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Stability of Ba,K/CeO_2 catalyst during diesel soot combustion: Effect of temperature, water, and sulfur dioxide

M.A. Peralta, V.G. Milt, L.M. Cornaglia, C.A. Querini *

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ, UNL-CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

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Abstract

In this work we study the stability of Ba,K/CeO_2 catalysts, which have been shown to be very active for soot combustion. The effects of high-temperature treatments and the presence of water or sulfur dioxide on the catalytic properties for soot oxidation are studied. Fresh and deactivated catalysts are characterized by XPS, FTIR, XRD, and high-frequency CO_2 pulses, and the activity is measured by TPO. Barium has only a minor effect on the activity for soot combustion, whereas potassium has a pronounced effect in decreasing the temperature needed to burn soot. In the case of Ba,K/CeO_2, optimum activity as a function of potassium content of around 7 wt% is found. The optimum, which is very smooth, is due to the synergistic effect between K and CeO_2. This catalyst is thermally stable up to 830 °C and does not deactivate even after 30 h at 800 °C. At higher temperatures, a decrease in the K/Ce surface ratio and formation of the $BaCeO_3$ perovskite, indicated by the XPS analyses, are the causes of activity loss. In these cases, there is a decrease in the level of interaction with CO_2. The presence of water at 400 °C does not lead to any significant modification of catalytic activity. However, the presence of water at 800 °C leads to both a drastic decrease in activity and a change in surface composition as indicated by XPS, with a high degree of hydroxylation and probably a spreading of BaO on the ceria surface. The presence of SO_2 (1000 ppm in air) at 400 °C deactivates the catalyst for soot oxidation even after rather short times (32 h). Under these conditions, FTIR and XPS analyses show that barium, potassium, and cerium sulfates are formed. Consequently, the activity for soot oxidation is lost, and there is no interaction between the catalyst and the CO_2. This type of catalyst has good thermal stability and very good tolerance to water at low temperatures (e.g., 400 °C). However, high concentrations of SO_2 lead to rapid deactivation. This should not be a major drawback, because in the near future a much lower level of sulfur in diesel fuel is expected.

Keywords: Diesel soot combustion; Potassium; Barium; Ceria; Stability

1. Introduction

Emissions from diesel engines contain soot and nitrogen oxides as main pollutants. Emission standards in many countries impose very stringent limits on the levels of these contaminants in engine exhaust gases. Current technologies need further improvement to reach the limits expected to be set in the near future; therefore, an intensive research effort is currently under way. The catalytic filter seems to be one of the most important methods to decrease the amount of soot in exhaust gases [1]. The catalyst deposited on a ceramic filter or foam must be sufficiently active to oxidize the soot at the temperature of the exhaust gases, which can be 400 °C for heavy-load engines and 300 °C or even lower for light-duty engines. Studies with a large number of catalytic formulations have been reported, including oxide materials and their mixtures [2–5], perovskite-type oxides [6–8], spinel-type Cu-chromite [9], Cu/K/Mo/Cl [10,11], Cu-V-K-Cl/TiO_2 [12], promoted vanadium oxides [13,14], and molten salts [11,15–17].

There are several requirements other than being active that a catalytic filter for diesel exhaust treatment should fulfill [18]: good thermal shock resistance, low-pressure drop, high soot filtration efficiency, and high soot–catalyst contact efficiency. In addition to these requirements, the catalyst must be stable in the presence of high concentrations of CO_2, water, and certain lev-

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[*] Corresponding author.
E-mail address: querini@fiqus.unl.edu.ar (C.A. Querini).

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els of SO_2. Even though this is a key issue, only a handful of papers are related to the stability of soot combustion catalysts [1,19,20] or, specifically, to the effect of water and SO_2 tolerance for these catalysts [21,22], but none of them [1,19–22] has carried out a systematic study of the effect of sulfur, water, and temperature on soot combustion activity. Badini et al. [23] analyzed the effect of water, temperature, and SO_2 on the catalytic behavior of Cu-K-V-Cl catalysts. They found good sulfur tolerance in their experiments using 200 ppm SO_2 for 96 h at 380 °C or 24 h at 600 °C. van Setten et al. [24] studied molten-salt catalysts supported on ceramic foams (based on Cs_2O, MoO_3, and Cs_2SO_4) to determine their mechanical strength, hydrothermal stability, and loss of catalyst due to solubility in water. On the other hand, a number of recent studies have examined the effect of SO_2 on the catalytic performance of three-way catalysts. It has been observed that the poisoning of automotive three-way catalysts by SO_2 occurs mainly through the formation of sulfate species, affecting the oxygen storage capacity. Even though the sulfate species can undergo oxidation and reduction in the same temperature range as that of ceria, the rate of oxygen transfer for the sulfate is lower [25]. Sulfate formation occurs mainly when the ceria is exposed to SO_2 at temperatures above 473 K in the presence of O_2 [26]. Nevertheless, Waqif et al. [27] found that heating ceria under SO_2 without oxygen results in the formation of surface and bulk-like sulfate species. Recently, Flouty et al. [21] found that for molybdenum-cerium catalysts, adding small quantities of molybdenum to the ceria improved the resistance of the catalysts to sulfur poisoning during the soot combustion reaction. In this study [21], the sulfated catalysts were prepared by treating the calcined solids under a flow of pure SO_2 gas at room temperature.

It has been reported that SO_2 in low doses promotes activity, as in the case of KVO_3/SiC catalysts [28]. Water was also found to increase the activity of this catalyst, which was attributed to improved contact between the catalyst and the carbon.

In preliminary studies, we also found a promotion effect of SO_2 at low doses on Co,K/MgO catalysts [29], and a moderate deactivation on powder or monolith supported K/La_2O_3 catalysts [30]. In addition, we found that potassium-promoted CeO_2 catalysts have very good activity for soot combustion, and when Ba is included in the formulation, they are able to work as a NO_x trap [31–33].

This paper addresses the stability of Ba,K/CeO_2 catalysts during the oxidation of diesel soot. The effect of temperature, water, and SO_2 is studied measuring the activity by temperature-programmed oxidation (TPO) to determine whether this material could be stable under real conditions. Preliminary results regarding aging treatment in liquid water are also presented. Catalysts are characterized by FTIR, XPS, XRD, BET, and high-frequency CO_2 pulses.

2. Experimental

2.1. Soot and catalyst preparation

The soot used in this work was prepared by burning commercial diesel fuel (Repsol-YPF, Argentina) in a glass vessel. After being collected from the vessel walls, it was dried in a stove for 24 h at 120 °C. Its specific surface area was 55 m^2/g. Temperature-programmed experiments performed using helium as carrier gas provided information regarding the amount of partially oxidized groups of the soot surface and the amount of hydrocarbons that could remain adsorbed after the diesel combustion. In this way, the amount of carbon released as CO, CO_2, and hydrocarbons represents 9.3% of the soot [33]. The same batch of soot was used in all of the experiments presented in this study, to avoid possible differences in surface oxygen groups, which could affect activity results.

The Ba,K/CeO_2 catalysts were prepared by the wet-impregnation method, using CeO_2 (Sigma, p.a.) as a support, to which a solution containing barium acetate and/or KNO_3 was added to obtain loads of 10, 16, and 22 wt% of Ba and loads of 2, 4.5, 7, 10, and 15 wt% of K. These values are referred to the CeO_2 support (e.g., 22 g of Ba per 100 g CeO_2). The initial concentration of the starting solutions was 0.1 M of both barium acetate and KNO_3. The suspension was evaporated at 85 °C while being vigorously stirred until achieving a paste, which was dried in a stove for 24 h at 120 °C and calcined for 2 h at 400 °C (fresh catalyst), heating from room temperature to the final temperature in 2 h. The nomenclature adopted for the catalysts was Ba(x),K(y)/CeO_2, where "x" indicates the weight percentage of barium and "y" is the weight percentage of potassium.

2.2. Activity test

The catalytic activity of Ba(x),K(y)/CeO_2 for the combustion of soot was determined by TPO. The soot and the different catalysts were mechanically mixed in an agate mortar for a prescribed period (6 min), so as to obtain a soot/catalyst ratio of 1/20 (wt/wt). A gaseous flow (40 mL/min) with 6% oxygen in nitrogen was used, and the temperature was increased at a rate of 12 °C/min, using 10 mg of the catalyst–soot mixture. A modified TPO technique [34] was used that involved passing the gases coming from the reactor through a methanation reactor, where CO and CO_2 were converted into CH_4. Afterward, methane was measured continuously with a flame ionization detector (FID). The methanation reactor contained a nickel catalyst and operated at 400 °C.

