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Soot combustion: Reactivity of alkaline and alkaline earth metal oxides in full contact with soot

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ABSTRACT

The activity in the soot combustion of K- and Ba-based catalysts in "loose" and "full" contact is investigated in this study. Under loose contact systems (obtained by mechanically mixing the soot and catalysts), the K-containing samples are very active in the oxidation of soot, as opposite to the Ba-containing samples. Also, a synergistic effect in this reaction is seen between K and Pt for the case of the K-containing samples. Under full contact conditions (obtained by impregnation of the soot with aqueous metal solutions), the reactivity of soot increases; in these conditions the performance of the poorly reactive Ba-containing samples becomes similar to the very active K-based system. This result points out the key-role played by both the selected alkaline or alkaline earth metal oxides in the soot combustion, and suggests that the poor activity of Ba under loose conditions is possibly due to the low mobility of the Ba surface species. Finally, it is found that the presence of NO favors the soot oxidation under loose contact, specifically over noble metal-containing samples, due to the oxidation of NO to NO_2. However the presence of the alkaline and alkaline earth oxide also affects the soot oxidation activity in the presence of NO. This has been ascribed to the formation of Ba- and K-nitrite/nitrate species which participate in the soot combustion process by giving rise to NO_x upon nitrite/nitrate decomposition and/or by directly reacting with soot.

1. Introduction

Over the past decade the utilization of Diesel engines has spread in to sectors traditionally covered by gasoline-powered Otto engines. In fact, while in the case of heavy-duty applications the use of Diesel engines is traditionally preferred, for light vehicles (sedan automobiles and mini-vans) we have witnessed in recent years a progressive increase of the Diesel engines' market share throughout Europe, up to 50% and beyond. The reasons for such an increase are essentially related to the good performance characteristics of modern Diesel engines, accompanied by low fuel consumption. However, Diesel engines are responsible for significant quantities of particulate matter (soot) and NO_x emissions. In particular, health studies indicating mutagenic activity by the particulate matter have prompted the National Institute for Occupational Safety and Health (NIOSH) to declare Diesel exhaust a potential and probable human carcinogen [1].

In view of increased concerns regarding the effects of soot and NO_x emissions on human health and the environment, legislated regulations on vehicle emissions have become more stringent so that in a near future, most vehicles will need to adopt suitable emission control devices to meet emission standards of Euro V (2009) in Europe and US'10 (2010) in the United States. For these reasons, considerable efforts have been devoted in recent years to the study of abatement technologies able to reduce both soot and NO_x emissions in the exhausts of Diesel engines.

In this respect, Toyota has developed the Diesel particulate-NO_x reduction (DPNR) technology for the simultaneous removal of NO_x and Diesel particulate matter [2,3]. This system consists of both a new catalytic filter and a new Diesel combustion technology; the new catalytic converter for DPNR is a porous ceramic filter coated with a catalytic layer consisting of a high surface area support (e.g. γ-alumina), a noble metal (Pt), and an alkaline or alkaline earth metal oxide which presents a high NO_x-storage capacity. This system accomplishes a simultaneous and continuous reduction of soot and NO_x under cyclic conditions, alternating a lean phase, during which the NO_x species produced by the engine are adsorbed on the alkaline or alkaline earth metal oxide component (via nitrate species formation), with a short rich phase, during which

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the nitrate species are reduced to nitrogen. The NO_x reduction mechanism in the DPNR system is similar to that already proposed by Toyota in NO_x-storage reduction (NSR) catalysts for lean-burn gasoline engines [4–7].

In previous work from our group [8], the reactivity of a typical DPNR Pt–Ba/Al_2O_3 catalyst in the simultaneous removal of particulate matter and NO_x was addressed. We found that this system shows good performance for the removal of both particulate matter and NO_x. More recently the reactivity of a K-based catalyst in the same reaction was also investigated and compared with that of the corresponding Ba-containing system [9]. The data pointed out that the K-containing catalyst has similar $DeNO_x$ activity when compared to the Pt–Ba/Al_2O_3 sample, but significantly higher activity for soot combustion.

To better understand the different reactivity of the K- vs. Ba-based catalytic systems in the oxidation of soot, and to identify the roles of the various catalyst components (K, Ba and Pt) and the key parameters involved in the reaction, we carried out a more fundamental study in which the combustion of soot was investigated both in the presence of alumina supported-Ba, -K and -Pt catalysts ("loose" contact) and after direct impregnation of soot with K, Ba and Pt precursors as well. These latter samples, referred in the following as "full contact" systems, are representative, in principle, of the intrinsic activity of the selected catalytic elements since their reactivity is not affected by the efficiency of the contact between the soot particle and the catalyst. Accordingly, mechanistic aspects on the role of the various catalyst components in the soot combustion, and on the relevance of the soot–catalyst contact could be clarified.

