Soot oxidation on a catalytic NO_x trap: Beneficial effect of the Ba–K interaction on the sulfated $Ba,K/CeO_2$ catalyst

V.G. Milt, M.A. Peralta, M.A. Ulla, E.E. Miró *

Instituto de Investigaciones en Catálisis y Petroquímica-INCAPE (FIQ, UNL-CONICET) Santiago del Estero 2829, 3000 Santa Fe, Argentina

Abstract

The $Ba,K/CeO_2$ catalyst is active both for NO_x trapping and soot combustion. In this work we report a Ba–K interaction that prevents K sulfation when NO_x is present, thus preserving the activity of K towards soot combustion during the working period of the trap. This effect is originated in the $K_2SO_4(s) + Ba(NO_3)_2(s) \rightarrow 2KNO_3(s) + BaSO_4(s)$ reaction, which is thermodynamically favored. In the absence of NO_x, the soot combustion reaction is strongly depressed by SO_2 whereas when NO_x is present both the sulfated and the non-sulfated catalysts present similar TPO patterns.
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1. Introduction

The combination of filters and oxidation catalysts appears to be the most effective after-treatment technique to eliminate soot particles [1] whereas NO_x adsorbers (traps) constitute a relatively new technology which is being developed for partial lean-burn gasoline engines and for diesel ones [2]. A handful of papers have been published in recent years on the soot combustion activity of catalytic traps to eliminate soot particles and NO_x in a single catalyst [3,4]. In this vein, we have reported that $Ba,K/CeO_2$ is an effective system which has barium for the trap function and potassium as the active site for soot combustion [5]. The effect of SO_2 on K-containing catalysts has also been recently reported. Tikhomirov et al. [6] found that the susceptibility of the $KNO_3–MnO_x–CeO_2$ catalyst to sulfur poisoning considerably decreases since potassium nitrate is more easily sulfated than cerium or manganese.

In a recent paper, we have reported that the presence of SO_2 (1000 ppm) at 400 °C leads to a dramatic deactivation of the soot combustion due to the formation of K_2SO_4 [7]. It is also well known that, under these conditions, the NO_x trap function deactivates due to the formation of $BaSO_4$, so that the trap should be periodically regenerated [7]. In the present work, we report an interesting effect by which the role of potassium towards soot combustion is preserved when NO_x is present and during the working period of the catalytic trap.

2. Experimental

2.1. Soot and catalysts preparation

The soot was obtained by burning commercial diesel fuel as described in [8]. The catalysts were prepared from a CeO_2 suspension to which a solution containing KNO_3 and/or barium acetate was added so as to obtain a load of 7 wt% of K and/or 22 wt% of Ba. The mixture was evaporated until achieving a paste, which was dried in a stove for 24 h at 120 °C and calcined at 400 °C. In order to study the effect of SO_2, the catalysts were pre-treated at 400 °C during 90 h in air containing 1000 ppm of SO_2. The sulfur loading of the sulfated $Ba,K/CeO_2$ catalyst was 2 wt% and

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* Corresponding author. Tel.: +54 342 4536861; fax: +54 342 4536861.
  E-mail address: emiro@fiqus.unl.edu.ar (E.E. Miró).

this value remained the same after the sample was treated in a NO + O$_2$ experiment, the percentage of sulfation being 40% referred to the saturation of Ba and K.

2.2. NO$_x$ adsorption

Experiments were performed in a Cahn 2000 microbalance. The sample was dried for 2 h at 400 °C in He and after this, a mixture of NO (4%) + O$_2$ (18%) (He balance) was fed. Then, it was heated up to 490 °C at 5 °C/min and maintained at this temperature for 10 min; then, it was cooled down to 70 °C. The feed was changed to He and then the procedure was repeated. During the treatments the changes in weight were recorded. The catalysts pre-treated in this way will be denoted as nitrated solids. For comparison, the NO + O$_2$ experiment was also done over a mechanical mixture of sulfated K/CeO$_2$ and sulfated Ba/CeO$_2$, prepared using equal proportions in weight.