The mixing procedure followed in this study was checked to determine its reproducibility. We found that it is possible to reproduce the TPO profile if the mixing time is controlled. The TPO maximum temperature falls in a window of ±10 °C when two mixtures are prepared using the same batch of catalyst and soot, which is a very good result, mainly if the heterogeneity of the system is taken into account. The loose-contact mixtures were also prepared with the selected catalysts by shaking the catalysts and the soot in a vial for 2 or 6 min.

The selectivity to CO_2 and CO was measured only with the potassium-containing catalysts in the TPO experiments, by analyzing the gases coming out of the cell with a gas chromatography column and a thermal conductivity detector.

2.3. Catalyst characterization

2.3.1. X-ray diffraction

The X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument with monochromator using Cu$K\alpha$ radiation at a scan rate of 1°/min, from $2\theta = 20$ to 100°.

2.3.2. IR spectroscopy

Infrared spectra were obtained using a Shimadzu 8101M spectrometer. Samples were prepared in the form of pressed wafers (ca. 1% sample in KBr). All spectra involved the accumulation of 80 scans at a resolution of 4 cm^{-1}.

2.3.3. High-frequency CO_2 pulse technique

This was carried out at different temperatures, by sending pulses of 0.135 µmol of CO_2 in 6% O_2 in N_2 carrier every 10 s. Thermal treatments between pulse cycles were also carried out. Typically, the procedure was as follows. The catalyst was heated up to 500 °C, at which point a series of 20 pulses was sent. Then the temperature was decreased to 400 °C, at which point a new series of pulses was carried out. Subsequently, the temperature was decreased to 25 °C, for the final set of pulses in the first cycle. After this first cycle of pulses, a thermal treatment in 6% O_2 in flowing N_2 was performed with heating up to 700 °C. During this treatment, CO_2 desorption was recorded to analyze the decomposition temperature of the bulk and surface carbonates that did not decompose at the pulse temperature. Afterward, a new set of pulses was carried out at 500, 400, and 25 °C to complete the second cycle. The CO_2 was detected with a FID after methanation, as described above.

The CO_2 peak comes out of the cell with a distortion, depending on the interaction with the catalyst. The absence of a CO_2 peak at the cell outlet means that the interaction is too high; a sharp peak indicates that there is no interaction at all. When several pulses are sent consecutively to the cell, the system might reach a pseudo-steady state, with constant amplitude of oscillation, as long as the adsorption–desorption process is sufficiently rapid. If the amplitude is lower than the reference (without catalyst or with a catalyst at a temperature at which there is no interaction), then the dynamics of the process allows the surface to adsorb–desorb the CO_2 at the same average rate as the injection.

2.3.4. X-ray photoelectron spectroscopy

The XPS measurements were carried out with an ESCA750 Shimadzu electron spectrometer using non-monochromatic Al$K\alpha$ X-ray radiation. The anode was operated at 8 kV and 30 mA, and the pressure in the analysis chamber was about 2×10^{-6} Pa during spectrum collection. The data were collected using an ESCAPAC 760 computer interfaced to the spectrometer and analyzed with appropriate software.

The spectra from the regions related to Ce 3d, Ba 3d, O 1s, K 2p, C 1s, and S 2p core levels were recorded for each sample. The binding energies (BEs) were referred to the C 1s signal (284.6 eV). Curve-fitting was performed using a Levenberg–Marquardt NLLSCF routine. The background contribution was considered assuming an integral-type background. Quantitative analyses were performed using the appropriate Scofield factors. Because of the approximations done in the calculations of the XPS composition, we had to consider the relative evolution of the ratios.

2.3.5. BET area

The BET surface area was determined for selected samples (both in fresh catalysts and after deactivation treatments) using a Quantachrome Nova 1000 sorptometer.

2.4. Stability tests

The thermal stability was studied by calcining the catalysts for 2 h at different temperatures, typically 700, 800, 810, 830, and 850 °C. In addition, calcination was carried out at 800 °C for 30 h. The stability was checked by both TPO analyses and high-frequency CO_2 pulses, and selected samples were characterized by XRD and XPS. In addition, total K content was analyzed by atomic absorption spectroscopy after sample dissolution in a perchloric–nitric acid mixture.

To study the effect of water and SO_2 on stability, catalysts were pretreated before the TPO experiments as follows. In the case of water, a stream of air was saturated with water at room temperature, then flowed through the catalyst bed at 400 and at 800 °C for different times (8–200 h). Then, the system was purged for 2 h with air at 400 °C. The resulting water concentration in the air stream is 3%, compared with the typical 6% in diesel engine exhausts. In the case of SO_2, air containing 1000 ppm of SO_2 was flowed for different times through the catalyst bed at 400 °C. After this treatment, the catalyst was purged with air for 2 h at the same temperature. High concentrations of SO_2 in air have also been used by other research groups to carry out accelerated deactivation tests; for example, Badini et al. [23] used 200 ppm SO_2 at 380 °C and 600 °C, Flouty et al. [21] used pure SO_2 at room temperature, and Neri et al. [22] used 1000 ppm SO_2 at 300 °C.

The effect of water was also addressed by washing the catalyst with water to simulate the effect of condensed water inside the pipe. A sample of fresh catalyst was washed with water, using a water/catalyst weight ratio of 15.

3. Results

3.1. Influence of barium and potassium content on the activity of fresh catalysts

Fig. 1A shows the TPO profiles of physical mixtures of soot and Ba(x)/CeO_2 catalysts. It can be seen that the maximum shifts slightly shifts toward lower temperatures as the barium content increases, being 500, 475, and 460 °C for 10, 16, and 22 wt% barium, respectively. The soot without catalyst displays a TPO profile with a maximum between approximately 550 and 600 °C [35], and the mixture of soot and CeO_2 calcined at 400 °C has a maximum at approximately 500 °C (not shown).

The influence of K content was studied on CeO_2 and on the catalysts containing 22 wt% barium. Results obtained with

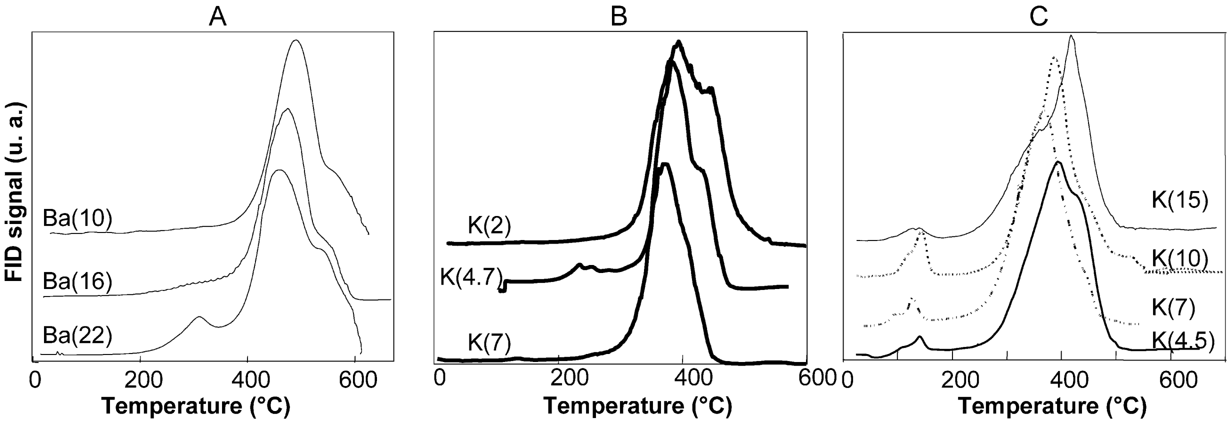

Fig. 1. TPO profiles of soot–catalyst mechanical mixtures. Catalysts calcined at 400 °C. (A) Ba(x)/CeO_2, (B) K(y)/CeO_2, and (C) Ba(22),K(y)/CeO_2.