2. Experimental

2.1. Catalysts preparation and characterization

A series of γ-alumina supported samples were prepared in this study, i.e. Pt/Al_2O_3, K/Al_2O_3, Ba/Al_2O_3, Pt–K/Al_2O_3 and Pt–Ba/Al_2O_3. The Al_2O_3 support was obtained by calcination at 700 °C of a commercial alumina (Versal 250 from UOP). Ba/Al_2O_3 (20/100, w/w), K/Al_2O_3 (5.4/100, w/w) and Pt/Al_2O_3 (1/100, w/w) catalysts were prepared by impregnation of γ-alumina with aqueous solutions of barium acetate, potassium acetate and dinitro-diammino-platinum (Strem Chemicals, 5% Pt in ammonium hydroxide), respectively. Pt–Ba/Al_2O_3 (1/20/100, w/w) and Pt–K/Al_2O_3 (1/5.4/100, w/w) catalysts were prepared by impregnation of the Pt/Al_2O_3 sample with solutions of barium acetate and potassium acetate, respectively. The powders were dried at 80 °C overnight and calcined at 500 °C for 5 h after each impregnation step. The catalysts were characterized by XRD (Philips PW 1050/70), surface area and pore size measurements (Micromeritics TriStar 3000 instrument), and determinations of Pt dispersion (H_2 chemisorption at 0 °C, TPD/R/O 1100 ThermoElectron Instrument).

Printex-U (Degussa), whose properties have been well described, e.g. in [10], was used as model soot. The catalyst–soot mixtures were prepared by gently mixing the catalyst powder with the soot for 24 h in a vial, thus realizing a loose contact. A catalyst/soot ratio of 9/1 (w/w) was always used in the various experiments.

For the case of the "full contact" systems, an intimate interaction of the catalytic elements with soot was obtained by direct incipient wetness impregnation of the soot powder with aqueous solutions of Ba acetate, K acetate and dinitro-diammino-platinum. After impregnation, the samples were dried overnight at 100 °C. Accordingly, the Ba/soot (20/100, w/w), K/soot (5.4/100, w/w) and Pt/soot (1/100, w/w) samples were obtained.

2.2. Reactivity tests

All reactivity tests were performed in a flow-reactor apparatus consisting of a quartz tube reactor (7 mm i.d.) connected to a mass spectrometer (Omnistar 200, Pfeiffer Vacuum) and to a micro GC (Agilent 300A) for the continuous on-line analysis of the outlet gases.

The behavior of the catalysts in the soot combustion reaction was investigated by means of temperature programmed oxidation (TPO) runs (from RT to 800 °C @15 °C/min) with O_2 (3%, v/v in He) or with O_2 (3%, v/v) + NO (1000 ppm) in He. An amount of 66 mg of the soot–catalyst (70–100 μm) mixture (loose contact) or 6 mg of impregnated soot (full contact) diluted 1/5 with quartz sand (70–100 μm) was used in each run, and the total gas flow was always set at 100 cm^3/min STP. Before each TPO test, the samples were heated at 500 °C in a He flow to promote the desorption/decomposition of weakly adsorbed species.

Additional catalytic tests were performed over pure soot, Ba/Al_2O_3–soot and K/Al_2O_3–soot mixtures under isothermal conditions. In these experiments, pulses of oxygen (3%, v/v in He, pulse length 10 min) were fed at various temperatures (from 350 to 470 °C) in the presence of CO_2 (0.3%, v/v) and water (1%, v/v) to the catalyst/soot mixture.

In all experiments the temperature of the catalyst–soot mixture was measured by a 0.5 mm o.d. K-type thermocouple directly immersed in the catalyst bed.

3. Results and discussion

3.1. Material characterization

The values of surface area (A_s), pore volume (V_p), average pore diameter (d_p) and Pt dispersion of the investigated catalytic systems are listed in Table 1. The specific surface areas of the bare γ-Al_2O_3 support and the Pt/Al_2O_3 sample are near 200 $m^2\,g^{-1}$; lower surface area values were determined for the K- and Ba-containing samples (180 and 176 $m^2\,g^{-1}$ for binary and ternary K-containing samples, respectively; 136 and 141 $m^2\,g^{-1}$ for binary and ternary Ba-containing samples, respectively). The surface area contraction is accompanied by a slight reduction of the pore volume, from 0.96 cm^3/g for γ-Al_2O_3 down to 0.71 cm^3/g for the Pt–Ba/Al_2O_3 catalyst and 0.65 cm^3/g for the Ba/Al_2O_3 catalyst, with the pore volume staying almost constant for the Pt/Al_2O_3 and K-containing catalysts. The pore diameter is in the range of 150–190 Å. The Pt dispersion measured by H_2 chemisorption is near 42% for Pt/Al_2O_3; a decrease is observed in Pt–Ba/Al_2O_3 (30%) and Pt–K/Al_2O_3 (18%).

The XRD patterns of the calcined Pt–Ba/Al_2O_3 and Ba/Al_2O_3 catalysts (Fig. 1) show both the monoclinic (JCPDS 78-2057) and orthorhombic (Whiterite, JCPDS 5-378) polymorphic forms of $BaCO_3$, in addition to γ-Al_2O_3 (JCPDS 10-425). Pt–K/Al_2O_3 and K/Al_2O_3 catalyst exhibited only the pattern of the γ-Al_2O_3 (JCPDS 10-425); no diffraction features related to K-containing phases could be detected. No XRD-detectable Pt phases were observed in the Pt-containing samples.

