Thermal analysis characterization of promoted vanadium oxide-based catalysts

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Abstract

Vanadium oxide-based catalysts promoted with KCl and a transition metal chloride (M = Cu, Ce, Fe, Co, Zn) have been investigated in the oxidation of diesel soot and characterized by thermal analysis techniques, such as temperature-programmed reduction (TPR) and differential scanning calorimetry (DSC). Aim of the study was to acquire information on the reaction mechanism of the catalytic soot combustion over these catalytic systems. Data presented suggest that the activity of investigated catalysts is correlated to their reducibility which favor the redox activity of the active vanadium species. The formation of eutectics between components of the catalyst also occur improving the catalyst–carbon contact. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Vanadium-based catalysts are the most promising systems for the combustion of diesel soot. Soot is a carbonaceous material made of amorphous carbon particles containing variable amount of toxic hydrocarbons and is the main environmental pollutant present in the exhaust gas of diesel engines. The development of suitable devices, i.e. catalytic traps, capable to oxidize the trapped soot at the temperature of exhaust gas (about 600–700 K) is nowadays a major challenge.

Besides the high interest, the reaction mechanism of soot combustion remains unclear. The high activity of vanadium oxide in the oxidation of soot and carbon

has been related to its low melting point which ensures a strong contact between the soot and catalyst [1]. The beneficial influence of a good contact between the soot and catalyst on the soot oxidation rate has been pointed by several authors [2,3]. The formation of liquid eutectic phases has been found to be a determinant factor on the activity of alkali-promoted vanadium catalysts [4]. On this basis, the catalysts with an induced particle mobility due to the formation of low melting point phases are favored over those which remain in the solid state [5].

However, other factors may contribute to the catalytic combustion of soot [6,7]. In particular, has been suggested that the oxidation of soot involves a redox mechanism in which the catalyst is partially reduced by extraction of oxygen from the catalyst which in turn is replaced by oxygen coming from gas phase [6]. This is favored by the capability of vanadium to change easily its oxidation state.

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In this work we present a thermal analysis characterization by means of TPR and DSC techniques of promoted vanadium-based catalysts. The results have been compared with the activity data in the combustion of diesel soot. The aim is to investigate the redox and thermal behavior of promoted vanadium-based catalysts in order to better understand the factors influencing the catalytic activity in the combustion of soot.

2. Experimental

2.1. Samples preparation

The catalysts were prepared by impregnation of an α-Al_2O_3 powder (Aldrich, 99.8%) with an aqueous solution of the appropriate inorganic salts. The salts used are: NH_4VO_3 (Fluka, >99.5%), KCl (Carlo Erba Reagenti, >99.5%) and chlorides of transition metals (M = Cu, Ce, Fe, Co, Zn). They were dissolved in a small amount of water in the molar ratio M:K:V = 2:2:1. The solution was added to alumina in order to obtain samples containing (after drying) 50 wt.% of α-Al_2O_3. The suspension was heated at 80 °C under stirring for 2 h and then dried at 393 K for 2 h. Then the powder was calcinated in static air at 973 K for 4 h.

2.2. Catalysts characterization

TPR experiments were carried out in a conventional apparatus using the following procedure: the sample (50 mg) was loaded in an U-type quartz glass microreactor and heated from room temperature (RT) to 1373 K (heating rate, 10 K/min) under 5% H_2/Ar (vol.%), with a constant flow rate of 20 cm^3/min. A molecular sieve cold trap and CO_2 trap were connected between the outlet of the reactor and the thermal conducibility detector (TCD). The flow rates were monitored by mass flow controllers. The catalyst was heated with a regulated furnace and the temperature was measured by a thermocouple placed inside the catalyst bed.

DSC analyses were performed by a Setaram TGDSC 111 thermobalance. The catalyst (10–20 mg) was put on the sample holder and was submitted to a linear rise of temperature from 298 to 973 K (scanning rate, 20 K/min) under an air flow.

XRD spectra were recorded on a Philips DY 765 diffractometer using the Cu Kα radiation. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS data file.