Table 1
Specific surface areas

Catalyst and treatment	BET surface area (m^2/g)
CeO_2	11.2
$CeO_2 + SO_2$	2.9
Ba(22)K(7)/CeO_2 calc. 400 °C	2.4
Ba(22)K(7)/CeO_2 calc. 700 °C	1.6
Ba(22)K(7)/CeO_2 calc. 800 °C	0.6
Ba(22)K(7)/CeO_2 calc. 400 °C, 100 h in H_2O	5.6
Ba(22)K(7)/CeO_2 calc. 400 °C, 90 h in SO_2	2.9

K(y)/CeO_2 are shown in Fig. 1B. In the range of 2–7 wt% K, the activity of K(y)/CeO_2 has a minor increment with increasing K content, being much better than that in the case of pure CeO_2. In the case of Ba(22),K(y)/CeO_2, there is also a significant effect of K on catalytic activity (Fig. 1C). The temperature of the maximum in the TPO profile decreases by approximately 100 °C when Ba(22)/CeO_2 is promoted with K. Whereas Ba(22)/CeO_2 displays a maximum at 460 °C, Ba(22),K(y)/CeO_2 profiles have a maxima between 365 and 410 °C. Increasing the K content from 4.5 to 7 wt% leads to an activity improvement, with the maximum of the TPO profile at 365 °C. However, further increases in K content to 10 and 15 wt% lead to a decrease in activity.

According to these results, the formulation selected to carry out the stability studies is Ba(22),K(7)/CeO_2. This catalyst was chosen to have both the largest NO_x trapping capacity (due to the highest Ba concentration) and the highest activity.

The TPO profile of the loose-contact mixture (not shown) displays a maximum at 460 and 480 °C after 6 and 2 min of shaking, respectively. The CO_2 selectivity is >90% at any temperature, continuously increasing with rising temperature.

Table 1 shows the BET surface area values for the support, for the fresh Ba(22),K(7)/CeO_2 catalyst, and for this catalyst after different treatments. The BET area decreases from 11.2 m^2/g for CeO_2 to 2.4 m^2/g for the Ba(22),K(7)/CeO_2 catalyst, indicating that at this level of loading, many small pores of the support are plugged. However, as reported previously [36], the surface area has very little influence on the soot oxidation reaction, because the soot particles are too large to fit inside any pore, and only the catalyst external surface takes place in the reaction.

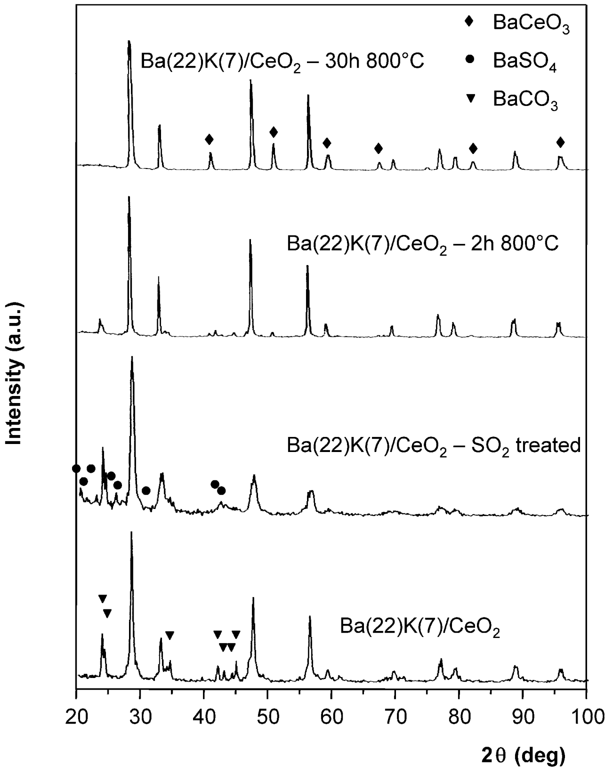

Fig. 2. XRD pattern of Ba(22),K(7)/CeO_2 catalysts, calcined at 400, 800 °C (for different times) and after SO_2 treatment for 90 h.

3.2. *Thermal stability of Ba(22),K(7)/CeO_2 catalyst*

The XRD analysis of the fresh Ba(22),K(7)/CeO_2 catalyst is shown in Fig. 2 and Table 2. The presence of $BaCO_3$ is clearly observed, as expected, because the spontaneous decomposition of $BaCO_3$ into $BaO + CO_2$ at appreciable rates occurs only at temperatures above 1337 °C [37]. The main XRD reflections of KNO_3 (JCPDS #5-377) coincide with that of $BaCO_3$ (JCPDS #5-378). Therefore, for the Ba(22),K(7)/CeO_2 catalyst, the presence of crystalline KNO_3 cannot be discarded. Moreover, the IR spectrum (not shown) indicates the presence of

Table 2
XRD crystalline phases

Solid	Treatment	Phase[a]
K(7)/CeO_2	Fresh[b]	CeO_2, [KNO_3]
	SO_2 treated	CeO_2
Ba(22)/CeO_2	Fresh[b]	CeO_2, $BaCO_3$
	SO_2 treated	CeO_2, $BaCO_3$, [$BaSO_4$]
Ba(22),K(7)/CeO_2	Fresh[b]	CeO_2, $BaCO_3$
	Solid calcined at 800 °C for 2 h	CeO_2, [$BaCO_3$], [$BaCeO_3$]
	Solid calcined at 800 °C for 30 h	CeO_2, $BaCeO_3$
	SO_2 treated	CeO_2, $BaCO_3$, [$BaSO_4$]

[a] Phases present at traces level appear between brackets.
[b] Solid calcined at 400 °C.

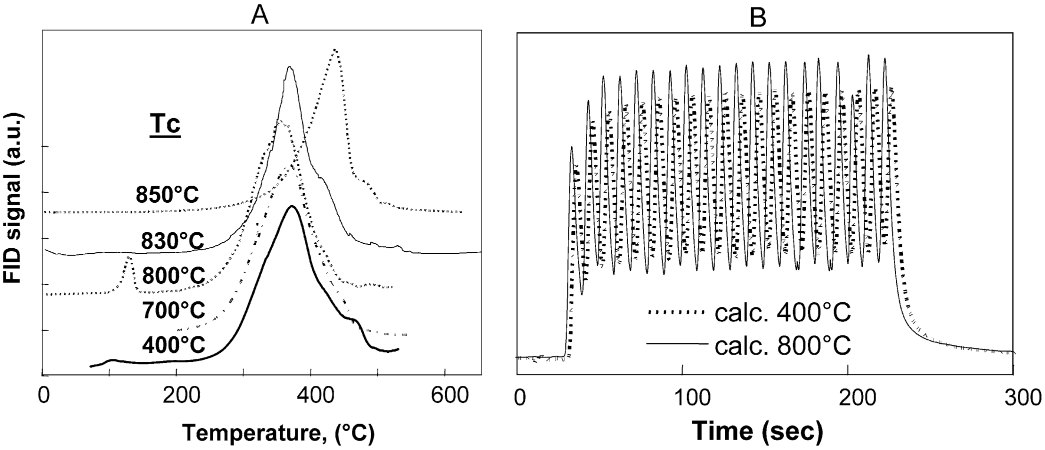

Fig. 3. Influence of calcination temperature (T_c) on Ba(22),K(7)/CeO_2 catalyst stability: (A) TPO profiles, (B) high frequency CO_2 pulses at 400 °C.

KNO_3, which decomposes at approximately 600–700 °C [38]. The diffractogram of the sample calcined at 700 °C (not shown) is not different than that of the catalyst calcined at 400 °C. Nevertheless, XRD analyses show differences between the catalysts calcined at 400 and at 800 °C for 2 h. Although the solid still contains $BaCO_3$ after the treatment at 800 °C, a new crystalline phase is detected after the high-temperature treatment, which corresponds to the $BaCeO_3$ perovskite, as indicated in the diffractograms shown in Fig. 2. The intensity of the $BaCeO_3$ diffraction lines increases when the treatment time at 800 °C increases from 2 h to 30 h. The calcination at 850 °C for 2 h produces the same effect as the longer treatment at 800 °C, with a very similar diffractogram.

Fig. 3A shows the effect of high temperatures on catalyst stability. There is no difference between the TPO profiles of catalysts treated at 400, 700, 800, and 810 °C (not shown). A sample was sequentially treated for 2 h at 800 °C, then for 2 h at 810 °C, 2 h at 830 °C, and 2 h at 850 °C. At each temperature, a sample was taken, and TPO and XRD analyses were carried out. The decrease in activity is observed as a noticeable shift in the TPO profile after the treatment at 850 °C. It must be taken into account that the catalyst treated at 800 °C for 30 h does not show any deactivation, as we shown below (Fig. 5).

Fig. 3B shows the CO_2 pulses carried out on the fresh catalyst and after calcination at 800 °C for 2 h. The amplitude of the oscillation exhibits a small increase after the treatment at high temperature, indicating that the interaction of CO_2 with the catalyst has a minor decrease.