Table 1
Material characterization: surface area, pore volume, average pore diameter and Pt dispersion

Catalytic systems	A_s ($m^2\,g^{-1}$)	V_p (cm^3/g)	d_p (Å)	Pt dispersion (%)
γ-Al_2O_3	207.4	0.96	153	–
Pt/Al_2O_3	198.4	1.00	168	42
K/Al_2O_3	180.0	0.82	152	–
Ba/Al_2O_3	136.2	0.65	167	–
Pt–K/Al_2O_3	176.3	1.01	191	18
Pt–Ba/Al_2O_3	141.6	0.71	166	30

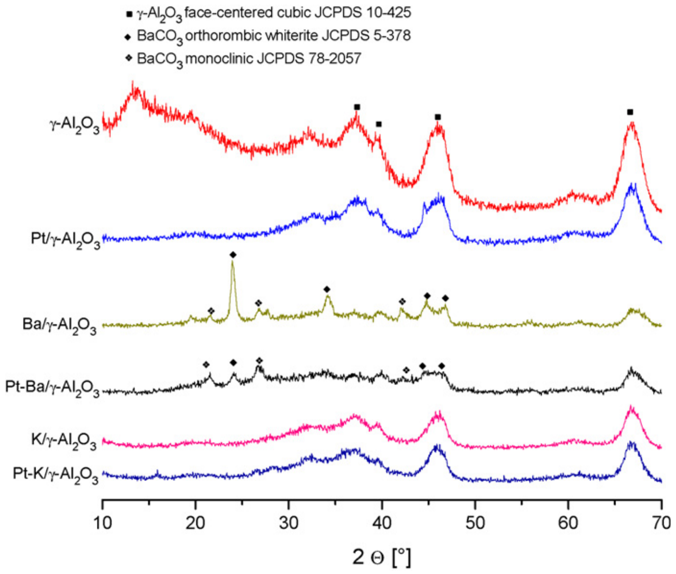

Fig. 1. XRD patterns of Al_2O_3, Pt/Al_2O_3, Ba/Al_2O_3, $Pt–Ba/Al_2O_3$, K/Al_2O_3 and $Pt–K/Al_2O_3$.

3.2. Soot oxidation in He + 3% O_2

3.2.1. Loose contact systems

Fig. 2A and B show the results obtained in the TPO experiments, carried out in He + O_2 (3%, v/v), for the catalyst–soot mixtures (loose contact). These figures show the CO_2 concentration and the soot conversion profiles with temperature, respectively. The O_2 consumption profiles (not shown) are always symmetrical to those of CO_2; CO is not detected in significant amounts (less than 2%) except for the Al_2O_3–soot and Ba/Al_2O_3–soot systems in which significant CO formation was observed. In these latter two cases, the selectivity towards CO_2 is near 60 and 84%, respectively. Notably, because in these experiments the temperature was measured by a thermocouple directly immersed in the catalyst bed, the recorded temperature (and hence the TPO profile) is not affected by the CO/CO_2 selectivity.

The soot–alumina sample gives rise to an ignition temperature (the temperature at which the CO_2 concentration exceeds 300 ppm) near 450 °C, whereas the peak maximum is observed at 680 °C. At this latter temperature, 50% of the soot initially loaded is combusted (Fig. 2B). The Ba/Al_2O_3 system shows a reactivity similar to that of the bare support; in fact, the CO_2 profiles of the Ba/Al_2O_3 system and that of Al_2O_3 support alone are almost superimposable. Accordingly, the data clearly show that the presence of Ba does not influence the soot oxidation, if one neglects the changes in the CO_2 selectivity (84 vs. 60%).

The Pt/Al_2O_3 system shows a similar ignition temperature compared to Ba/Al_2O_3, but after ignition the soot combustion proceeds more rapidly than in the case of the Ba/Al_2O_3 sample. Accordingly, the peak temperature is shifted to lower temperatures by about 100 °C. Hence the presence of Pt does not affect the temperature onset for soot oxidation, but instead increases the rate of oxidation, in line with the results reported by Setiabudi et al. [11]. Finally, the $Pt–Ba/Al_2O_3$ sample shows a behavior which is essentially intermediate between that of the Pt/Al_2O_3 and Ba/Al_2O_3 samples. However, very different results are obtained for the case of the K-containing samples. Indeed for K/Al_2O_3 and $Pt–K/Al_2O_3$, the onset for soot oxidation is observed at temperatures near 300–350 °C, i.e. 100 °C below that of the Ba-containing and Pt/Al_2O_3 samples. Hence the soot conversion curves (Fig. 2B) are shifted to lower temperatures, so that for the $Pt–K/Al_2O_3$ and K/Al_2O_3 samples, 50% soot conversion is achieved at 530 and 550 °C, respectively. We stress that the sample containing only K (i.e. the K/Al_2O_3 sample) shows a reactivity which is well above that of the Pt/Al_2O_3 catalyst. This result indicates a very high reactivity of potassium in the oxidation of soot. Indeed, 47% and 57% of soot is combusted below 550 °C with K/Al_2O_3 and $Pt–K/Al_2O_3$, respectively, while only less than 5% of soot is converted at the same temperature for the other samples.

