Combustion of carbon particulate catalysed by mixed potassium vanadates and KI

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A K–V–I-containing catalyst for low-temperature combustion of carbonaceous materials was studied so as to check its potential in diesel particulate removal. X-ray diffraction (XRD) and scanning electron microscopy (SEM-EDS) showed that its main constituting compounds are KVO_3, KI and $K_4V_2O_7$. Differential scanning calorimetry (DSC) and temperature-programmed oxidation (TPO) tests enlightened that the catalyst is active well below 400 °C (peak combustion temperature: $T_p = 380\,^{\circ}C$). Thermal treatments carried out at this temperature with dry or humid air did not entail detrimental effects on the catalyst performance. Similar treatments at higher temperatures (600 and 750 °C) resulted in a modification of the catalyst composition and in a slight decrease of its activity (T_p increases of about 60 °C). These last treatments caused the progressive loss of active components due to either evaporation of eutectic liquid formed at about 450 °C or production of gaseous iodine through a reaction between KI and KVO_3, which also gave rise to the formation of $K_4V_2O_7$. However, the consequent deactivation was moderate owing to the high intrinsic activity displayed by the formed potassium pyrovanadate.

Keywords: K–V–I catalyst, diesel particulate, catalytic combustion

1. Introduction

Diesel engine emissions are potentially harmful for human health especially because of their particulate content. For this reason most industrial countries are tightening their emission regulations [1]. One of the possible ways to reduce particulate emission lies in filtering it with traps, and continuously burning it out thanks to the presence of a catalyst which promotes its combustion at the rather low temperatures of the exhaust pipe (below 400 °C). Most studies performed in the last years were focused on systems based on the combination of halides, oxides, molybdates or vanadates of alkali and transition metals. Two systems have shown a particularly high activity: a Cu–K–Mo–Cl-based catalyst [2] and a Cu–K–V–Cl-based one [3–5]. The above materials are active through a gas-phase and a liquid-phase mobility mechanism, respectively, which are responsible for their superior activity because of the improved contact conditions between the catalytically active species and diesel particulate. Nevertheless, both these systems contain copper chloride, which is toxic and is, moreover, a known oxychlorination catalyst that can lead, in contact with diesel exhausts, to formation of toxic chlorinated compounds, such as dioxins [6]. Hence, the authors have recently addressed their research on new Cu-free catalysts based on halides and vanadates [7]. Recent investigations have shown that these catalysts display their activity through the formation of low melting eutectics; on the other hand, the formation of liquid phases makes them prone to degradation by loss of some active components as vapours.

In this context, a KI–KVO_3 catalyst supported on α-alumina has been considered. In this paper, its activity is investigated as well as its reaction mechanism, which turned out to be quite different from that of the twin catalysts based on mixed halides and vanadates mentioned above. Moreover, its hydrothermal stability was checked so as to evaluate its potential for practical application.

2. Materials and methods

2.1. Catalyst preparation

The catalyst was prepared by incipient-wetness impregnation of an α-Al_2O_3 powder (grain size 38–63 μm) with aqueous solutions of potassium metavanadate and potassium iodide in a 1 : 1 molar ratio (for more details about the impregnation procedure and apparatus, see [5,7]). The impregnated powder was then dried at 120 °C for 1 h and calcined at 700 °C for 4 h in calm air. The formation of some eutectic liquids among catalyst components at these temperatures helps to achieve a better coverage of the support, as demonstrated for similar catalytic systems [8]. The potassium metavanadate used for this purpose was obtained by melting together potassium carbonate and vanadium pentoxide at 600 °C. In a similar manner, but changing properly the molar ratio of the precursors, the vanadate $K_4V_2O_7$ was also prepared as a reference material at 750 °C, because it was assessed to be one of the major components of the

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$KVO_3 + KI$ catalyst after thermal exposure, as discussed later. Reference catalysts, containing only single vanadates supported on α-alumina, were also prepared. For all the catalysts the weight ratio between the precursor salts and the α-Al_2O_3 support after the drying step was set equal to 1.

2.2. Catalyst ageing

The catalyst was submitted to several isothermal treatments, so as to check its stability under different conditions:

- in dry air at 380 °C for 96 h;
- in humid air (containing about 12 vol% of water, a concentration representative of diesel exhaust conditions) at 380 °C for 96 h;
- in dry air at 600 °C for 24 h;
- in humid air (same as above) at 600 °C for 24 h;
- in dry air at 750 °C up to 65 h.