Tables 3 and 4 show XPS results for the Ba(22),K(7)/CeO_2 catalyst. The K/Ce ratio decreases from 2.2 to 0.6 when calcination temperature increases from 400 to 800 °C, whereas the Ba/Ce ratio increases slightly from 0.6 to 0.7. The total potassium content, measured by atomic absorption spectroscopy after sample dissolution, was 7 wt% for the fresh sample and 1.3 wt% after the treatment carried out at 850 °C, as described previously.

The sample treated at high temperature (800 °C) displays a binding energy of 779.6 eV that could be assigned to Ba in a perovskite structure [39,40]. For Y-Ba-Cu-O mixed-oxide systems, Fukuda et al. [40] concluded that the 778.9 eV peak is due to Ba^{2+} in the superconducting-oxide structure by comparing the BE differences between Ba $3d_{5/2}$ and O 1s for various Ba compounds.

Table 1 shows the values of the specific surface for catalysts treated at 700 and 800 °C. It can be observed that the area clearly decreases with increasing treatment temperature.

3.3. Stability of the Ba(22),K(7)/CeO_2 catalyst in the presence of water

Ba(22),K(7)/CeO_2 catalysts calcined at 400 and 800 °C for 2 h were treated at 400 and 800 °C, respectively, with wet air

Table 3
Surface atomic ratio for Ba,K/CeO_2 samples after treatments in air + water and air + SO_2 at 400 °C

Samples	Calcination temperature	Treatment	Ba/Ce	K/Ce	S/Ce	$O/C_{CO_3^=}$[a]	O/Ce
Ba(22),K(7)/CeO_2	400 °C	–	0.6	2.2	–	nm	8.8
	400 °C	8 h air + H_2O	0.58	1.6	–	nm	nm
	400 °C	100 h air + H_2O	0.6	1.9	–	nm	nm
	400 °C	30 h air + SO_2	1(0.06)[b]	2.3(0.13)	3.9(0.22)	nm	9.4(0.53)
	400 °C	90 h air + SO_2	0.8(0.05)	2.2(0.12)	3(0.17)	nd	11.2(0.61)
	800 °C	–	0.7	0.6	–	nm	5.5
	800 °C	30 h air + H_2O[c]	0.8(0.06)	1.3(0.09)	–	4.2	8.9(0.63)
	800 °C	90 h air + H_2O[c]	1.2(0.05)	5(0.18)	–	7.2	18.8(0.66)
K(7)/CeO_2	700 °C	14 h air + SO_2	–	1.6	2.3	nd	9.2
CeO_2	400 °C	8 h air + SO_2	–	–	0.5	nd	4.1

[a] nm: not measured. nd: not detected.
[b] The M/At ratios are shown between parenthesis, where At is equal to the sum of all element measured intensities.
[c] These treatments were performed at 800 °C.

Table 4
Binding energies for Ba,K/CeO_2 samples after treatments in air + water and air + SO_2 at 400 °C

Samples	Calcination temperature	Treatment	Ba $3d_{5/2}$[a]	K $2p_{3/2}$	S 2p	O 1s	
Ba(22),K(7)/CeO_2	400 °C	90 h air + SO_2	780.3	292.1	168.0	531.5	100%
			(2.6)	(2.5)	(2.7)	(2.5)	
	800 °C	–	779.6	292.5	–	530.7	–
			(2.4)	(2.4)		(4.2)	
	800 °C	30 h air + H_2O	779.4	292.4	–	531.8[b]	54%[c]
			(2.3)	(2.2)		529.5	46%
	800 °C	90 h air + H_2O	779.5	292.6	–	532.4	51%
			(2.3)	(2.3)		530.8	49%
K(7)/CeO_2	700 °C	14 h air + SO_2	–	292.4	168.5	531.4	84%
				(2.1)	(2.5)	529.0	16%
CeO_2	400 °C	8 h air + SO_2	–	–	168.1	531.6	46%
					(2.9)	529.0	54%

[a] FWHM are given between parenthesis.
[b] FWHM of O 1s component was 2.4 ± 0.1 eV.
[c] Relative intensities of the O 1s contributions.

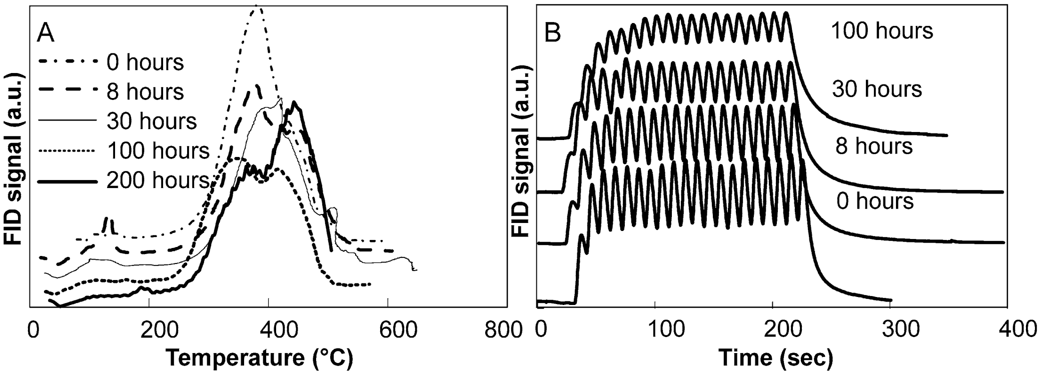

Fig. 4. Influence of water on Ba(22),K(7)/CeO_2 catalyst stability: (A) TPO profiles; (B) high frequency CO_2 pulses at 400 °C. Solid calcined at 400 °C and then treated at 400 °C with air saturated with water at room temperature for different periods of time.

during different times. The air was saturated with water at room temperature, as described in Section 2.4.

Fig. 4A shows the TPO profiles obtained with the catalyst calcined at 400 °C, treated during 8, 30, 100, and 200 h with wet air at 400 °C. It can be observed that the activity at low temperatures is essentially the same (see the low-temperature side of the TPO profiles). The high-temperature side shifts toward higher temperatures as time in wet air increases, although there is no systematic change. Fig. 4B shows the CO_2 pulses experiments carried out on the samples treated with wet air. The amplitude of oscillation decreases as the time of treatment with wet air increases, indicating that water produces higher interactions with CO_2.

Fig. 5 shows results obtained with the Ba(22),K(7)/CeO_2 catalyst treated both with wet air and with dry air at 800 °C for 30 h. A shift of the TPO maximum toward higher temperatures indicates that the catalyst deactivates during treatment with wet air at high temperatures. It is very interesting to note that even

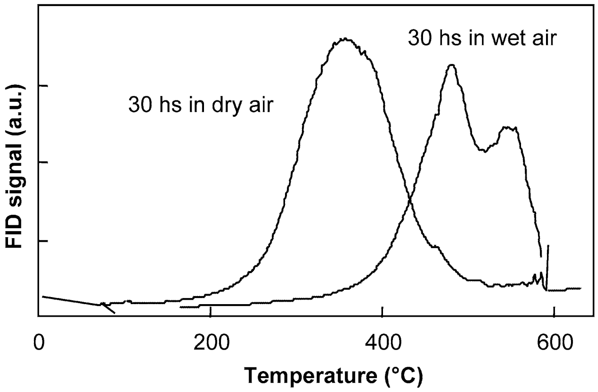

Fig. 5. Effect of temperature and water on the activity of the Ba(22),K(7)/CeO_2 catalyst: TPO profiles of soot–catalyst treated at 800 °C during 30 h with either dry air or wet air.

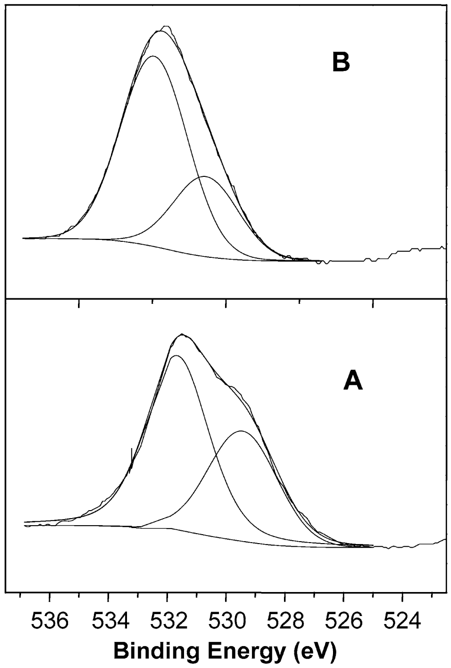

Fig. 6. XPS spectra of the O 1s region of Ba(22),K(7)/CeO_2 sample calcined at 800 °C after wet air treatments at 800 °C: (A) during 30 h, (B) during 90 h.

after 30 h at 800 °C, in dry air the catalyst is stable (compare with the TPO profiles shown in Fig. 1C). The CO_2 pulses (not shown) show decreased interaction between the CO_2 and the catalyst due to the high-temperature treatment in both dry air and wet air.