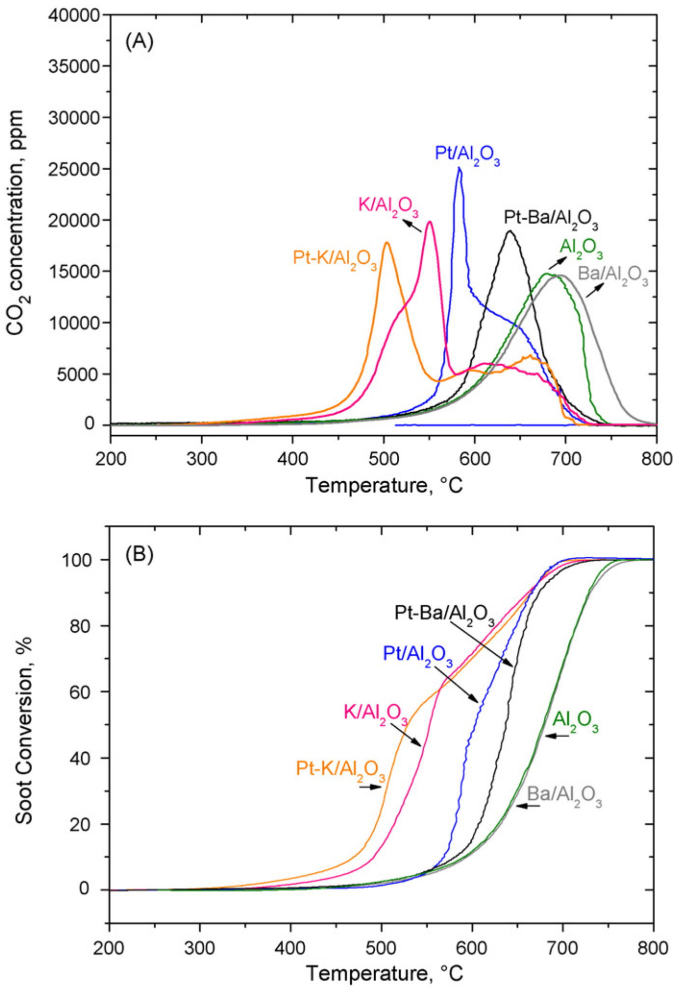

Fig. 2. Results of TPO experiments in He + O_2 3% (v/v) over loose contact systems. (A) CO_2 evolution; (B) soot conversion.

In contrast, Krishna and Makkee [12] did not observe significant differences in the un-catalyzed and catalyzed soot combustion when the oxidation was carried out in the presence of Pt/Al_2O_3 and $Pt–Ba/Al_2O_3$. However, in line with our results, a valuable effect of the presence of K/Al_2O_3 and $Pt–K/Al_2O_3$ catalysts on the soot oxidation was pointed out. Notably, as also pointed out by Krishna and Makkee [12], a synergistic effect is seen for the case of the K-containing samples in that the $Pt–K/Al_2O_3$ sample outperforms the catalytic behavior of both the Pt/Al_2O_3 and K/Al_2O_3 samples (see Fig. 2). The same effect is not apparent in the case of the Ba-containing catalysts since the reactivity of the $Pt–Ba/Al_2O_3$ sample is lower than that of the Pt/Al_2O_3 catalyst. In this respect, the K promoter shows unique features in the soot combustion reaction.

To further compare the soot oxidation activity and selectivity of the Ba and K promoters, soot oxidation tests were performed under isothermal conditions at temperatures between 350 and 470 °C by feeding oxygen pulses (3% O_2 in He) over Ba/Al_2O_3 and K/Al_2O_3 catalysts in loose contact with soot, with the results shown in

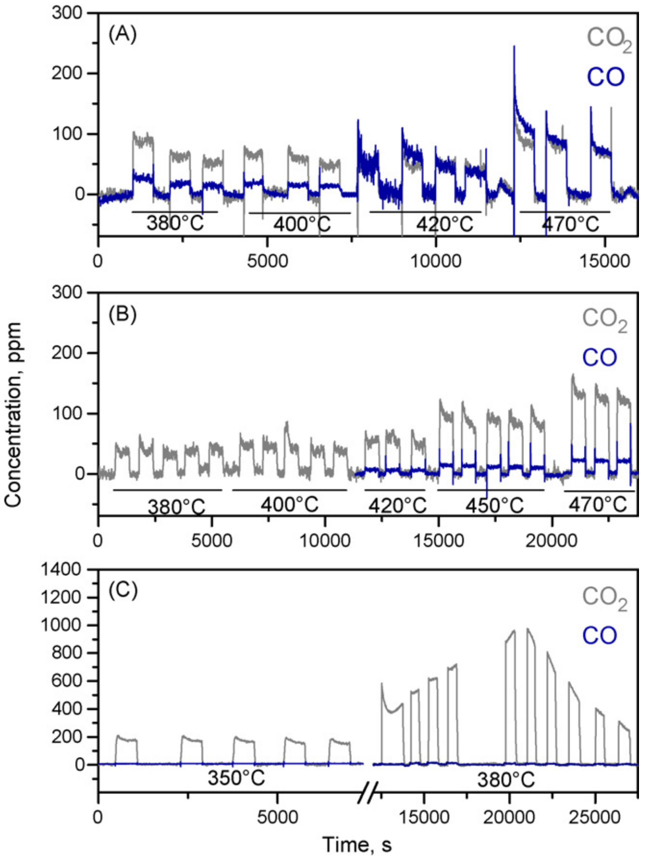

Fig. 3. Isothermal oxidation over soot (A), Ba–Al_2O_3/soot (B) and K–Al_2O_3/soot (C) upon steps of He + O_2 3% (v/v).

Fig. 3B and C, respectively. The results obtained for the case of soot alone are also shown for comparison purposes (Fig. 3A).

