. In table 2 the DTGA peak temperatures for catalyst–particulate mixtures prepared using samples of catalyst calcinated at 700°C for different periods of time are reported. Calcination periods longer than 4 h at 700°C cause a decrease of the catalyst activity (table 2). The comparison of XRD patterns of catalyst specimens calcined for different times also put into evidence only a variation of the relative intensities of the reflexes.

Looking for an explanation of such catalyst deactivation, the weight loss of a catalyst treated in air flow, at different temperatures (700–1000°C) and for different periods of time, was evaluated (fig. 4), starting from the reference catalyst. Further, in fig. 5 the time-dependency of the weight percentages of Cu, K, V and Cl, evaluated in the same operating conditions is shown.

From fig. 4 it appears clear that the catalyst loses weight for prolonged treatment at high temperatures, the weight loss being rather dramatic for 900 and 1000°C. At such temperatures a plateau is reached within a few hours corresponding to an about 15% weight decrease. A similar behaviour can be observed in fig. 5 concerning the Cu, K and Cl residual concentrations in the catalyst referred to its final weight, the limiting concentrations being approximately: Cu = 2%; K = 1.7%; Cl = 0.2%. Due to the loss of these elements, the percentage of V increases at beginning of the thermal treatments, then it slowly decreases showing as long term exposure causes a slight depletion of V, too.

From these data it can be concluded that the catalyst loses essentially copper and potassium chlorides during prolonged stay at temperatures higher than 700°C. This phenomenon is more and more rapid at increasing temperature. On the other hand, only a slight decrease of the content of vanadates can though be noticed at the same operating condition.

A kinetic study was then performed on a few samples treated under different representative conditions (static air in either open or closed vessels; inert gas) by the Ozawa method so as to better understand the effect of such treatments on the catalyst activity. The results of

Table 1
Peak temperatures of DTGA curves for mixtures of particulate and samples of the Cu–K–V catalyst calcined for 4 h at different temperatures (scanning rate: 20°C/min)

Calcination temperature (°C)	DTGA peak temperature (°C)
650	387
700	380
750	498
800	492

Table 2
Peak temperatures in DTGA curves for a mixture of particulate and samples of Cu–K–V catalyst calcined at 700°C for different times (scanning rate: 20°C/min)

Calcination time (°C)	DTGA peak temperature (°C)
1	374
4	380
5	429
8	475
10	476

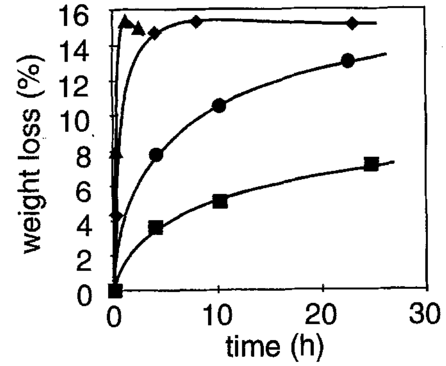

Fig. 4. Catalyst weight loss vs. time during calcination in calm air at different temperatures ((■) 700°C; (●) 800°C; (◆) 900°C; (▲) 1000°C).

such experiments are shown in fig. 6, where plots for the basic catalyst and for the uncatalysed combustion of soot are also reported.

In this figure the activation energy calculations refer to a fraction of burned particulate corresponding to the 50% of the combustion enthalpy. The values of apparent activation energy for catalysed (reference catalyst) and uncatalysed particulate combustion, calculated from DTA data referring to different fractions α_i, are reported in table 3.

As expected, the activation energies in table 3 vary with the percentage of heat of combustion used as a reference. In fact, as the combustion process progressively involves all the components of the particulate (i.e., volatile and solid), these apparent activation energy values refer to different sets of single chemical reactions which cause the emission of the 25, 50 and 75% of the combustion heat respectively. The volatiles burn first, the solid after.

However, table 3 shows that the activation energy decrease given by the Cu–K–V catalyst is not changing seriously with the fraction of combustion enthalpy considered. The 50% combustion heat fraction was chosen as a reference for all runs whose results are plotted in fig. 6, since the corresponding temperature can be evaluated more precisely than those related to the other two fractions.

The weighted-mean apparent activation energies for catalytic combustion of coal greatly depend on the volatiles content of these solid fuels [13,15,19,20], and can range between 56 kJ/mol (for lignite with 54 wt% of volatiles) and 176 kJ/mol (for petroleum coke anthracite with 7.8 wt% of volatiles). However, according to literature, also the activation energy for the uncatalysed combustion of diesel particulate can change with the soot characteristics, ranging from 102 to 178 kJ/mol [7,10]. The values of apparent activation energies obtained in the present study for the catalysed and uncatalysed reaction are consistent with the literature data taking into account the volatile content in the particulate under investigation.

Table 4 lists the apparent activation energies (calculated by least squares fitting of the data in fig. 6) and the DTA peak temperatures for the various catalyst samples which underwent additional thermal treatment.