Table 3 gives the XPS results for these experiments. The K/Ce ratio increases from 0.6 up to 5 when the fresh catalyst calcined at 800 °C is treated with wet air at 800 °C for 90 h. On the other hand, the ratio O/Ce increases from 5.5 up to 18.8, and Ba/Ce also increases from 0.7 to 1.2.

Fig. 6 shows the XPS spectra in the O 1s region after the wet treatments. The O 1s recorded from the Ba(22),K(7)/CeO_2 solid calcined at 800 °C after wet treatment at 800 °C for 30 h exhibited two contributions, at 529.5 eV and 531.8 eV, whereas after 90 h, these two contributions correspond to 530.8 and 532.4 eV, respectively. A low Ba BE similar to that assigned to Ba in a perovskite structure was measured after the wet treatment (Table 4).

The aging treatment in liquid water at room temperature led to a loss of potassium from the catalyst. Using a mass of water equal to 15 times the mass of catalyst flowing through the catalyst, a K loss equivalent to 7% of the initial content was observed. This means that after this treatment, the K loading on the catalyst dropped from the initial 7 to 6.5 wt%.

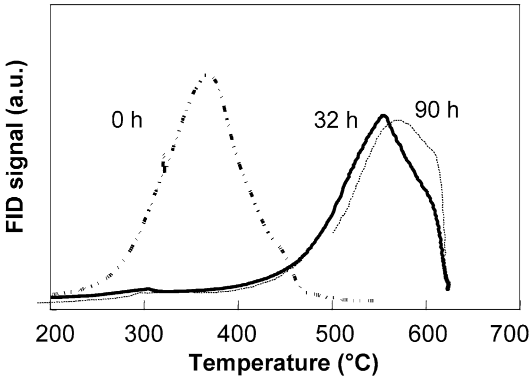

Fig. 7. Influence of the treatment time with SO_2 on the catalyst activity. Catalyst: Ba(22),K(7)/CeO_2 calcined at 400 °C, flowing gas: 1000 ppm SO_2 in air, temperature: 400 °C.

Table 5
Temperature of the TPO maximum obtained with fresh and SO_2-treated catalysts

Catalyst	Temperature of TPO maximum	
	Fresh	SO_2-treated
CeO_2	523	558 (31 h)
Ba(22)/CeO_2	460	524 (30 h)
K(7)/CeO_2	369	586 (8 h)

3.4. Effect of SO_2 (1000 ppm) on activity and solid properties

Samples of the Ba(22),K(7)/CeO_2 catalyst calcined at 400 °C were treated in an air stream containing 1000 ppm of SO_2 at 400 °C for different times. Afterward, the catalyst was mixed with soot and the activity was measured by TPO. Fig. 7 shows the TPO profiles for the soot mixed with the Ba(22),K(7)/CeO_2 catalyst both fresh and treated in air + SO_2. This treatment produced an important loss of activity. After 30 h in the presence of SO_2, the maximum in the TPO profile shifts by approximately 200 °C. Each individual supported component of the catalyst and the ceria support were also treated with the air + SO_2 mixture. Results are shown in Table 5. Both Ba(22)/CeO_2 and CeO_2 displayed a significant decrease in activity after the treatment. The K(7)/CeO_2 catalyst displayed a similar shift toward the high-temperature side as that shown in Fig. 7 for Ba(22),K(7)/CeO_2.

The XRD pattern of the Ba,K/CeO_2 catalyst (Fig. 2) treated in SO_2-containing air shows the CeO_2 and $BaCO_3$ phases. Nevertheless, the presence of $BaSO_4$ at trace levels could be observed (Fig. 2; Table 2).

Table 3 shows the XPS analyses of samples treated in SO_2. There are no important modifications in the K/Ce surface ratio, whereas the Ba/Ce ratio increases from 0.6 to 0.8–1. Sulfur is detected on the surface of the Ba(22),K(7)/CeO_2 catalyst with a S/Ce ratio of around 3. The S 2p BE (∼168 eV) corresponds to sulfates [41] (Table 4). This signal is detected on CeO_2, K(7)/CeO_2, and Ba(22),K(7)/CeO_2 treated in SO_2. For the barium-containing catalyst, a signal coincident with the barium sulfate is observed at 780.3 eV [41].

Fig. 8 shows the K 2p–C 1s region spectra for the Ba(22), K(7)/CeO_2 catalyst after treatment with SO_2 and with water. BEs for K 2p for the supported catalysts are summarized in Table 4. The BE of the K 2p peak was 292.4 ± 0.2 eV, which relates to K^+. The C 1s spectra (Fig. 8) indicate two kinds of carbon species. The lower energy peak is taken as adventitious carbon and assigned the value of 284.6 eV as reference. Besides, the C 1s peak at 288 eV can be assigned to carbonate species [41]. The samples treated with wet air (Figs. 8A and 8B) display the signal that corresponds to carbonates. It can be observed that after the SO_2 treatment, the C 1s carbonate peak vanishes.

XPS spectra in the O 1s region after the SO_2 treatment were fitted to analyze the proportions of different oxygen species, assigning a BE of 529.0 eV to the oxide lattice oxygen and a BE of 531.6 eV to the oxygen of the sulfate species [41,42].

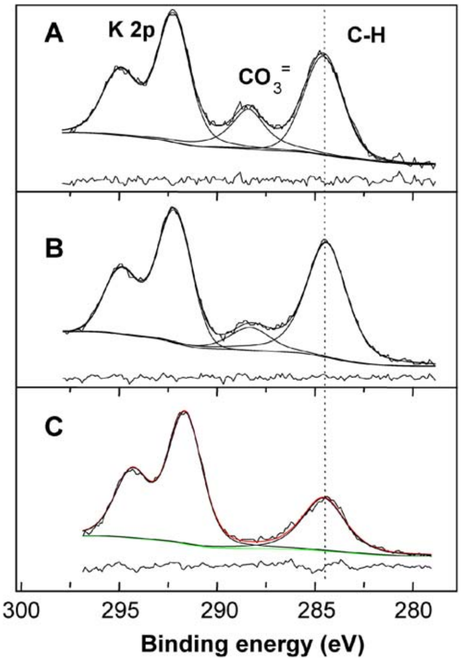

Fig. 8. Variation in the C 1s–K 2p XPS region of Ba(22),K(7)/CeO_2 catalysts: (A) calcined at 800 °C and treated in wet air during 30 h at 800 °C, (B) calcined at 800 °C and treated in wet air during 90 h at 800 °C, (C) calcined at 400 °C and treated in air + SO_2 during 90 h.

The results of the spectrum adjustment are displayed in Table 4. For the CeO_2 support (8 h in SO_2), both peaks are in similar proportions, whereas in the K(7)/CeO_2 solid (14 h in SO_2), the intensity of the higher BE peak is 84% of the total signal. In the case of the Ba-containing catalyst, after 90 h in an SO_2 flow, the only peak observed corresponded to surface sulfate, with no signals detected coming from the oxides.

Table 6 shows the IR vibrational frequencies for compounds that could be present in these samples: CeO_2, K(y)/CeO_2, Ba(x)/CeO_2 and Ba(x),K(y)/CeO_2. Fig. 9B shows the FTIR spectra of CeO_2 and K(7)/CeO_2 either fresh or treated with SO_2. The K_2SO_4 and $Ce(SO_4)_2$ spectra are also included for comparison. The fresh K(7)/CeO_2 solid shows the characteristic bands (at 1384 and 826 cm^{-1}) of KNO_3 (Table 6). The sulfated catalyst displays the peaks that correspond to the K_2SO_4 at 1120, 980, and 620 cm^{-1}. (This last signal does not appear in Fig. 9B, due to the range shown.) A broad band in the 1000–1200 cm^{-1} region may correspond to bulk cerium sulfate formation, as suggested by the spectra shown in Fig. 9B for this compound. KNO_3 is still present on the K(7)/CeO_2 solid treated with SO_2; therefore, during the treatment with SO_2, both K and Ce would react, leading to the corresponding sulfates. The pure CeO_2 sample treated with SO_2 displays bands in the same regions as the $Ce(SO_4)_2$ (main broad band in the 1000–1200 cm^{-1} region). Waqif et al. [27] also found the formation of surface and bulk cerium sulfate when CeO_2 was treated in the presence of SO_2 and excess O_2 at 400 °C. Fig. 9A shows IR spectra for barium-containing catalysts. It is evident that the catalysts treated with SO_2 form $BaSO_4$. The bands at 1437, 1059, 858, and 694 cm^{-1} corresponding to $BaCO_3$ also appear in the spectra of the fresh and sulfated catalysts (Fig. 9A).