2.3. Catalyst characterisation

The composition and microstructure of the investigated catalyst were studied by X-ray diffraction (XRD) using a Philips PW1710 apparatus equipped with a monochromator (Cu K_α radiation). On some particular samples, mostly related to the above described thermal stability tests, specific elemental analyses were also carried out: the catalyst active components were dissolved in an acid concentrated solution ($HCl : HNO_3 = 1 : 1$) and quantitative analyses were performed by atomic absorption spectroscopy (for K and V) and by liquid ionic chromatography (for I). The chemical characterisation was completed by SEM-EDS analysis. Finally, in order to investigate the chemical reactions or the physical state transitions that might occur in the catalyst at high temperatures, mixtures of KVO_3 and KI were submitted to differential scanning calorimetry (Dupont DSC 910, scanning rate 10 °C/min).

2.4. Activity tests

The catalytic activity towards the combustion of amorphous carbon (particle diameter: 45 nm in diameter; ashes and adsorbed moisture content: 0.34 and 12 wt%, respectively) was studied by differential scanning calorimetry (DSC) and temperature-programmed oxidation (TPO). DSC tests with a scanning rate of 10 °C/min up to 550 °C were performed in air on a mixture of carbon and supported catalyst held in aluminum crucibles. The samples for TPO analyses were prepared by mixing the supported catalyst and the carbon in a 1 : 1 weight ratio either by accurate mixing in a mortar (tight contact conditions) or by shaking the powders in a bottle (loose contact conditions). Afterwards, these samples were submitted to a linear rise of temperature (up to 700 °C, 10 °C/min rate) with an air flow in the TPO equipment. The TPO experimental set-up is described in detail elsewhere [9]. The fixed bed in the reactor consisted of 20 mg of a 1 : 1 by weight mixture of carbon and supported catalyst (prepared as described above) and 100 mg of inert SiO_2 granules (0.3–0.7 mm), just used to reduce the specific pressure drop and prevent thermal runaways. Three tests were carried out on each sample so as to determine an average temperature value (T_p) corresponding with the maximum of the CO_2 outlet concentration peak. In a particular TPO run, performed to assess the catalytic effect of the vapours released by the catalyst at high temperature, the catalyst (200 mg) and the carbon (10 mg), each one mixed with SiO_2 grains, were placed in two consecutive fixed beds separated by a quartz wool layer, in order to avoid any direct contact. This way, only the vapours released by the catalyst into the flowing air could reach the carbon. Since these vapours contained iodine, a further TPO run was carried out with a carbon–silica mixture as fixed bed through which air containing about 20 vol% of I_2 vapours was flowing.

3. Results and discussion

3.1. Catalyst activity and reaction mechanism

The $KVO_3 + KI$ catalyst shows appreciable activity in the combustion of amorphous carbon by lowering the TPO combustion peak in tight contact conditions from the value of 660 °C, typical for the not-catalysed reaction, to 382 °C (table 1); therefore its activity seems at least comparable to that of the best catalytic systems reported in the literature [2,4].

In figure 1 the X-ray diffraction patterns (XRD) of the supported $KVO_3 + KI$ catalyst, after calcination periods of 4 and 6 h, respectively, are compared with that of KVO_3. It can be seen that if the calcination step is prolonged over 4 h a new compound, namely potassium pyrovanadate ($K_4V_2O_7$), forms in appreciable amount. Probably a small amount of $K_4V_2O_7$ is already present in the sample calcined for 4 h only, but its percentage is too low to give well evident peaks in the XRD pattern. The prevalent activity of this new compound is proven by the comparatively low peak temperature (360 °C) measured with pure pyrovanadate as the only catalyst (table 1).

Table 2, where the TPO peak temperatures measured for samples with different carbon-to-catalyst ratios or mixing

Table 1

Alumina-supported catalysts: peak temperatures (T_p) of carbon combustion TPO curves. Catalyst-to-carbon ratio 1 : 1.