2.3. Catalytic activity

Catalytic tests were performed in a temperature-programmed oxidation (TPO) apparatus. The soot (collected from a diesel filter mounted in a Renault diesel car) was accurately mixed with the catalyst in the weight ratio of 1:20 in an agate mortar. An U-type quartz glass microreactor was then loaded with 325 mg of the mixture and the oxidation was carried out in the range 298–973 K in flowing air (50 ml/min). In all experiments, a heating rate of 5 K/min was applied. The product gas stream was analyzed by a mass quadrupole spectrometer (VGQ Quadrupole). The MS apparatus was calibrated before each measurement with a standard mixture of CO_2.

3. Results and discussion

Vanadium oxide has been reported from long time as a catalyst for the combustion of carbonaceous materials [8]. The high activity of V_2O_5 in this reaction has been related to

1. the low melting point (963 K), which provides a high mobility of the vanadium species during burn-off [1,8]. The surface mobility of the active species is a key factor in the oxidation soot. It can be supposed that the formation of liquid phases enables the mobility of the active species, thereby improving the contact with the carbon through a wetting process;
2. the ability of vanadium to change easily its oxidation state. This provides a high reactivity of the oxygen in the V=O bond, making favorable the oxygen needed for the oxidation of soot [9]. The oxygen content in the catalyst is restored by exposure to air.

Ciambelli et al. have proposed a ternary-based vanadium catalyst promoted with K and Cu chlorides for the oxidation of diesel soot which still stands as one of most active catalysts [6]. In this last decade

many other catalysts based on vanadium oxide promoted with different transition metals have been investigated [10]. In order to explain the enhanced activity of the promoted systems, the formation of low-melting mixed phases has been reported to be the key factor by several authors [4–6,10]. The influence of the redox properties of the catalytic system has been also pointed out [11,12].

So far no systematic thermal analysis characterization has been carried out on these systems. In this study, DSC and TPR techniques were used with the aim to investigate the catalytic behavior, i.e. to detect the formation of low-melting phases and to test the reducibility of vanadium oxide-based catalysts, respectively.

Table 1 list the vanadium catalysts investigated. The formulation-type of the catalysts comprise V as the base metal, K as alkali metal and a transition metal, M = Cu, Fe, Ce, Zn, Co, supported on α-Al_2O_3. A pure vanadium catalyst, V/Al_2O_3, and a binary catalyst, KV/Al_2O_3, are also reported for comparison.

First, we focused our attention on the combustion of soot on the pure vanadium oxide (V/Al_2O_3), K-doped vanadium oxide (KV/Al_2O_3) and K–Cu-doped vanadium oxide catalysts (KCuV/Al_2O_3). TPO experiments were carried out to evaluate the activity of the catalysts in the combustion of soot. In order to compare the catalytic activity of the investigated systems the "T_{ox}" temperature was used. T_{ox} represents the temperature at which the highest formation of CO_2 is observed. Of course, lower T_{ox} corresponds to a higher activity of the catalyst. T_{ox} values for the investigated catalysts are shown in Table 1.

The related TPO are reported in Fig. 1. The uncatalyzed combustion of soot shows a peak at a temperature >823 K. In the presence of vanadium-based
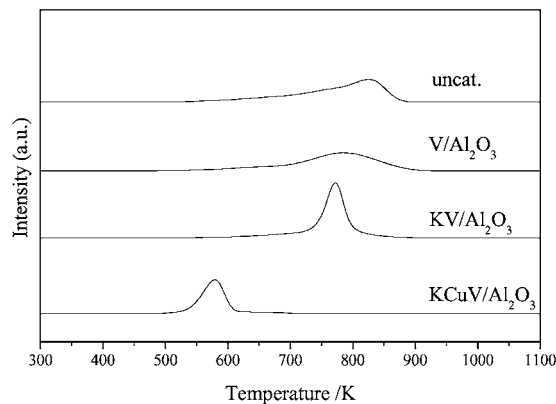

Fig. 1. TPO of K- and Cu-promoted vanadium oxide catalysts.

catalysts, a lower T_{ox} have been obtained. The undoped vanadium catalyst shows a TPO peak at about 793 K. The addition of K and Cu chlorides to V/alumina system decreases further the soot combustion temperature. T_{ox} registered on VK/Al_2O_3 and VKCu/Al_2O_3 were 773 and 583 K, respectively.