In the case of the SO_2-treated Ba(22),K(7)/CeO_2 solid (Fig. 9A), the signals at 620, 980, and 1120 cm^{-1} indicate the presence of K_2SO_4. Note also that the 900–1200 cm^{-1} region, typical of the $\nu_{S\text{–}O}$ [43], is wider than the spectra of either $BaSO_4$ or SO_2-treated Ba(22)/CeO_2. According to Lercher and coworkers [44], the signals at 1060 and 1120 cm^{-1} could be assigned to surface sulfate species. Along the same lines, the bands appearing in the 1420–1350 cm^{-1} region could be assigned to surface S=O vibration in covalent sulfates, as reported by Kustov et al. [43].

The results shown in Fig. 9 clearly indicate that in Ba(22), K(7)/CeO_2, sulfates of barium, potassium, and cerium are formed on exposure to SO_2 at 400 °C. These results correlate with the surface studies previously shown. The specific surface area of the catalyst treated for 90 h with SO_2 is practically the same as that of the fresh catalyst.

Table 6
Characteristic IR vibrational frequencies

Species	IR vibrational frequencies (cm^{-1})
$BaCO_3$	1437 (s), 1059 (w), 858 (m), 694 (m)
$BaSO_4$	1470 (m), 1190 (s), 1130 (s), 1080 (s), 980 (w), 860 (w), 640 (m), 610 (s)
KNO_3	1433 (sh), 1384 (s), 1354 (sh), 1273 (sh), 826 (m)
K_2SO_4	1120 (s), 980 (w), 620 (s)

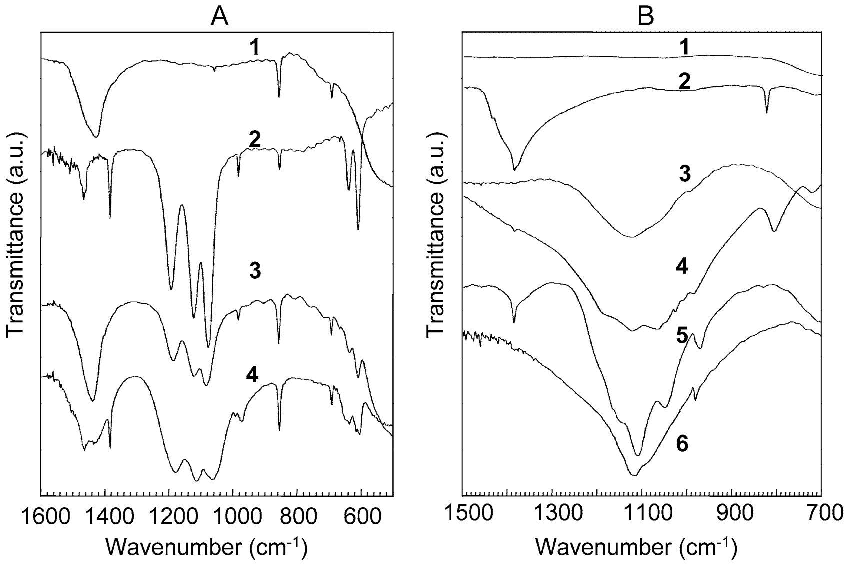

Fig. 9. FTIR spectra of (A) (1) Ba(22)/CeO_2; (2) $BaSO_4$; (3) Ba(22)/CeO_2, SO_2 treated; (4) K(7)/Ba(22)/CeO_2 SO_2 treated and (B) (1) CeO_2; (2) K(7)/CeO_2; (3) CeO_2, SO_2 treated; (4) $Ce(SO_4)_2$; (5) K(7)/CeO_2, SO_2 treated; (6) K_2SO_4.

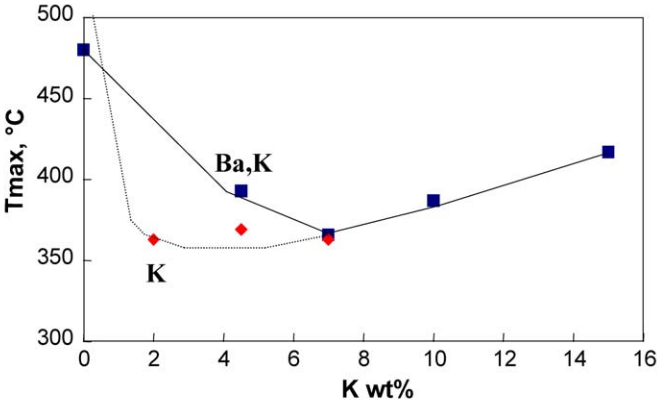

Fig. 10. Temperature of the maximum of the TPO profile (T_{max}) as a function of K content (wt%).

4. Discussion

4.1. Effect of composition on catalytic activity

The results shown in Fig. 1A indicate that barium has little influence on the direct combustion of soot. Although Ba was not so effective in increasing catalytic activity, it is an important element in the NO_x storage capacity of the catalysts. This has been extensively studied in three-way catalysts [45] and, with less emphasis, in diesel exhaust gas treatment [33].

On the other hand, K has a significant effect on catalytic activity, as indicated by the TPO profiles shown in Fig. 1B. This component is key to obtaining good activity. However, there is no linear relationship between its composition and activity. Fig. 10 shows that activity has a smooth maximum as a function of K wt% of around 7 wt% in the case of Ba(22),K(y)/CeO_2, and of 2–7 wt% in the case of K(y)/CeO_2. These results are in complete agreement with the synergistic effect between ceria and potassium in this catalytic system that we proposed earlier. If the K content is too high, then ceria is fully covered, and its well-known redox capacity is no longer available. This is observed when the K content is increased to above 7 wt%. Similar results were previously found on K/La_2O_3 catalysts [30]. Following this same trend, Shangguan et al. [46] found that the doping of potassium effectively promoted the catalytic performance of $CuFe_2O_4$ for the simultaneous removal of NO_x and diesel soot particulate. They also found an optimum composition of potassium above which the activity decreased. In addition, An et al. [47] studied different alkali-metal doped systems and found that K was the best promoter of soot oxidation, and that K-rich samples had the lowest soot oxidation temperatures.

The very good activity of our K/CeO_2 catalytic system is due to the synergistic effect between K and CeO_2. It is well known that CeO_2 has a redox capacity, providing active oxygen to oxidize the soot. We have proposed that K may act to form a carbonate-type intermediate with the partially oxidized soot, which then decomposes and releases the CO_2. The high mobility of the K compounds due to the relatively low boiling point improves the effective contact between active phases and soot. This fact is also related to the volatility of K hydroxides and oxides, which contributes to the improved effectiveness of the catalyst in this reaction, mainly at high temperatures. This possible mechanism was previously proposed by our group [29,31,32,35,38]. The correlation between the CO_2–catalyst interaction and the activity supports the idea of a carbonate-type intermediate. Therefore, if the CeO_2 redox capacity and/or the K carbonate formation capacity are lost, then a decrease in activity can be expected due to the corresponding decrease in the synergistic effect.