Long-time thermal exposure at 400 and 800°C of the catalyst contained in sealed silica tubes does not affect

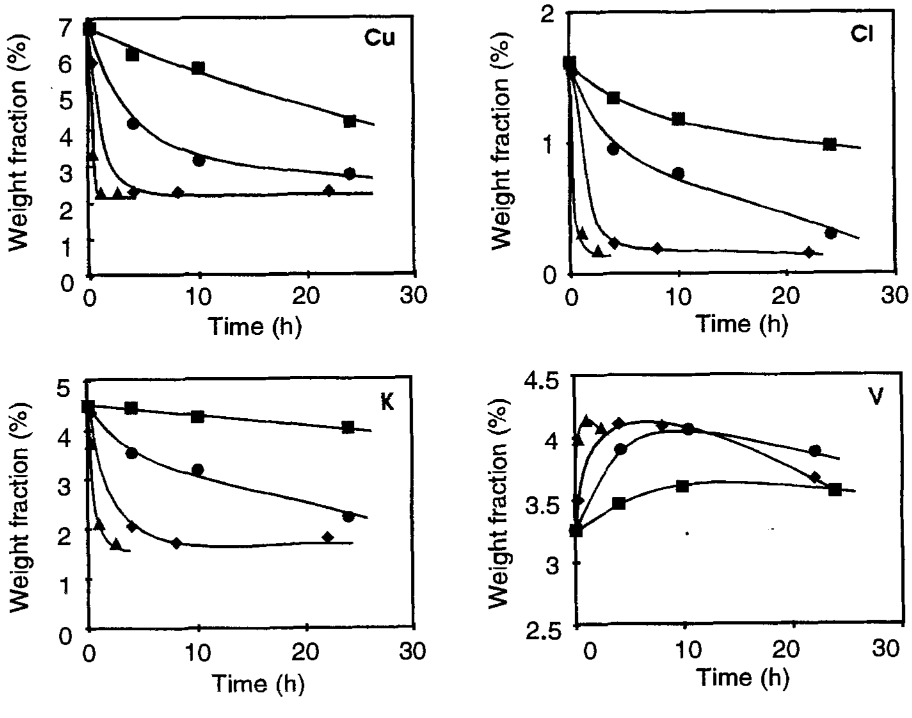

Fig. 5. Time-dependency of the weight fraction of elements Cu–K–V–Cl in catalyst samples treated at different calcination temperatures ((■) 700°C; (●) 800°C; (◆) 900°C; (▲) 1000°C).

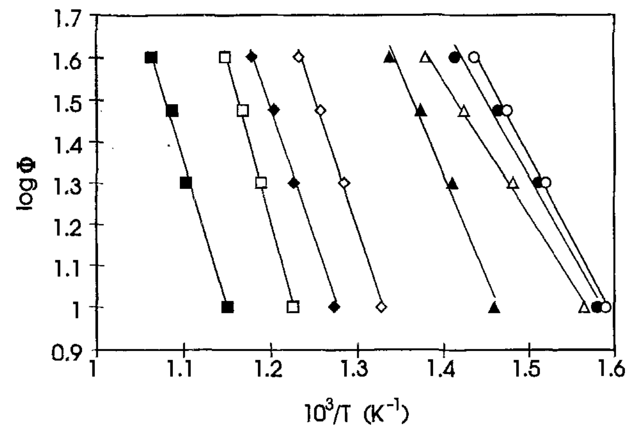

Fig. 6. Ozawa's plots for uncatalysed and catalysed particulate combustion, enlightening the effect of various heat treatments on the apparent activation energy of the reaction. Legend: (■) uncatalysed combustion; (●) reference catalyst; (▲) after 15 d at 400°C in air; (△) after 15 d at 400°C in a sealed silica vessel; (○) after 8 d at 800°C in a sealed silica vessel; (◇) after 8 d at 800°C in air; (◆) after 3 h at 1000°C in static air; (□) after 3 h at 1000°C in inert gas.

its activity: only slight variations in the apparent activation energy (see table 4) and in the particulate combustion temperature were observed. This is a clear sign that no chemical degradation of the catalyst takes place during these treatments.

On the contrary, similar thermal treatments performed in static air (at 400, 800 and 1000°C) cause a reduction in the catalyst activity which is more and more important as long as the treatment temperature increases. Since this behaviour cannot be attributed to chemical degradation, this phenomenon should also occur during the treatments of specimens sealed in silica tubes, partial evaporation of active components of the catalyst has to be regarded as the most likely cause for the deactivation obtained. X-ray diffraction analysis does not show the formation of new phases or the complete disappearance of any component of the catalyst, however the peaks attributed to KCl and $CuCl_2 \cdot Cu(OH)_2$ become very weak. This is perfectly in line with the observations made concerning the weight loss experiments (figs. 4 and 5), which lead to the conclusion that K and Cu chlorides are prone to leave the catalyst by evaporation at high temperatures. The active role of some chlorides in catalytic combustion of carbonaceous material was assessed by some researchers [21], which confirms that the observed loss of activity has to be attributed to the at least partial disappearance of chlorides. The residual activity of the catalysts (especially for those treated at 800 and 1000°C) is likely to be referred to their residual content of vanadates, which also showed a significant activity towards soot combustion [22].