Fig. 2(a) shows the XRD spectra of the catalysts after calcination at 973 K and before TPR. The strong diffraction peaks of α-Al_2O_3 dominate the spectra. XRD of the V/Al_2O_3 sample shows that V_2O_5 is formed. However, it should be noted that, despite the high loading of vanadium, the V_2O_5 diffraction peaks present a low intensity. This can be due to the scarce tendency of vanadium species to crystallize under the conditions used. KVO_3 and KCl were found on the sample doped with K. On the KVCu/Al_2O_3 catalyst, KCl and $CuCl_2 \cdot 3Cu(OH)_2$ have been identified. The low amount of KCl found on this latter catalyst, is an indication that part of it can be linked to Cu and/or V with formation of mixed phases. However, neither KVO_3 and/or KCuV mixed phases were observed. It is likely that these phases are in an amorphous state and therefore undetectable by XRD. The results shown are in agreement with data reported by Ciambelli et al. [13] and Badini et al. [14].

XRD collected after TPR are also reported in Fig. 2(b) and show changes occurring on the catalysts under TPR conditions (flowing H_2 up to 1273 K). XRD pattern registered on all samples show only the V_2O_3 diffraction peaks. This suggests that the mixed phases formed are not stable under TPR conditions.

Table 1
Vanadium oxide-based catalysts investigated and related T_{ox} temperature in the combustion of soot

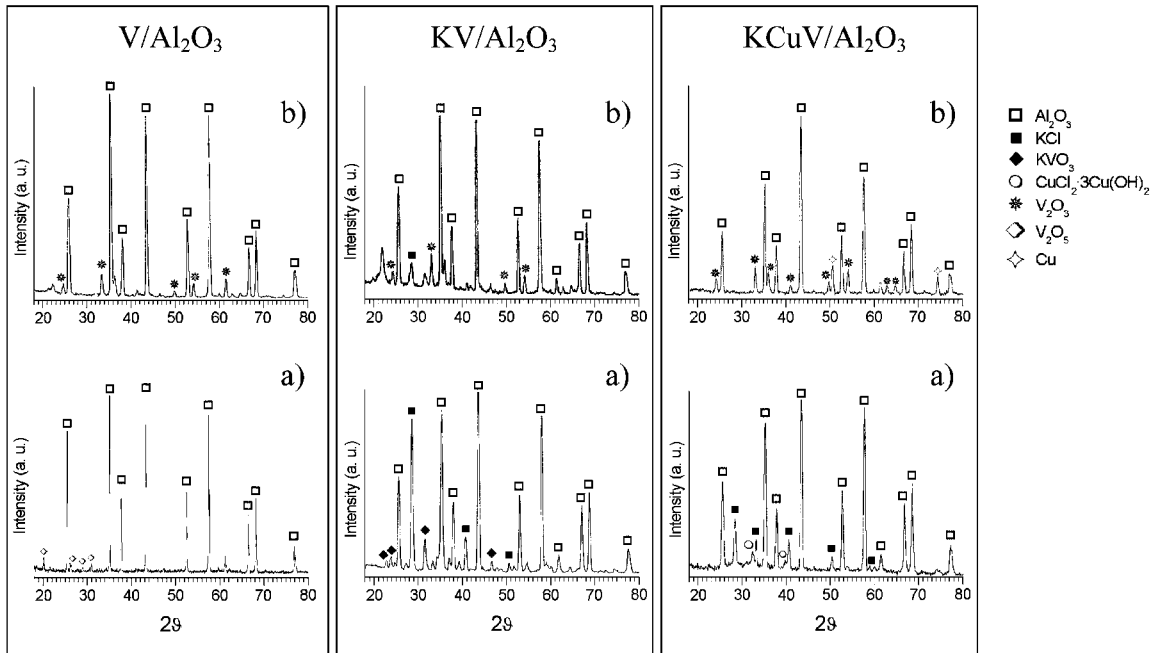| Catalysts	V (wt.%)	K (wt.%)	M (wt.%)	T_{ox} (K)
V/Al_2O_3	7.03	–	–	793
KV/Al_2O_3	5.83	8.95	–	773
KCuV/Al_2O_3	4.19	6.44	10.46	583
KCeV/Al_2O_3	2.52	3.86	13.85	723
KCoV/Al_2O_3	3.43	5.27	7.94	708
KFeV/Al_2O_3	3.15	4.84	6.92	683
KZnV/Al_2O_3	4.73	7.25	12.14	655