2.3. Soot combustion in a NO + O$_2$ mixture

Experiments were carried out with fresh and sulfated solids mixed with soot (soot/catalyst ratio 1/20). The mixture was treated in the microbalance, feeding NO (4%) + O$_2$ (18%) (He balance) and heating from 70 °C to 490 °C at 5 °C · min^{-1}.

2.4. Catalysts characterization

X-ray diffractograms (XRD) were obtained with a Shimadzu XD-D1 instrument with monochromator using Cu Kα radiation at a scan rate of 1°/min. Infrared spectra (FTIR) were obtained with a Shimadzu 8101 M spectrometer. Samples were prepared in the form of pressed wafers (ca. 1% sample in KBr). All spectra involved the accumulation of 80 scans at 4 cm^{-1} resolution.

3. Results

3.1. NO$_x$ adsorption and soot combustion

Fig. 1 shows the microbalance experiments performed with the Ba/CeO$_2$ and the Ba,K/CeO$_2$ solids before and after the treatment with SO$_2$. The microbalance results obtained on the mechanical mixture of sulfated K/CeO$_2$ and sulfated Ba/CeO$_2$ are also included in this Figure, in addition to the sulfated K/CeO$_2$ solid. The left part of the graph corresponds to the heating with NO + O$_2$ and the right one to the heating under He. The discontinuity observed in the curves is due to the isotherm at 490 °C, followed by the cooling in the NO + O$_2$ flow.

At 70 °C both Ba/CeO$_2$ and Ba,K/CeO$_2$ adsorb NO + O$_2$, the adsorption for the solid containing K being higher because K also traps NO$_2$ forming KNO$_3$. During the heating, increasing weights are observed due to the interaction of the solids with NO + O$_2$. The nitrate species formed are stable under the inert atmosphere and the K-containing solid exhibits a higher interaction with NO + O$_2$. Table 1 contains the NO$_2$ adsorption capacities.

For the SO$_2$ treated solids, significantly decreased interactions with NO + O$_2$ were observed (see Fig. 1 and Table 1). Besides, the interaction was higher for the solid containing potassium. The behavior of the mechanical mixture of sulfated K/CeO$_2$ and sulfated Ba/CeO$_2$ was an average of those of individual component catalysts. This is because the mixture was prepared from an equal amount
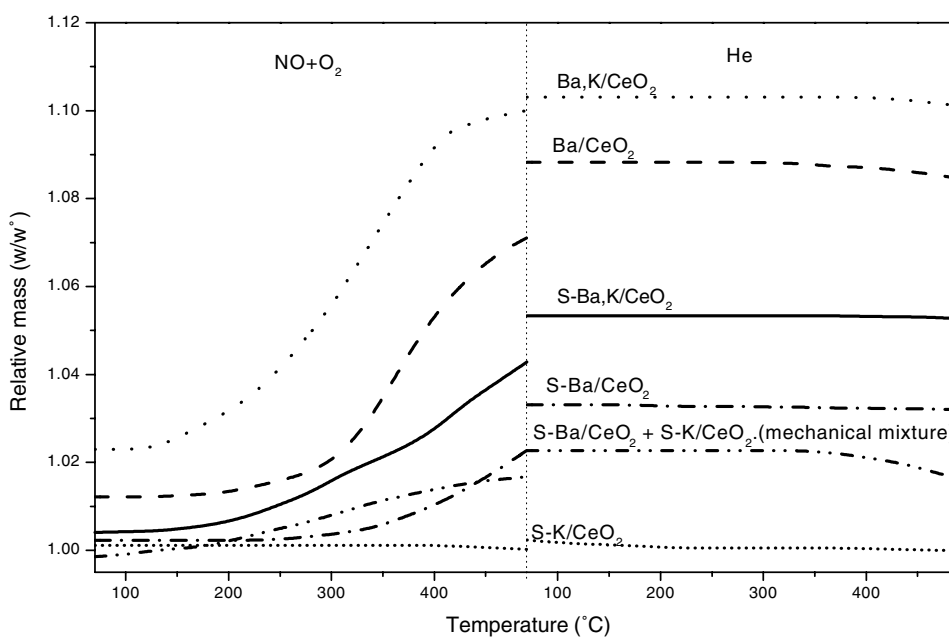

Fig. 1. Effect of sulfation upon NO$_x$ adsorption capacity of Ba,K/CeO$_2$ solids. Catalyst weight: 150 mg, total flow rate: 20 cm^3/min and heating rate: 5 °C/min. S indicates sulfated solids.