Catalyst and ageing conditions	T_p (°C)
Not catalysed combustion	660
$KVO_3 + KI$ catalyst calcined for 4 h at 700 °C in dry air	382
$KVO_3 + KI$ catalyst calcined for 6 h at 700 °C in dry air	379
$KVO_3 + KI$ catalyst aged 96 h at 380 °C in dry air	382
$KVO_3 + KI$ catalyst aged 96 h at 380 °C in humid air	386
$KVO_3 + KI$ catalyst aged 24 h at 600 °C in dry air	437
$KVO_3 + KI$ catalyst aged 24 h at 600 °C in humid air	443
KVO_3 catalyst	500
$K_4V_2O_7$ catalyst	360

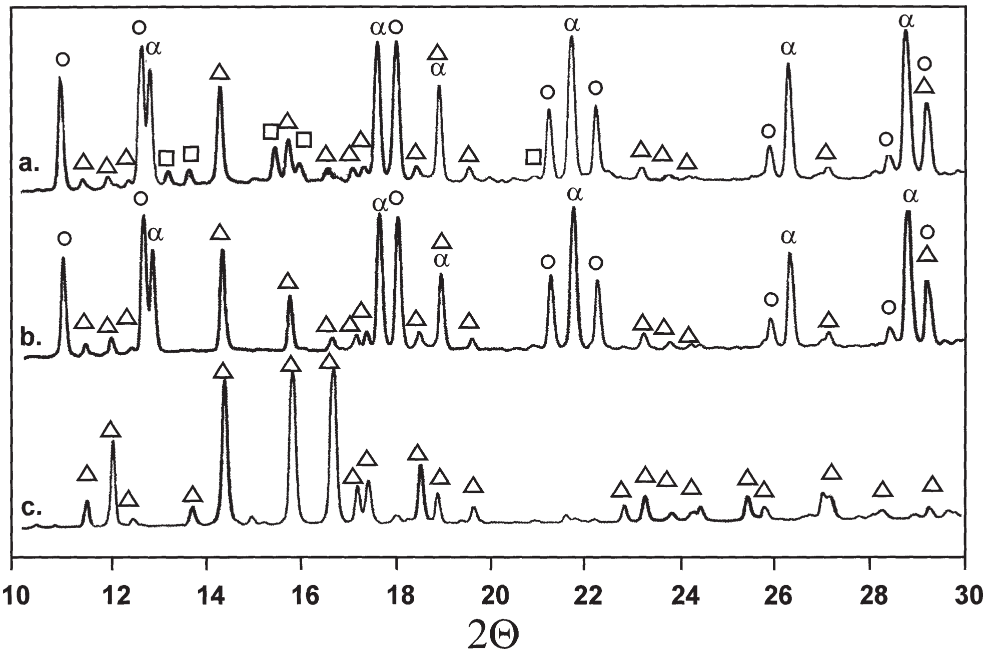

Figure 1. XRD patterns of: (a) catalyst based on KI + KVO_3 supported on α-Al_2O_3 calcined for 6 h at 700 °C, (b) catalyst based on KI + KVO_3 supported on α-Al_2O_3 calcined for 4 h at 700 °C, (c) pure KVO_3. (△) KVO_3, (○) KI, (α) α-Al_2O_3, (□) $K_4V_2O_7\cdot 2H_2O$.

Table 2
KVO_3 + KI catalyst: combustion TPO peak temperatures (T_p) obtained under different experimental conditions.

Catalyst/carbon ratio	T_p (°C)	
	Tight contact	Loose contact
8 : 1	378	565
4 : 1	380	570
2 : 1	385	585
1 : 1	382	600
1 : 2	429	614
1 : 5	484	645

methods (loose or tight contact) are listed, gives some information about the catalytic mechanism governing the activity of the catalyst under investigation. Independently of the contact mode, T_p decreases by increasing the catalyst-to-carbon ratio in the sample, at least for ratios lower than 1. Beyond this limit, the TPO peak temperature of tight-contact samples does not change significantly. This is rather obvious, since according to this intensive way of putting catalyst and carbon into contact, beyond a certain catalyst mass nearly all the carbon available comes into good contact with the catalyst itself. Conversely, for loose-contact conditions, a further progressive decrease of the peak temperature occurs for catalyst-to-carbon ratios higher than 1.

The samples prepared by tight contact burn systematically at temperatures much lower than those of the samples characterised by loose contact. For the heterogeneous reaction between solid carbon and oxygen catalysed by a solid catalyst, a close contact between the particles of carbon and those of the catalyst is required in order to allow the best catalytic effect. On the other hand, since T_p for tight contact does not decrease significantly by increasing the catalyst-to-carbon ratio over 1 : 1, this last value seems to be sufficient for maximising the overall catalytic performance. As discussed in a previous paper [9] and reported in the literature [10], on the basis of the grain size of both carbon and alumina support, a 1 : 1 ratio should not be sufficient to allow a complete solid–solid contact, leaving a considerable fraction of carbon untouched by the catalyst. Therefore, since the solid–solid contact does not seem to be controlling the catalyst activity, some degree of mobility of catalyst components should be inferred.