Fig. 2. XRD spectra of the V/Al$_2$O$_3$, KV/Al$_2$O$_3$, and KCuV/Al$_2$O$_3$ catalysts before (a) and after TPR (b).

DSC analyses are presented in Fig. 3. On the V/Al$_2$O$_3$ catalyst, the endothermic peaks at 933 K was assigned to the melting of vanadium oxide on alumina. Pure V$_2$O$_5$ have a melting point of 963 K. The presence of impurity and/or the higher dispersion on the support can be responsible of the lower melting temperature in comparison to bulk V$_2$O$_5$. On
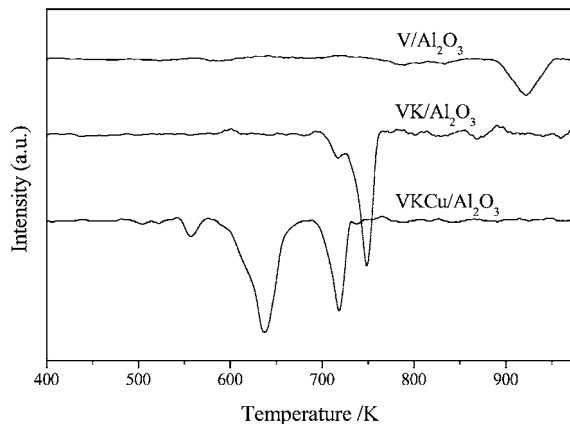

Fig. 3. DSC analysis of K- and Cu-promoted vanadium oxide catalysts.

addition of KCl, an endothermic peak (shifted at lower temperature (753 K) compared to that observed on the undoped catalyst) is present. As suggested by XRD this is the consequence of the formation of KVO$_3$ having a melting point (793 K) lower than pure V$_2$O$_5$. This compound, has been reported to melt at about 753 K in the presence of KCl [4]. On the sample KVCu/Al$_2$O$_3$, the presence of two main endothermic peaks at 638 and 718 K was observed. These peaks can be assigned to melting of mixed phases containing Cu, V and K of different compositions. These results are in agreement with data reported by Serra et al. on similar catalytic systems [4].

TPR profiles of these catalysts are compared in Fig. 4. The reduction of the pure vanadium(V) oxide catalyst proceeds in a step-wise manner. According to literature data, V$_6$O$_{13}$ is formed after the first reduction step [15,16]. Then it is completely reduced to VO$_2$ in the second step. In the final step the reduction to vanadium(III) oxide, V$_2$O$_3$, occurs.

The addition of K and Cu chlorides modify the TPR pattern of the catalytic system. On the K-promoted vanadium catalyst, the relative intensity of the peaks are changed and the reduction temperature is strongly
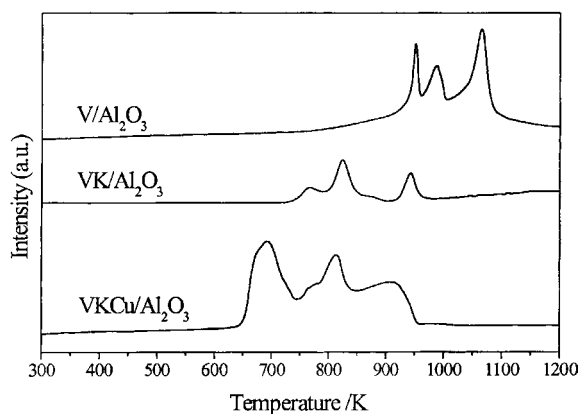
Fig. 4. TPR analysis of K- and Cu-promoted vanadium oxide catalysts.