Both composition and precursors may have an effect on activity. In the present study, catalysts were prepared from a solution containing nitrates. We have previously reported studies carried out on K/CeO_2, and K/La_2O_3 catalysts prepared using KOH as a precursor without the addition of any nitrate [30–32,38]. Both catalysts have activity very similar to that reported in the present study obtained with Ba,K/CeO_2 catalysts prepared from KNO_3 [32]. These results demonstrate that even though NO catalyzes soot oxidation via NO_2 formation, the catalytic effect of K in the catalyst formulated in this work does not depend noticeably on the anion combined with K, mainly taking into account that NO is not fed to the system. Therefore, the reaction occurs using oxygen from the gas phase and is not due primarily to nitrate decomposition. It is difficult to directly compare the activity of catalysts from different laboratories for soot burning, because of the varying intensities of the mixing procedures that the groups use. We have found that changing the mixing time, leading to different levels of contact between the soot and the catalyst, can shift the maximum in the TPO profiles by several degrees. For example, changing the mixing time from 2 to 15 min produces a decrease in TPO maximum temperature of as much as 150 °C. The different activities for loose contact and tight contact for several catalysts were shown by Neeft et al. [48]. Nevertheless, it is useful to compare the catalysts studied in different laboratories, keeping in mind that the differences are due not necessarily to differences in intrinsic activity, but to differences in the level of contact. Some examples of the most active catalysts found in the literature are catalysts based on Cu-K-V, which displayed peaks at 380 °C [49]; Cu,K,Mo,(Cl)/ZrO_2, which displayed a peak at 330 °C or above in a tight contact mode [50]; K/La_2O_3, which burnt the soot with a maximum at ca. 350 °C [30,32,33]; and Cs_3VO_4 [51], which showed a maximum in the TPO profile at 279 °C. In the latter case, the hydrophilic nature of CsO_2 limited the application to stationary sources with exhaust gases at high temperatures [51].

The loose-contact experiments indicate a difference of 100 °C in the maxima in the TPO profiles of these experiments and those of the tight-contact mode. Neeft et al. [48] reported differences of 30–150 °C when this type of comparison was carried out with a large variety of catalysts. Our catalyst displays an intermediate behavior, meaning that the ability of the active phases to reach the soot particles is good. Because high activity in a loose-contact mode is related to high volatility and/or mobility, such as has been observed in a molten-salt systems, the loss of active phase due to these mechanisms (i.e., volatilization and/or dripping) must be considered when designing catalyst formulations.

4.2. *Thermal stability*

There is no difference between the TPO profiles of the Ba(22),K(7)/CeO_2 catalyst treated at 400, 700, 800, and 830 °C, which indicates that the catalyst has a very good thermal stability in this temperature range. However, when the catalyst is calcined above 830 °C, the activity decreases, as indicated by a shift of the main peak toward higher temperatures in the TPO profiles.

Both K and CeO_2 are needed to obtain good activity, because a synergetic effect is obtained as reported previously [31,32]. This means that the optimum activity is obtained for a given K/Ce ratio, and large modifications of this in any directions lead to a drop in activity. The decrease in the K/Ce ratio on treatment at 800 °C indicates a K loss on the surface. However, this final ratio of 0.6 is still sufficient to maintain good activity. Considering results obtained with K(y)/CeO_2, which have practically the same activity between 2 and 7 wt%, and results obtained with Ba(22),K(y)/CeO_2, which have almost the same activity for 4.5 and 7 wt%, it can be concluded that a decrease of K/Ce ratio to $1/3$ of its initial 7 wt% should not have a significant effect on activity. This is what we found on the catalyst calcined at 800 °C, on which the K/Ce surface ratio decreased from 2 to 0.6. At higher temperatures or longer treatment times, the K content will keep decreasing to a level below the minimum required to maintain the activity. The total K content after the treatment at 850 °C was 1.3 wt%, and because of this low value, a decrease in activity was found. These results clearly indicate that at these high temperatures, an irreversible K loss occurs by volatilization. However, it must be emphasized that in this case the catalyst was sequentially treated for 2 h at 800 °C and then for 2 h at 810 °C, 2 h at 830 °C, and finally 2 h at 850 °C.

Recently, Eberhardt et al. [52] reported that the reaction between CeO_2 and $BaCO_3$ to form $BaCeO_3$ mixed oxide occurs above 780 °C. This phenomenon is another cause of catalyst deactivation, because K alone has low activity for soot combustion, CeO_2 with its redox capacity being necessary to supply oxygen in the reaction mechanism [32]. Because the perovskite is less effective than the CeO_2 for oxygen transfer or not effective at all, the activity decreases. These are the causes of the lower activity of the catalyst treated at 850 °C. Perovskites studied by Fino et al. [4,8] displayed the maximum in the TPO profile above 450 °C in a tight contact mode or in some cases at 400 °C, as in the case of $LaCrO_3$ [53].

The CO_2 pulses results (Fig. 3B) also indicate a lower concentration of K on the catalytic surface after calcination at 800 °C, in complete agreement with the XPS results. K is needed to promote interaction between CO_2 and the Ba(x),K(y)/CeO_2 catalyst. Neither Ba nor CeO_2 interacts with the CO_2 [31]. In the case of barium, after calcination at 400 °C, it is already saturated in CO_2 (barium is present in this solid as $BaCO_3$, as observed by XRD and FTIR, and could also be present as $BaCO_3$ on the surface). In the case of CeO_2, no distortion of the CO_2 pulse signal was found at this temperature. This indicates either that the kinetics of formation of cerium carbonate is sufficiently low and cannot be observed at 500 °C or below, or that cerium carbonate is thermodynamically very unstable and is not formed at all. Hilaire et al. [54] found that this carbonate is unstable in an oxidizing atmosphere. Therefore, the higher the K concentration, the higher the interaction with the CO_2 and the smaller the amplitude of oscillation in the CO_2 pulse experiment. One possible reaction mechanism for soot oxidation involves the formation of a carbonate-type intermediate [32], as mentioned earlier. Then, if the proposed mechanism is correct, the lower activity of the catalyst calcined above 830 °C is due in part to a decrease in the catalyst's ability to form such a carbonate intermediate, as a consequence of a K content below the minimum needed to obtain the optimum activity.

The shift in Ba BE toward lower values indicates that after calcining at 800 °C, part of the barium carbonate decomposes to form the Ba perovskite. Also note the lower intensity of the $BaCO_3$ peaks in the XRD spectra compared with the Ba(22),K(7)/CeO_2 solid calcined at 800 °C for 2 or more hours and at 400 °C. The same Ba BE was also observed when the catalyst calcined at 800 °C was treated with wet air at 800 °C.

We have previously reported [55] a similar behavior in the Co,K/La_2O_3 catalysts calcined at 700 °C. An increase in the concentration of the out-layer perovskite species was observed when the potassium content increased, following the same tendency observed in the bulk. Those $LaCoO_3$ species would limit the interaction of lanthanum with CO_2. This result allowed us to correlate the presence of surface perovskites with the lower activity of these catalysts. For the Ba(22),K(7)/CeO_2 catalyst, the loss of cerium due to the formation of the $BaCeO_3$ perovskite contributes to the deactivation of the catalyst.

The specific surface area decreases as treatment temperature increases from 400 to 700 and finally to 800 °C, indicating that a sinterization process is occurring. No agglomeration of Ba can be expected because the XPS results show a constant Ba/Ce ratio. In the case of K, a decrease in the K/Ce ratio was found, but as discussed in this section, this is due mainly to K volatilization. However, even though the specific surface decreases, the activity of these three samples is the same, also in agreement with the concept of the low dependency of activity for soot oxidation on specific surface area.

4.3. Stability in wet atmosphere

The results shown in Fig. 4A indicate that exposure of the catalyst to wet air at low temperature (400 °C) has a minor catalytic effect. Comparing the TPO profile obtained with the catalyst treated for 200 h in wet atmosphere with that obtained with the fresh catalyst shows a relative increase in the second peak as the only difference, which in the fresh catalyst appears as a shoulder. The low-temperature maximum in the profile is around 360 °C in both cases.

The CO_2 pulses results (Fig. 4B) indicate a small increase in its interaction with the catalyst with increasing duration of treatment. During the treatment with water, CO_2 and H_2O compete for the basic sites of Ba, changing the initial state of Ba from carbonate to barium hydroxide. Therefore, as the treatment in water proceeds, the transformation $BaCO_3 \rightarrow Ba(OH)_2$ occurs, with the $Ba(OH)_2$ thus formed able to interact with CO_2. Because the XRD diffractogram displays only the presence of barium carbonate (not shown), the transformation to $Ba(OH)_2$ could occur only on the surface of the $BaCO_3$ particles. A similar contribution to the increase in CO_2 interaction could be the transformation of KNO_3 to KOH. However, because the activity is almost indifferent to the K precursor, this increase in the interaction with CO_2 does not lead to an increase in activity.

After the high-temperature treatment in air (800 °C), there is a decrease in the amount of $BaCO_3$ and KNO_3 and a decrease in the interaction with CO_2. In contrast, the treatment in dry air at 800 °C leads to a K loss, as indicated by a decrease in the K/Ce surface ratio from 2.2 to 0.6. Because the composition of K is still sufficient to be in the quasi-plateau of the curve activity composition, practically no deactivation is observed after the treatment in dry air. The treatment in wet air at 800 °C leads to a dramatic decrease in activity. The catalytic surface undergoes a profound reorganization, as indicated by the significant changes in the O/Ce, Ba/Ce, and K/Ce ratios. These modifications lead to a modification in the K/CeO_2 ratio, resulting in a loss of synergistic effect and thus of activity.