Table 3
Comparison between the apparent activation energy for uncatalysed and catalysed particulate combustion, calculated for different fractions of the heat of combustion

Fraction of the heat of combustion considered (%)	Activation energy (kJ/mol)	
	uncatalysed reaction	catalysed reaction (basic Cu–K–V catalyst)
25	141	55
50	128	67
75	117	52

An almost complete loss of activity was observed after a 3 h treatment at 1000°C under inert gas flow. The catalyst damage seems to be irreversible, because a subsequent calcination in air at the same temperature and for the same time length does not restore completely the catalyst activity.

The X-ray diffraction pattern of the catalyst after 3 h at 1000°C under inert gas flow is reported in fig. 7. This spectrum is appreciably different from that of the catalyst before the thermal treatment, in fact the reflexes for KCl and CuO disappear in the X-ray pattern.

The presence of V_2O_3 and Cu characteristic peaks in this spectrum shows that the oxidation numbers of vanadium and copper decrease. During the subsequent treatment in air the vanadium is oxidised (probably up to an oxidation number of 5) and the peaks of V_2O_3 disappear. The loss of activity consequent to the high temperature treatment in inert gas is then likely attributed to chemical degradation of the vanadates, which were stabilised by the presence of oxygen in the treatments with static air.

Table 4
Influence of some thermal treatments on catalyst activity and apparent activation energy

Thermal treatment temperature	Time	Activation energy (kJ/mol)	DTA peak temperature (scanning rate: 10°C/min)
400°C in air	15 d	91	420
400°C in sealed quartz vessels	15 d	59	365
800°C in air	8 d	116	487
400°C in sealed quartz vessels	8 d	72	347
1000°C in air	3 h	118	530
1000°C in inert gas	3 h	144	556
reference catalyst	–	67	354
uncatalysed combustion	–	129	616

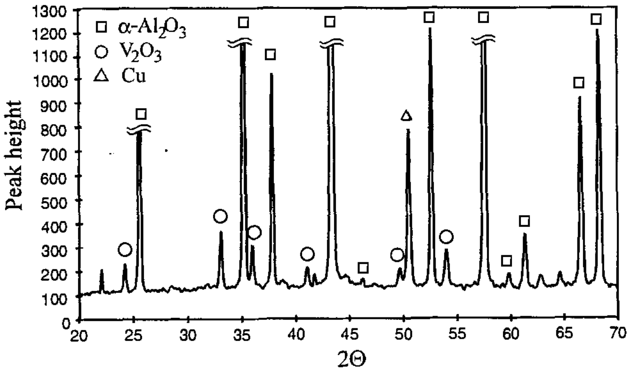

Fig. 7. X-ray diffraction pattern of the Cu–K–V catalyst after treatment for 3 h at 1000°C under inert gas flow.

4. Conclusions

The performance and the thermal stability of catalyst Cu–K–V for catalytic combustion of diesel soot were assessed. The temperature range and activation energy for the combustion of soot particulate are greatly lowered by the Cu–K–V catalyst, though long-term isothermal treatment under air or inert gas flow at a temperature higher than that adopted in the processing of the catalyst (700°C) results in appreciable decrease of the catalyst activity.

This behaviour is due to evaporation of part of the active components of the catalyst. In particular, Cu, K and Cl leave the supported catalyst to a certain extent depending on both the temperature and the treatment time. Twin isothermal treatments performed keeping the samples in sealed silica tubes did not affect the catalyst activity. Actually, in this last case equilibrium conditions between the gaseous phases and the catalyst are probably achieved, thus hindering the evaporation of active components.

High temperature treatment in inert gas flow though leads to chemical decomposition of vanadates, together with the evaporation of potassium and copper chlorides.

As a final consideration it has to be underlined how, despite the Cu–K–V catalyst appears a promising candidate for diesel soot combustion applications, a soot trap activated with such catalyst has to be capable of burning out all the soot produced by the diesel engine. Otherwise, any soot accumulation in the trap itself, leading to periodic thermal regeneration of the trap, would probably result in a progressive catalyst damage, due to the high temperatures reached during this regeneration step. Despite the high activity of the catalyst such goal seems difficult to attain at low engine loads unless external heaters are used to keep the trap temperature just above 350°C. In this case, the catalyst would be able to continuously burn out the soot produced by the engine, without any accumulation.

Further studies, performed in order to achieve a better understanding of the catalyst chemical and physical structure and of the role played by any component (vanadates, chlorides, ...) on the catalyst activity, are in progress. Perhaps, the effect of SO_2 and NO_x on the catalyst activity at high temperatures (> 400°C) might also be worthwhile investigating, extending the aforementioned studies by Ciambelli and coworkers [14], to such extreme operating conditions.

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