For the case of the bare soot (Fig. 3A), very low levels of CO_2 production are observed starting from 380 °C: peaks near 70 ppm are indeed observed at this temperature upon O_2 admission to the reactor. Formation of CO is also observed in non-negligible amounts. Upon progressively increasing the temperature up to 470 °C, a small increase in the production of CO_2 (80 ppm) is observed, whereas CO formation increases considerably so that at the maximum investigated temperature the amounts of CO and CO_2 produced are nearly the same.

When the soot oxidation runs are carried out in the presence of the Ba/Al_2O_3 sample (Fig. 3B), similar results are obtained. However, in this case CO is detected in lower amounts when compared to the pure soot sample (Fig. 3A). Hence, apparently the presence of the Ba/Al_2O_3 sample does not significantly modify the rate of soot oxidation but instead favors the oxidation of CO to CO_2.

A different picture is apparent for the case of the K/Al_2O_3 sample (Fig. 3C). Indeed in this case a much higher soot oxidation rate is measured, even at lower temperatures: the CO_2 concentration is near 200 ppm already at 350 °C. Furthermore, it is noteworthy that the production of CO is negligible. When the temperature is increased to 380 °C, the CO_2 formation rate is greatly enhanced, with CO still remaining negligible. Notably, at this temperature the CO_2 production changes with time-on-stream, increasing during the initial oxygen pulses, reaching a maximum near 1000 ppm, and then beginning to decrease. It may be speculated that the increase in the soot combustion activity which is observed during the initial pulses is related to changes in the soot particles characteristics due to the ongoing oxidation reaction, eventually leading to an increase in the reactivity. On the other hand, the decrease observed after the initial peaks are likely due to a decrease in the total amount of soot.

In line with the TPO data previously shown (Fig. 2), the results just described demonstrate that alumina-supported K shows a significant decrease in the soot oxidation temperature even under loose conditions. These data parallel those reported by Krisnha and Makkee [12] who reported that K/Al_2O_3 and Pt–K/Al_2O_3 decrease the soot oxidation temperature (even under loose contact) with respect to un-catalyzed soot combustion. These authors attributed the high activity in the soot combustion of the K-containing samples to the volatile nature of the K species that, due to its high mobility, is responsible for the observed effects on soot combustion. It has also been suggested that potassium can promote the formation of low melting point compounds that wet the soot surface, increasing its contact with the catalyst and thus improving activity [13–18].

Thus, it can be speculated that K, possibly due to the formation of a low melting point species, may give rise to highly mobile species on the soot surface which enhances the soot–catalyst contact. In fact, it has also been reported that, due to the volatile nature of the K species, K-based catalysts suffer deactivation by loss of the active elements [12]. In order to check this point, the K–Al_2O_3 catalyst was used for repeated soot oxidation cycles with He + 3% O_2 under isothermal conditions at 400 °C, followed by TPO runs up to 500 °C to complete the soot oxidation. The data (herein not reported for brevity) indicated a significant decrease in activity (rate of CO_2 formation) from the first to the second cycle (activity was reduced by a factor of 2–3); the activity in subsequent cycles, however, was found to be stable and reproducible.

3.2.2. *"Full contact" systems*

Fig. 4A–C shows the results obtained during the TPO experiments carried out for the case of the soot samples directly

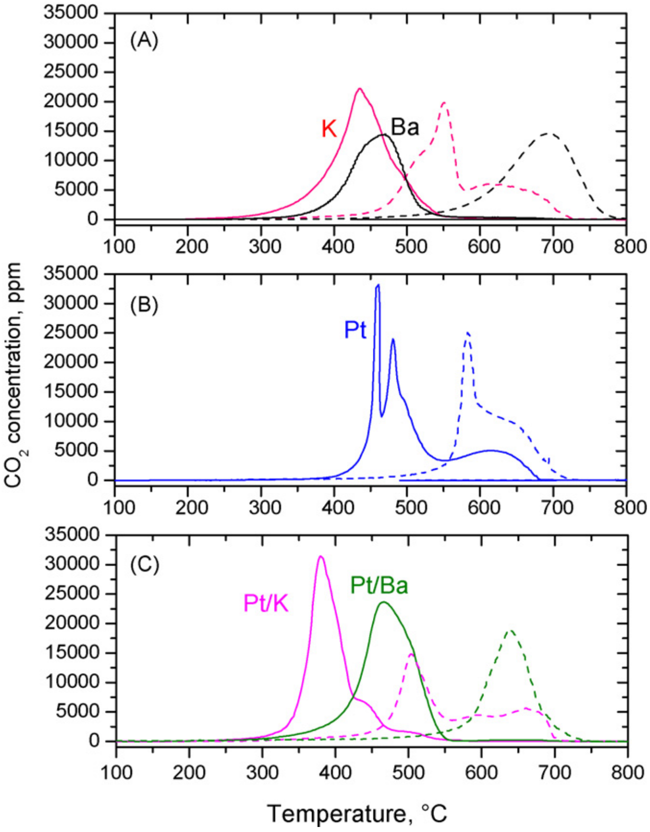

Fig. 4. Results of TPO experiments in He + O_2 3% (v/v) over loose contact systems (dashed lines) and full contact systems (solid lines).

impregnated with the different metal salts (i.e. K/soot, Ba/soot, Pt/soot, Pt–K/soot, Pt–Ba/soot). The data are shown as solid lines in the figure and compared with the results of the corresponding experiments obtained for the case of the loose contact systems (dashed lines). As reported above, the impregnated soot samples (“full contact” systems), in which the active elements are embedded in soot, are representative of an intimate contact between the soot and the catalytic elements. This is a more reproducible technique than the classical tight contact methods obtained by mechanically grinding the soot and the catalysts in a mortar. Indeed, the physical processes occurring during the mechanical mixing do not allow the achievement of an optimum and reproducible contact between the soot particles and the active sites.