Table 1
NO$_2$ storage capacities

Catalyst[a]	w/w° at 300 °C[b]	w/w° at 490 °C[b]	% NO$_2$ stored at 300 °C[c]	% NO$_2$ stored at 490 °C[c]
Ba,K/CeO$_2$	1.103	1.101	77.74	76.16
Ba/CeO$_2$	1.088	1.084	66.57	63.76
S-Ba,K/CeO$_2$	1.053	1.053	40.16	40.01
S-Ba/CeO$_2$	1.033	1.032	24.90	24.04
S-Ba/CeO$_2$ + S-K/CeO$_2$ (mechanical mixture)	1.023	1.015	17.09	11.08
S-K/CeO$_2$	1.000	1.000	0.35	0.03

[a] S indicates sulfated samples.
[b] Relative mass data from Fig. 1, after NO + O$_2$ treatment, in He atmosphere.
[c] Calculated with respect to the total adsorption capacity of Ba and K.

of sulfated Ba/CeO$_2$ and sulfated K/CeO$_2$ thus resulting half of the Ba and K loadings if compared with the Ba,K/CeO$_2$ sample. In the case of the K/CeO$_2$ solid treated with SO$_2$, a low interaction with NO + O$_2$ was observed (Fig. 1).

Fig. 2 displays the resulting behavior of the simultaneous NO$_x$ adsorption and soot combustion for both the sulfated and the non-sulfated Ba,K/CeO$_2$ catalysts. For both solids, the weight decreases (up to 450 °C and 490 °C, respectively) and then it begins to increase. After all the soot has been burnt-off, the weight increases because Ba(NO$_3$)$_2$ formation and other reactions involving carbonates, sulfates and nitrates may also be occurring. Fig. 2 also shows that in the 250–450 °C temperature range the weight of the sulfated sample is lower than that of the non-sulfated one due to the loss of NO$_x$ adsorption capacity for the sulfated solid (Fig. 1). Thus, it is shown that the soot combustion occurs in a similar temperature range in both samples.
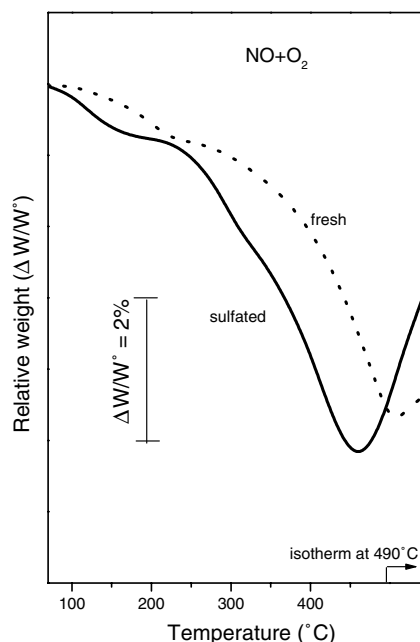

Fig. 2. Soot combustion on the Ba,K/CeO$_2$ catalyst mixed with soot (ratio: 20/1, wt/wt) in the presence of NO + O$_2$: (solid line) sulfated and (dash line) fresh. Conditions: Catalyst + soot weight: 150 mg, total flow rate: 20 cm^3/min and heating rate: 5 °C/min.

3.2. IR characterization

The IR spectrum of the fresh Ba/CeO$_2$ solid exhibits all the bands associated with BaCO$_3$ (Table 2) and, in addition, the sulfated Ba/CeO$_2$ catalyst shows the bands associated with BaSO$_4$ (spectra not shown). Although the solid is poisoned with sulfur during the treatment with SO$_2$, not all the barium present in the catalyst is converted into BaSO$_4$.