In the presence of wet air, the drastic increase in the surface K/Ce ratio is a very interesting effect. One of the main contributions in the O 1s XPS spectrum, obtained with the catalyst treated at 800 °C with wet air for 32 h at 529.5 eV, is characteristic of metal–oxygen bonds and could correspond to Ce–O [56] and Ba–O [57]. The second one, at 531.8 eV, is typical of oxygen in a $CO_3^{=}$ group and strongly supports the presence of barium carbonate on the surface [41,58]. In the case of the catalyst exposed to wet conditions for 90 h, a high BE peak at 532.4 eV appears that could be assigned to surface hydroxyl group. Moreover, the peak at 529.5 eV almost vanishes, suggesting hydroxylation of the catalyst surface. The calculated $O/CCO_3^{=}$ ratio shown in Table 3 is equal to 4.2 and 7.2 for samples treated in wet air for 30 and 90 h, respectively, which is higher than the value expected from carbonates stoichiometric composition ($O/CCO_3^{=} = 3$). These higher values found for the wet samples should be attributed to the presence of other oxygen species together with carbonates, such as partial hydroxylation of the samples.

These results support the explanation given above. When the hydroxylation of the catalyst increases, as indicated by the O/Ce ratio, the interaction with CO_2 increases a little. The effect of hydroxylation could be more important when the treatment is carried out at high temperature due to a faster rate of interaction between water and CeO_2, as revealed by the high increase in O/Ce ratio (compare the O/Ce ratios for the different treatments at 800 °C in wet air).

Another major effect of the treatment at 800 °C in a wet atmosphere is the increase in K surface concentration (see the K/At and K/Ce ratios in Table 3). The K migrates to the surface; the effect of this is a dramatic increase in the observed K/Ce ratio, while the Ce/At ratio decreases from 0.07 to 0.029 with increasing time treatment, which could be due mainly to the fact that ceria is buried in a layer of other compounds. The main consequence of these changes is that both catalytic functions, K and CeO_2, become unbalanced and a decrease in activity is found, as shown in Fig. 5. The increased Ba/Ce ratio from 0.6 to 1.2 could indicate that after the long treatment (90 h) at 800 °C, the BaO spreads out on the ceria surface, covering the catalytic functions needed for soot oxidation. Further investigation is needed to confirm this hypothesis.

The aging treatment in liquid water indicates that 7% of the K is lost on contacting the catalyst with a large flowing volume of water. The result is promissory, because under real conditions, water will condense on the catalyst, leading to some extent to the K loss, but it will not be equivalent to a large volume of water flowing through the catalyst, leaching the active phase. This particular issue requires further investigation, because the precursor, calcination temperature, and other promoters might help lower the solubility of the K active phase.

4.4. Stability in SO_2

The temperature needed to burn soot after SO_2 treatment of the Ba(x),K(y)/CeO_2 catalyst is similar to that needed for the uncatalyzed reaction, which means that the catalyst is almost completely deactivated. For this reason, no difference is observed between the TPO profile obtained with the catalyst treated for 30 h and the catalyst treated for 90 h in air + SO_2.

Both Ba(22)/CeO_2 and CeO_2 without the promoting effect of K are not very active catalysts for soot combustion; therefore, the sulfation of the surface leads to a smaller drop in activity as compared with the Ba(22),K(7)/CeO_2 catalyst, as shown in Fig. 7 and Table 5.

The increased O/Ce surface ratios during sulfation shown in Table 3 agree with the sulfate formation on the catalyst surface. XPS data analysis of O 1s BE indicates that sulfate formation occurs, in agreement with the C 1s spectrum, where the peak assigned to $CO_3^=$ is not observed. The different oxygen proportions (lattice oxygen and oxygen in sulfates) reported in Table 4 could be related to the different times of the SO_2 treatments. These results show that all of the components of the catalyst (i.e., potassium, barium, and cerium) form surface sulfates at 400 °C. This indicates that the surface sulfates were formed from carbonates at this temperature at an appreciable rate. As an example, the SO_2 could react through the following reaction: $BaCO_3 + SO_2 + 0.5O_2 \leftrightarrow CO_2 + BaSO_4$, in the case of the Ba-containing solid. This reaction also indicates that the effect of SO_2 would be different were CO_2 present in the gas phase, most likely increasing the resistance to sulfate formation due to a competition between both components. XRD results indicate that the sulfates are highly dispersed.

Therefore, sulfate formation is a process that at this time scale (up to 100 h) occurs only on the surface of the support. In the case of barium, it seems that the sulfate spreads out easily on the catalyst surface, because barium carbonate is present as large particles on the fresh catalyst, whereas after sulfidation, a very weak signal is observed by XRD and no carbonate peak is detected by XPS, which could be explained by a spreading of the barium sulfate. The sulfate formation takes both active functions out of the catalytic cycle. Cerium sulfate is not a good redox component, and potassium sulfate has a much lower capacity to interact with the CO_2, as shown by the high-frequency pulse experiments, and thus the carbonate-type intermediate path is canceled out. The result of these changes is a dramatic decrease in activity.

After the treatment with SO_2, the specific surface area is the same as or somewhat larger than the fresh catalyst. However, the catalyst is almost completely deactivated. This result also agrees with those shown above, for which no correlation between activity and surface area is observed in the soot oxidation reaction.

5. Conclusion

It has been shown that the Ba(22),K(7)/CeO_2 catalyst has good activity for soot combustion. In a dynamic analysis such as TPO, the catalyst displays the beginning of the reaction at 280 °C. At 344 °C, the rate of soot combustion is 0.19 g C/g cat h for a catalyst containing 5 wt% soot. This is a very interesting result, because this temperature is similar to or lower than that of the exhaust gases for heavy-load engines and not very far from that of light-duty engines. The effect of K content on CeO_2 and Ba(22)/CeO_2 clearly indicates the synergistic effect between K and CeO_2. An interesting finding in this study is that the activity has a smooth maximum as a function of the K content being around 7 wt%. The activity decreases at K concentrations above 10 wt%, as well as at very low K content (<2 wt%).

The thermal stability of this catalyst is very good. It can tolerate high temperature excursions up to 830 °C without activity changes, even though there are surface modifications as shown by XPS, CO_2 pulses, and XRD analyses. However, a loss of activity occurs when the catalyst is treated at 850 °C, due to the formation of a perovskite phase as $BaCeO_3$ and also due to a decrease in the surface K content below the minimum needed to maintain good activity, as found by XPS. At this temperature, the decomposition of KNO_3 occurs. Longer treatments at 800 °C (e.g., for 30 h) also lead to perovskite phase formation at a level where deactivation occurs.

The presence of steam at 400 °C does not affect the catalytic performance of Ba(22),K(7)/CeO_2, as indicated by TPO, XPS spectra, and XRD diffractograms, which are very similar to those of the fresh catalysts. However, when wet treatment is carried out at 800 °C, a drastic decrease in activity is found. This is mainly due to the fact that the treatment at high temperature in wet air leads to decreased availability of CeO_2 and loss of K, with a significant increase in the K/Ce surface ratio. This means that the catalytic functions become unbalanced, with a resulting activity loss. An interesting effect of the presence of water at high temperature is a significant increase in the surface ratios of Ba/Ce, O/Ce, and K/Ce, due to the rapid hydroxylation of the surface, which also modifies the interaction of the catalyst with the CO_2, and also probably to a spread of BaO. This point will be addressed in a future study, because it may have important consequences in the formulation and preparation of this catalyst.

The high-frequency CO_2 pulse technique is very sensitive in detecting minor changes in the catalyst surface, and the dynamics of the interaction between the CO_2 and the catalyst and its modification on different treatments support our previously proposed mechanism of soot combustion involving a carbonate-type intermediate formation. The catalyst is not stable under an atmosphere containing SO_2. There is a major loss of activity for soot combustion when the catalyst is treated in air + 1000 ppm SO_2 for 30 h. All of the species form sulfates: barium, cerium, and potassium. Barium carbonate is partially decomposed, forming barium sulfate.

The impact of all these changes on NO trapping/reducing capacity is currently being addressed in our group. The combined effect of SO_2, CO_2, and water will also be analyzed to determine whether the competition between these compounds to react with cerium, potassium, and barium modifies the final sulfur tolerance of the catalyst.

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