The comparison among DSC runs performed on the pure catalyst and on carbon–catalyst mixture helps to clarify this point. Curve (a) in figure 2, referring to the catalyst–carbon mixture, shows a sharp exothermic effect at about 380 °C related to the catalytic combustion. Conversely, for curve (b), concerning the pure catalyst, an endothermic phenomenon takes place starting from about 450 °C. This temperature is well above the obtained T_p value for the catalysed carbon combustion, but it is lower than the melting point of each single component of the catalyst: in fact, KVO_3 melts at 520 °C, KI at 681 °C and $K_4V_2O_7$ at 675 °C. The endothermic peak can very likely be attributed to the melting of an eutectic phase formed between the catalyst components. However, since the eutectic liquid forms well above 400 °C, it cannot be responsible for the catalyst mobility at the combustion peak temperature.

Two tests were thus carried out to investigate a possible catalyst mobility due to vapour phases.

First, the supported catalyst was kept in the TPO reactor in isothermal conditions at 380 °C under air flow; the outlet gas was bubbled in an aqueous solution of KI which became brown coloured because of the dissolution of io-

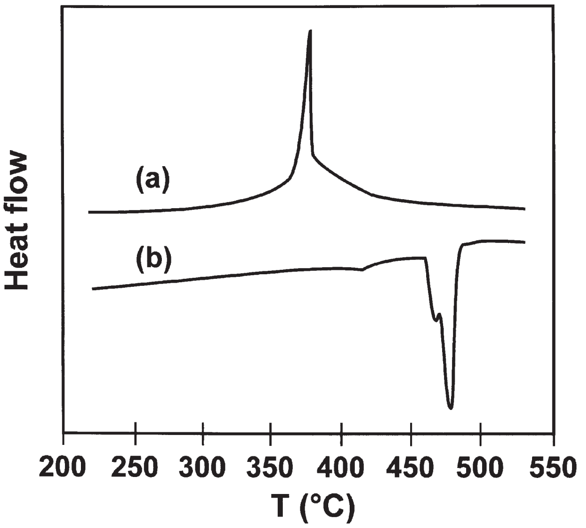

Figure 2. Comparison of DSC plots related to: (a) catalyst/carbon 1 : 1 sample under air flow, (b) catalyst only, sealed in the sample holder to avoid iodine escape possibly damaging the experimental apparatus.

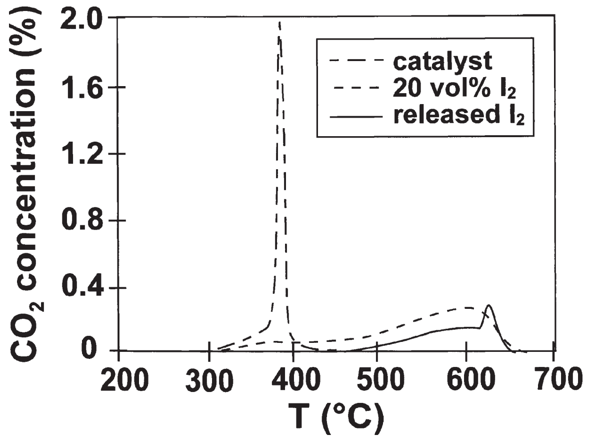

Figure 3. Comparison of carbon combustion TPO curves obtained under three different operating conditions: for a carbon/catalyst mixture in tight contact, in the presence of the vapours released by the solid catalyst, with an air flow containing 20 vol% of sublimed iodine vapours.

dine vapours, as demonstrated by the chemical analysis too. Moreover, the thermal stability in air flow at 380 °C of KI and of a mixture of $KI + KVO_3$ was also checked, noticing a progressive weight loss to an asymptotic value of about 1% only for the $KI + KVO_3$ mixture.