shifted towards lower values. The TPR profile of V/K/Cu shows a complex pattern due to the contemporary reduction of the Cu species. Moreover, the temperature at which the reduction starts, T_{red}, is remarkably lower (648 K, compared to 743 K of the K-doped catalyst and 873 K of the undoped catalyst). T_{red} was taken as a measure of the reducibility of the catalytic system. The above data shows that doping vanadium oxide catalysts with K- and Cu-chlorides increases the reducibility of the catalyst.

Fig. 5 shows the relationship between catalytic activity (expressed by T_{ox}) and the reducibility of the catalysts. The trend observed suggests that the
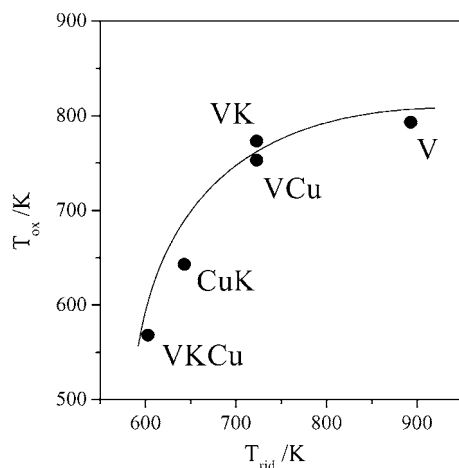

Fig. 5. Comparison between T_{red} and T_{ox} of K- and Cu-promoted vanadium oxide catalysts.

reducibility of the catalytic system is an important factor in determining the catalytic activity in the combustion of soot.

The catalytic activity has been successfully correlated with the reducibility of the catalyst for many oxidation reactions. Regarding the combustion of soot, different opinions are reported. Moulijn and coworkers [17] pointed out that the reduction of metal oxides by hydrogen follows a different mechanism than the reduction of soot. Therefore, in their opinion, the use of the reduction temperature to explain the activity of catalysts for the combustion of soot, is a priori not applicable [17]. On the other hand, Querini and coworkers correlated directly the activity of a K, Co/MgO catalyst to its reducibility, as determined by TPR, suggesting that a redox mechanism is involved in the combustion process [18].

DSC data above reported evidentiated the formation of low-melting phases at the addition of K- and Cu-promoters. As reported by Serra et al. the formation of eutectic mixtures improves the soot–catalyst contact by wetting the carbon particles [4]. This favor the combustion reaction according to a redox mechanism involving vanadium and copper compounds.

In order to have information on different metal vanadates, ternary catalysts with various transition metals have been investigated. Fig. 6(a) reports the XRD spectra of the as-prepared catalysts. A detailed microstructural characterization of these catalysts is beyond of our scope. Some main characteristics will be outlined. The first is the different intensity of the peaks of the potassium chloride indicating the different reactivity of the potassium towards the various components of the catalysts to form mixed phases. Strong diffraction peaks attributed to the oxides of the corresponding transition metal were observed in the case of Ce- and Fe-promoted catalysts. XRD spectra confirm that phases (pure or mixed) containing vanadium are mainly in an amorphous state.

XRD registered after TPR are shown in Fig. 6(b). V_2O_3 and the reduced phases of the transition metal oxides (up to the elemental state) are the main diffraction peaks identified.