As shown by Fig. 4, when an intimate contact is guaranteed between the active elements and soot, significant changes in the TPO spectra are observed. In fact, in all cases both the ignition and peak temperatures for soot oxidation significantly decrease with respect to those of the corresponding loose contact systems. The observed shift is nearly 100–150 °C for the Pt- and K-containing samples; an even greater (nearly 200 °C) decrease is observed in the temperature onset for soot combustion for the case of the Ba-containing samples (Ba/Al_2O_3 and $Pt–Ba/Al_2O_3$). In fact, under “full contact” conditions, the reactivity of the Ba-containing samples, which was found to be very poor under loose contact conditions, is similar to the very active K-based system. The positive effect of contact was also well evident for the case of the Pt/soot and Pt/Al_2O_3–soot samples, a result that contrasts with what has been reported in the literature for the effect of contact in the case of Pt [12].

Thus, when an intimate contact is guaranteed between the active elements and soot, the soot combustion reaction is greatly enhanced, in line with literature indications [12,15]. In particular, when an intimate contact is guaranteed, even the poorly reactive Ba-containing samples show similar activity as K-containing catalysts.

The beneficial role of alkali or alkaline earth metal oxides in the gasification of carbonaceous materials is well known. It has been suggested that the alkaline or alkaline earth metal oxides form higher surface oxides (e.g. superoxides or peroxides) which may initiate the soot oxidation [19,20] via the formation of atomic O_{ad} species. The electropositive nature of alkali and alkaline earth metal oxides could result in a strengthening of carbon–oxygen bonds and a corresponding weakening of carbon–carbon bonds by electron transfer to the carbon substrate [17,21,22].

In these mechanisms the nature of the soot/active component contact is essential. Accordingly, when the contact is poor (loose contact systems), the active element contact with the soot may be blocked by the alumina support material. On the other hand, if the active element has high mobility, or it is volatile, a good catalyst/soot contact is attained and this improves activity. This would explain the observed difference between the K- and Ba-based systems, with Ba species having intrinsic high activity in the soot combustion but low mobility on the surface.

A role for Pt in the soot combustion mechanism is also evident in these results although, under “full contact” conditions, Pt shows a lower reactivity with respect to K and Ba. However the rate of soot combustion after the onset temperature is significantly higher than that of the Pt-free samples. This may suggest that Pt promotes the mobility of active oxygen species formed over the alkaline or alkaline earth metal oxide. In this way, higher soot combustion activity (under full contact conditions) is seen for the Pt–K and Pt–Ba samples (see Fig. 4).

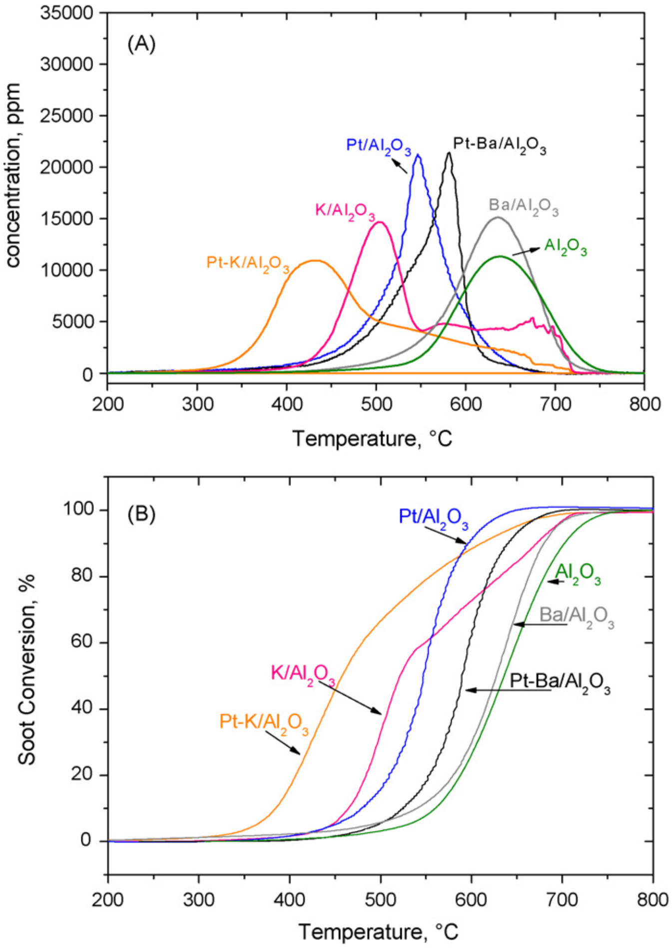

Fig. 5. Results of TPO experiments in He + NO 1000 ppm + O_2 3% (v/v) over loose contact systems. (A) CO_2 evolution; (B) soot conversion.