Second, a carbon sample was submitted to two TPO runs, one with a flow of air carrying the vapours released by the catalyst and the other with an air flow containing 20 vol% of sublimed iodine. These TPO curves are compared in figure 3 with the reference curve pertaining to a catalyst–carbon sample heated with an air flow. While a concentration of 20 vol% of iodine in the combustion air is capable of lowering the combustion onset temperature down to about 380 °C, the iodine vapours produced while heating the catalyst can only slightly decrease the T_p value compared with carbon uncatalysed combustion. Hence, iodine vapours display a certain catalytic activity towards carbon combustion which increases with their concentration in the gaseous phase. However, it is very hard to assess the actual concentration of iodine vapours which locally occurs inside the mixture of carbon and $KVO_3 + KI$ at the TPO temperature peak.

As confirmed by the ageing tests, detailed in section 3.2, the following reaction (which causes the formation of a new vanadate, $K_4V_2O_7$, with an increased K-to-V ratio compared with KVO_3) very likely takes place:

$$4KI + 4KVO_3 + O_2 \rightarrow 2K_4V_2O_7 + 2I_2 \qquad (1)$$

$K_4V_2O_7$ displays an intrinsic catalytic activity towards carbon combustion better than that of KVO_3. The performance of supported catalysts prepared by using each of these vanadates alone was tested by TPO measurements in tight contact conditions, obtaining T_p values of 500 and 360 °C for KVO_3 and $K_4V_2O_7$, respectively (see table 1).

In conclusion, the appreciably low TPO combustion temperature resulting from the $KI + KVO_3$ catalyst can be attributed to a synergetic effect among all its solid and gaseous components: in particular, pyrovanadate is capable of promoting carbon combustion in tight contact conditions already at about 360 °C, at which a moderate iodine vapours production allows a weak mobility and a consequent, further increase of the catalytic activity (figure 3).

However, the catalyst under investigation suffers to some extent from the drawbacks that characterise all the catalysts for particulate combustion, showing mobility through the formation of vapours [2]: a progressive change of composition and environmental impact due to release of gaseous compounds.

3.2. Catalyst ageing tests

The catalyst activity variations eventually occurring during thermal exposure under different atmospheres are listed in table 1.

T_p increases of about 55 °C when the catalyst is aged for 24 h at 600 °C: this increase is somewhat higher in the presence of humid air (T_p increase of about 60 °C). By contrast, the ageing at 380 °C, which might be regarded as more representative of the normal operating conditions in a catalytic trap, does not seem to affect significantly the catalytic activity, independently of the presence of moisture. The results of XRD analyses allows to correlate the variation of activity with composition changes. As discussed previously, the thermal exposure generally causes a decrease of iodine content in the catalyst sample, which occurs more rapidly at higher temperatures: for instance, the potassium iodide decrease during 24 h of ageing at 600 °C is appreciably larger than that after 96 h at 380 °C (figure 4). The formation of $K_4V_2O_7$, with an enhanced potassium-to-vanadium ratio, is the consequence of this loss. Also, in the case of catalyst samples aged in humid air the potassium iodide decrement increases with the treatment temperature. SEM-EDS analysis of the sample aged at 600 °C with humid air confirmed the strong removal of iodine.