TPO spectra for promoted vanadium catalysts are shown in Fig. 7. The corresponding values of T_{ox} (see Table 1) indicate that the catalytic system containing Cu was the most active. The substitution of Cu with other transition metals results in higher values of T_{ox}
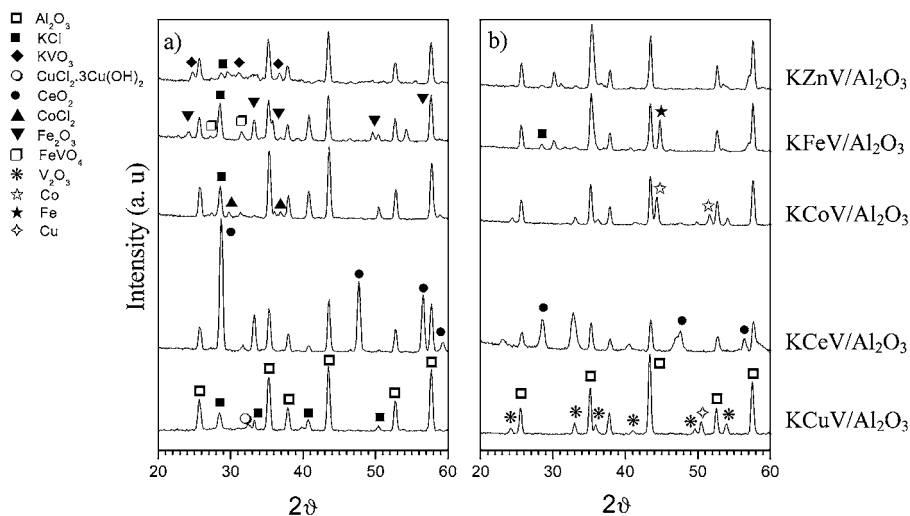
Fig. 6. XRD of K–vanadium oxide catalysts promoted with different transition metals: (a) as-prepared; (b) after TPR.

(lower activity). The following scale of activity was observed: KVCu > KVZn > KVFe > KVCo = KVCe.

Figs. 8 and 9 report the DSC and TPR profiles of the different promoted vanadium-based catalysts investigated. DSC analysis show endothermic peaks at temperature from 573 to 933 K depending on the catalyst nature. These peaks can be attributed to the melting of amorphous mixed phases.

Promoted samples show complex TPR patterns (Fig. 9). It can be noted that the onset reduction temperature of catalyst, T_{red}, increases when Cu is

substituted with other transition metals. The same trend previously observed in Fig. 5 has been evidentiated on the KVM/Al$_2$O$_3$ catalysts (Fig. 10) confirming further that the reducibility of the catalyst play a key role in this reaction.

On the basis of results reported in this work, some considerations on the reaction mechanism of soot combustion over KVM/Al$_2$O$_3$-type catalysts can be made. It is well known that the activity of the vanadium oxide in oxidation reaction is linked to the reactivity of the oxygen in the V=O bond [9]. On
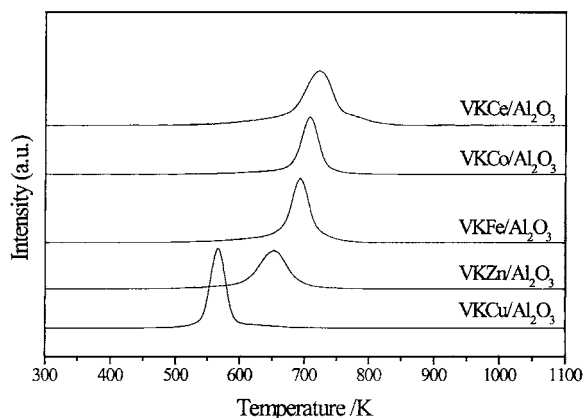

Fig. 7. TPO of K–vanadium catalysts promoted with different transition metals.
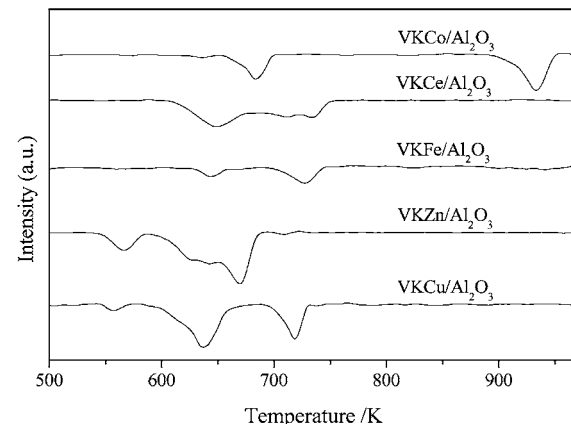