3.3. *Soot oxidation in He + 3% O_2 + 1000 ppm NO*

Fig. 5 shows the results obtained in the TPO experiments carried out in He + NO (1000 ppm) + O_2 (3%, v/v) for the various investigated catalyst–soot mixtures (loose contact). Fig. 5A and B show the CO_2 concentration profiles and the soot conversion with temperature, respectively.

For the case of the bare alumina support, the temperature threshold for soot oxidation is not significantly affected with respect to the same experiment carried out in the absence of NO (see Fig. 2). On the other hand, for all the other systems the presence of NO in the gas feed decreases the temperature onset for the reaction; the decrease is particularly evident for the case of the Pt-containing samples in which a shift towards lower temperatures of 50–100 °C is observed. The beneficial effect of NO on soot combustion is well established in the literature, specifically over noble metal-containing samples [8,12,23]. The suggested mechanism is based on the oxidation of NO to NO_2 promoted by Pt; NO_2 then rapidly oxidizes soot to CO_2. As discussed by Krishna and Makkee [12], in Pt-containing samples soot may be oxidized by NO_2 with formation of CO_x and NO; NO is then oxidized again by O_2 over Pt and hence it is “recycled”. However, a mechanism involving the soot oxidation by O_2 assisted by NO_2 should also be invoked in view of the high rate of soot oxidation with respect to the amounts of NO_2 formed by NO oxidation.

Notably, for the case of the Pt-free systems (Ba/Al_2O_3 and K/Al_2O_3), the presence of NO does not significantly affect the temperature threshold for soot oxidation; however, over these samples the oxidation proceeds faster than in the pure O_2 flow (the maximum in the CO_2 concentration is shifted by about 50 °C). Sullivan et al. [24] have reported the promotional effect of NO over Na/Al_2O_3, suggesting that NO adsorbs as nitrites which are subsequently oxidized to nitrates. These nitrate species are then desorbed as NO_2 that then oxidizes the soot.

It is noteworthy that, at variance with results reported by Krishna and Makkee [12], the synergetic effect between K and Pt, which is seen in the case of the K-containing samples in a NO-free environment, is again evident in the presence of gaseous NO. In fact, the $Pt–K/Al_2O_3$ sample outperforms the catalytic behavior of both the Pt/Al_2O_3 and K/Al_2O_3 samples in decreasing the soot oxidation temperature. The synergetic effect is not apparent for the case of the Ba-containing catalysts, as in the absence of NO (see Fig. 2), since the reactivity of the $Pt–Ba/Al_2O_3$ sample is intermediate between that of the Pt/Al_2O_3 and Ba/Al_2O_3 samples.

As previously discussed, the suggested soot oxidation mechanism in the presence of NO is driven by the oxidation of NO to NO_2 promoted by Pt. Moreover, the data reported above point out that the alkaline and alkaline earth oxides play a role as well. Since it has been previously shown that $Pt–K/Al_2O_3$ and $Pt–Ba/Al_2O_3$ catalysts have similar NO oxidizing properties but different activity for soot combustion [9], their different reactivity in the soot combustion in the presence of NO cannot be uniquely related to the activity for the oxidation of NO to NO_2. It is well known that NSR-type catalysts undergo nitration when exposed to NO/O_2 [9,12] via the formation of nitrite and nitrate species bonded to the alkaline or alkaline earth metal oxides. Nitrates are also formed on the exposed alumina surface. Krishna and Makkee [12] pointed out that soot is oxidized at significantly lower temperatures over NO_x treated $Pt–K/Al_2O_3$ and $Pt–Ba/Al_2O_3$ catalysts compared to fresh catalysts, respectively. The increase in the reactivity for soot combustion has been ascribed to the decomposition of the nitrates leading to NO_2 evolution; the different thermal stability of the nitrates formed on Ba, K or alumina affects the activity for soot combustion. The direct participation of surface nitrates as soot oxidants can also be invoked; accordingly, it is speculated that upon exposure of NO, mobile and/or reactive surface nitrates species are formed over the $Pt–K/Al_2O_3$ and $Pt–Ba/Al_2O_3$ samples, which promotes soot combustion. As a matter of fact, the presence of mobile surface nitrate species in NSR catalysts has been invoked by several authors [25]; thus, the different nature and mobility of nitrate species formed over K- and Ba-based catalysts may explain the different activity in the soot combustion of $Pt–K/Al_2O_3$ and $Pt–Ba/Al_2O_3$ samples in the presence of NO.

Finally, the effect of the presence of NO was also investigated in the case of the full contact samples. Fig. 6 compares the TPO experiments carried out with He + 3% (v/v) O_2 both in the presence and in the absence of 1000 ppm NO. Notably, in all cases the CO_2 profiles do not show appreciable differences both in terms of soot ignition and oxidation rate, thus indicating that when an intimate contact is guaranteed between the active elements and the soot particles, the presence of NO does not lead to any significant effect on soot combustion, even for the case of the Pt-containing samples. This is possibly related to the fact that, under full contact conditions, the presence of the alkaline or alkaline earth metal oxides is so effective in the reaction that the NO oxidation to NO_2 and the participation of NO_2 in the soot combustion does not lead to significant added benefits for the reaction.