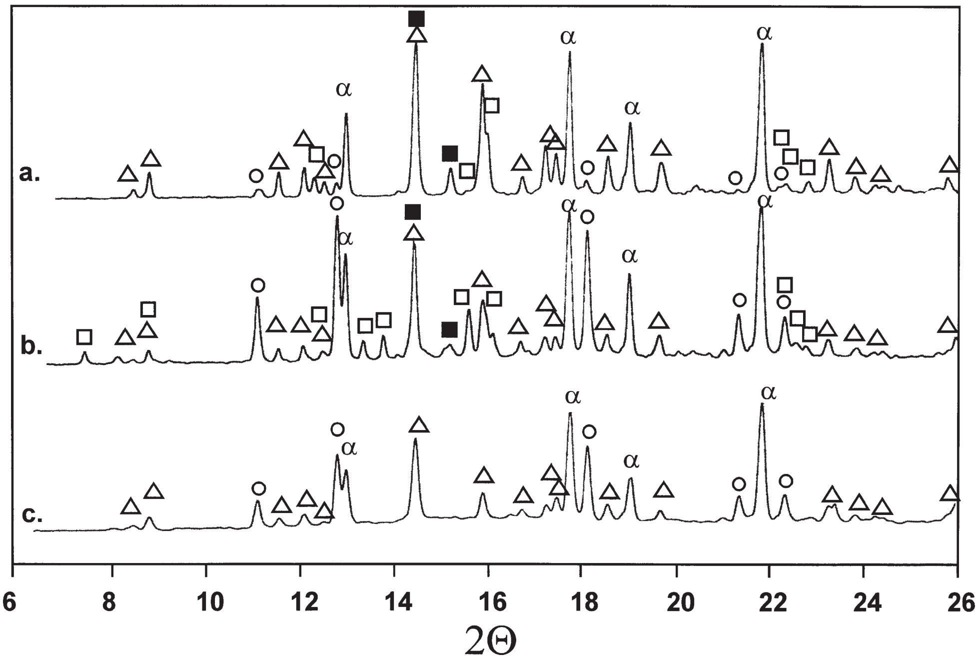

Figure 4. XRD diffraction patterns of KI + KVO_3 catalyst supported on α-Al_2O_3: (a) after 24 h of ageing at 600 °C in air, (b) after 96 h of ageing at 380 °C in air, (c) calcined for 4 h at 700 °C. (△) KVO_3, (○) KI, (α) α-Al_2O_3, (□) $K_4V_2O_7 \cdot 2H_2O$, (■) $K_4V_2O_7 \cdot H_2O$.

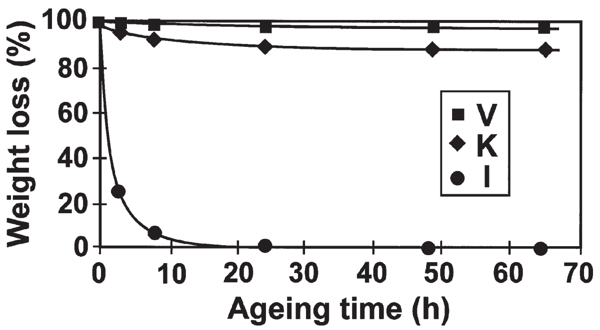

Figure 5. Weight losses vs. time for the single elements (I, V, K) contained in a KI + KVO_3 catalyst heated at 750 °C in air.

The inferred reaction (1) is also in agreement with chemical analyses performed on catalyst samples submitted to a severe isothermal treatment (at 750 °C) for periods up to 65 h. In these conditions it was observed that the percentages of K and V decrease very slowly during ageing while iodine is lost completely during about the first 20 h of treatment (figure 5).

In spite of the progress of reaction (1) during ageing, the contents of $K_4V_2O_7$ detected by XRD analyses in the catalyst samples treated with humid air were lower than those present in specimens treated at the same temperature with dry air. Probably this is due to the very high $K_4V_2O_7$ vanadate sensitivity to moisture. In fact, at room temperature potassium pyrovanadate is highly hygroscopic and becomes deliquescent at the contact with the air humidity, thus its preparation by melting K_2CO_3 and V_2O_5 results in the formation of a mixture of $K_4V_2O_7$ with two hydrates: $K_4V_2O_7 \cdot H_2O$ and $K_4V_2O_7 \cdot 2H_2O$ (figure 6).

A certain instability of this compound at high temperature in a humid environment should be inferred to explain the related catalyst partial deactivation and the XRD results.

Nevertheless, the catalyst under investigation shows a fair stability at temperature around 380 °C because reaction (1) occurs slowly in these conditions. Furthermore, only after the formation of eutectic liquid at about 450 °C can also K and V leave the catalyst by evaporation.

In conclusion, when the ageing is carried out at 600 °C or higher temperatures, the loss of either the active catalyst components by evaporation of eutectic liquid or gaseous iodine from the chemical reaction (1) are responsible for the activity decrease of the catalyst. In these ageing conditions, notwithstanding the good intrinsic catalytic activity towards carbon combustion of the formed pyrovanadate, the relative amount of this latter is not sufficient to counterbalance the loss of active components and to completely avoid the catalyst activity decrease. In particular, at high temperature the pyrovanadate content seems to be lowered, probably by some interaction with humidity.

As potassium pyrovanadate promotes catalytic carbon combustion at about 360 °C, that is, when it is in the solid state, its effectiveness is mainly due to its crystalline structure and to the nature and orientation of its chemical intramolecular bonds. Potassium metavanadate is also known to have a catalytic activity, but, on the basis of TPO peak temperatures obtained with these two pure substances, the pyrovanadate seems to be much more active.

For this reason, further investigations about catalysts based on similar pyrovanadates of metals (Rb, Cs), less susceptible to water vapour than $K_4V_2O_7$, are in progress. Such studies are somewhat complicated by the almost complete lack of literature information about these promising compounds.