Fig. 8. DSC analysis of K-doped vanadium oxide catalysts promoted with different transition metals.
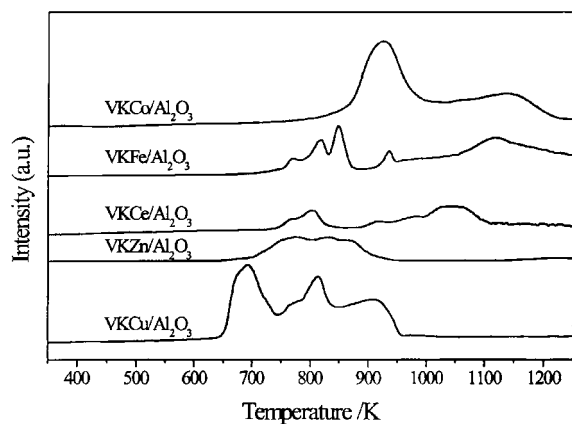
Fig. 9. TPR analysis of K-doped vanadium oxide catalysts promoted with different transition metals.

addition of alkali metal compounds to vanadium oxide their electron-donating effect increase the reactivity of the oxygen atom [19]. Ermini et al. have shown, by means of FT-IR measure, that the addition of the alkaline promoter to vanadium oxide shift the V=O stretching to lower wave number, reflecting the lower bond order on the K-promoted catalysts [20]. The strong decrease of the reduction temperature of the vanadium species in the presence of potassium we observed suggests a weakening of the V=O bond. In addition, when transition metals having different oxidation states are present in the catalytic formulation, they may favor the ability of vanadium to change the
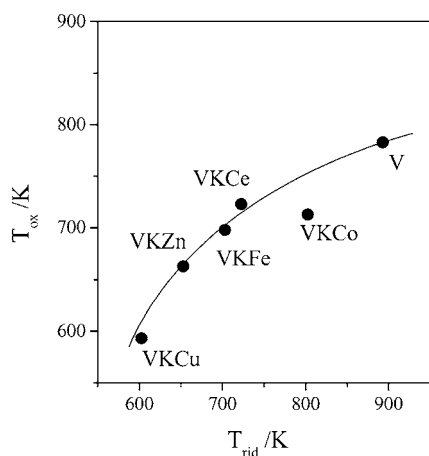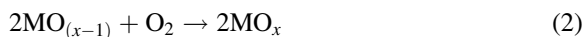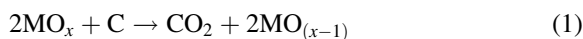
oxidation state and then promote the catalyst to act as oxygen pumps combining and delivering oxygen through a reduction/oxidation mechanism (Mars and Van Krevelen) proposed by Ciambelli et al. [21]

$$2MO_x + C \rightarrow CO_2 + 2MO_{(x-1)} \tag{1}$$

$$2MO_{(x-1)} + O_2 \rightarrow 2MO_x \tag{2}$$

During step (1) the catalysts undergoes a partial reduction due to the removal of lattice oxygen. An attempt was therefore done to detect these reduced intermediate catalytic species. XRD analysis carried out after reaction however has not showed any reduction of catalytic species. Two explanation can be given: (a) the oxidation reaction could interest only the surface and therefore, due to the low concentration of the reduced catalytic species, they cannot be detected by XRD; (b) the partial pressure of oxygen in the reactant feed is high, lattice oxygen consumed during step (1) can be replenished by gaseous oxygen so that the oxidation may proceed continuously and no intermediate reduced active species can be observed.

In conclusion, thermal analysis results here reported suggest that the higher activity of promoted vanadium oxide catalysts can be related to the ability of the added components to favor the redox cycle of the active vanadium species. The formation of eutectic liquids between the components of the catalyst contribute to improve the catalyst–carbon contact. This synergy of actions is fundamental in promoting the soot combustion.

Fig. 10. Comparison between T_{red} and T_{ox} of K-doped vanadium catalysts promoted with different transition metals.

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