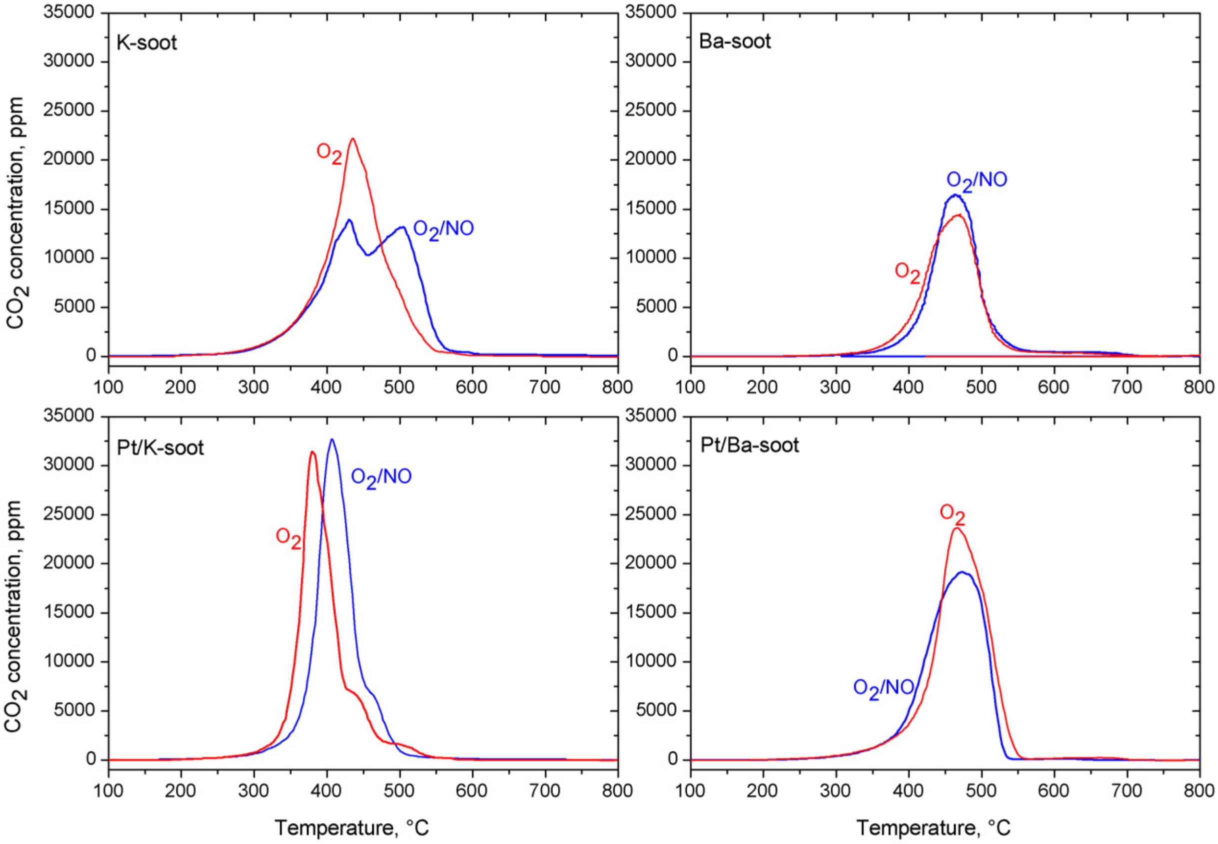

Fig. 6. Results of TPO experiments over full contact systems in He + 1000 ppm NO + 3% O_2 (solid blue lines) and in He + 3% O_2 (dot red lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

4. Conclusions

The activity for soot combustion of K- and Ba-based catalysts in "loose" and "full" contact was investigated in this study. In line with other literature reports, it is found that the K-containing samples (i.e. K/Al_2O_3 and $Pt–K/Al_2O_3$) are very active for the oxidation of soot even under loose contact conditions. As a matter of fact, a decrease in the soot ignition temperature of around 100 °C is observed using 3 vol.% O_2. Also, a synergistic effect is observed for the case of the K-containing samples in that the $Pt–K/Al_2O_3$ sample outperforms the catalytic behavior of both the Pt/Al_2O_3 and K/Al_2O_3 samples. The same effect is not apparent for the Ba-containing catalysts when in loose contact with the soot.

When an intimate contact is guaranteed between the active elements and the soot (full contact), the reactivity in the soot combustion reaction is enhanced for both K- and Ba-based samples. Notably, under these conditions the reactivity of the poorly active Ba-containing samples becomes similar to the very active K-based system. Accordingly, the poor activity observed in the soot combustion reaction for the case of the Ba-based catalysts under loose conditions is possibly due to the low mobility of the active Ba surface species.

The presence of NO promotes the soot oxidation over all the investigated samples when they are loosely contacting soot, but specifically over noble metal-containing samples, due to the oxidation of NO to NO_2 which in turn oxidizes the soot. However, the presence of the alkaline and alkaline earth oxide also affects the soot oxidation activity in the presence of NO. This has been ascribed to the formation of Ba- and K-nitrite/nitrate species which participate in the combustion of soot via the formation of NO_x upon nitrite/nitrate decomposition and/or by directly reacting with soot. In this case, the greater activity of the $Pt–K/Al_2O_3$ sample with respect to the $Pt–Ba/Al_2O_3$ catalyst in the presence of NO may be related to the different nature and mobility of nitrate species formed over K- and Ba-based catalysts.

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