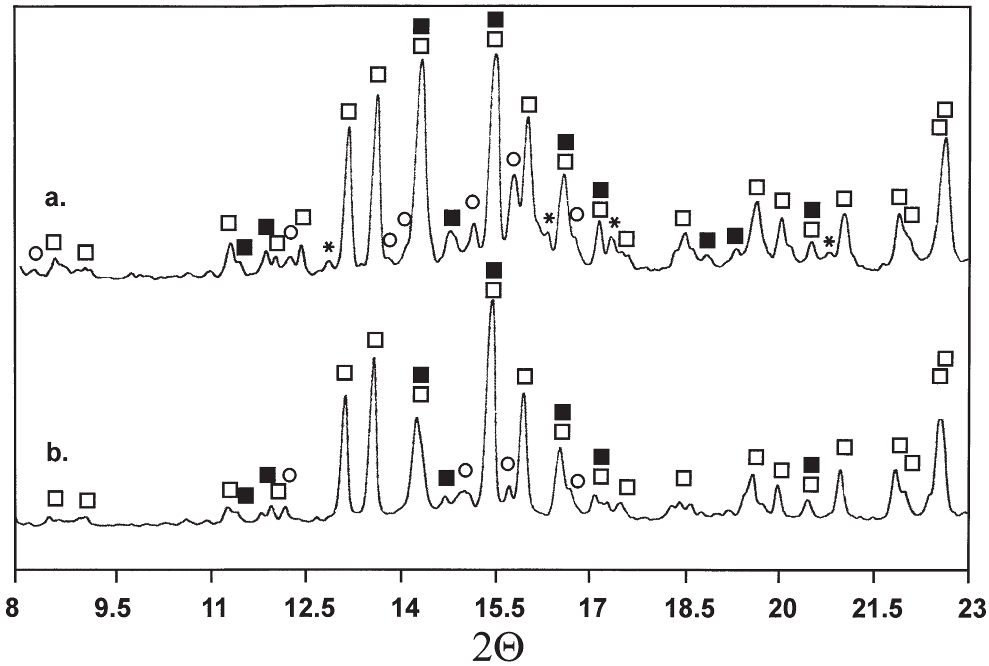

Figure 6. XRD patterns related to a sample of $K_4V_2O_7$ prepared by reaction between K_2CO_3 and V_2O_5 after progressive hydration at room temperature by humid air: (a) 30 min after preparation, (b) 60 min after preparation. (∗) unidentified peak, (○) $K_4V_2O_7$, (□) $K_4V_2O_7\cdot 2H_2O$, (■) $K_4V_2O_7\cdot H_2O$.

4. Conclusions

A catalyst prepared starting from KVO_3 and KI, containing after preparation these two precursors and $K_4V_2O_7$, shows a catalytic activity toward carbon combustion analogous to that displayed by the best catalysts proposed to date. Contrary to these latter, however, the catalytic reaction mechanism is primarily based on the solid–solid contact between carbon and catalyst, even though a weak degree of mobility might be attributed to the formation of iodine vapours.

This catalyst achieves the maximum catalytic combustion rate at 380 °C and maintains this activity also when it is aged at this temperature, which may be considered as a representative working temperature about the actual diesel exhaust gases.

Exposure to air at higher temperatures causes a rapid change of the catalyst composition, with both an increase of $K_4V_2O_7$ content and a corresponding decrease of the KI percentage. This behaviour does not affect seriously the catalyst performance due to the high specific activity of potassium pyrovanadate. However, at ageing temperatures above 450 °C the catalyst components form an eutectic liquid which makes the loss of active compounds by evaporation comparatively easy.

Finally, the main drawback of the catalyst consists in the instability of pyrovanadate in humid environment, in particular at the high temperatures which can be occasionally reached in diesel traps. This lack could be overcome by the development of catalysts based on pyrovanadates less sensitive to moisture.

In line with previous work on similar catalytic systems [7], current research efforts, carried out within the framework of activities of a Brite-Euram project (acronym: CATATRAP), are aimed at developing catalysts based on the very active potassium pyrovanadate, coupled with promoters of low-temperature eutectic liquid formation. Provided degradation mechanisms such as volatility are kept at an acceptable level, this new catalyst could achieve even better performance than the catalysts proposed here, owing to improved catalyst-to-soot contact conditions.

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