The IR spectrum of the fresh Ba,K/CeO$_2$ solid shows the presence of BaCO$_3$, KNO$_3$ and small amounts of potassium carbonate. KNO$_3$ is present because this salt was used for the catalyst preparation. The sulfated catalyst shows the characteristic bands of BaCO$_3$, K$_2$SO$_4$, and BaSO$_4$. Consequently, both potassium and barium react with SO$_2$ leading to the formation of sulfates. These spectra are not shown.

Fig. 3(a–b) shows a comparison between the IR spectra of the non-sulfated and sulfated Ba,K/CeO$_2$ solids after soot combustion in the presence of NO + O$_2$. The spectra for the sulfated and nitrated Ba,K/CeO$_2$ and K/CeO$_2$ catalysts are also included in Fig. 3(c–d). In the case of the non-sulfated Ba,K/CeO$_2$ solid mixed with soot and treated under the NO + O$_2$ atmosphere, the only species detected by IR are Ba(NO$_3$)$_2$ and KNO$_3$ (Fig. 3a), whereas the sulfated solid after the same treatment shows BaSO$_4$, Ba(NO$_3$)$_2$, KNO$_3$ and traces of BaCO$_3$ (Fig. 3b).

For the SO$_2$ treated Ba,K/CeO$_2$ catalyst, the IR spectrum of the solid extracted from the microbalance after the NO + O$_2$ treatment (Fig. 1) shows the presence of BaSO$_4$, Ba(NO$_3$)$_2$ and KNO$_3$ (Fig. 3c). Although surface free NO$_3^-$ species would also be present, their characteristic signal at 1385 cm^{-1} would overlap those of bulk nitrate compounds. This spectrum has two interesting features to be remarked: the absence of K$_2$SO$_4$ signals and the better

Table 2
Characteristic IR vibrational frequencies [5,7]

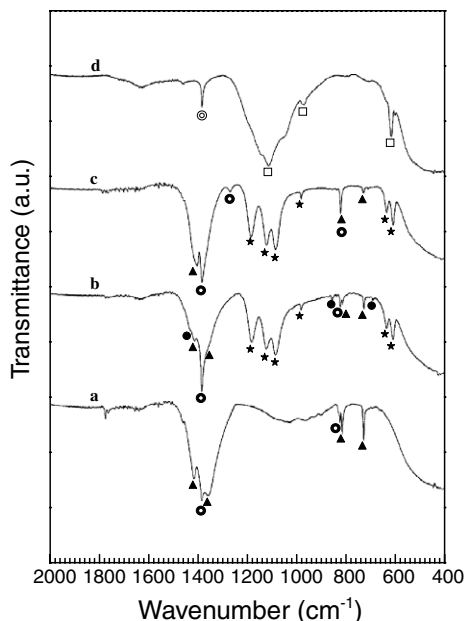| Species	IR vibrational frequencies (cm^{-1})
BaCO$_3$	1437 (s), 1059 (w), 858 (m), 694 (m)
Ba(NO$_3$)$_2$	1416 (s), 1358 (s), 818 (m), 730 (m)
KNO$_3$	1433 (sh), 1384 (s), 1354 (sh), 1273 (sh), 826 (m)
BaSO$_4$	1470 (m), 1190 (s), 1130 (s), 1080 (s), 980 (w), 860 (w), 640 (m), 610 (s)
K$_2$SO$_4$	1120 (s), 980 (w), 620 (s)
Free NO$_3^-$	1385 (s)

Fig. 3. IR spectra of samples used in the experiments shown in Fig. 2 (soot combustion in the presence of NO + O$_2$): (a) fresh Ba,K/CeO$_2$ and (b) sulfated Ba,K/CeO$_2$. The spectra (c) sulfated and nitrated Ba,K/CeO$_2$ and (d) sulfated and nitrated K/CeO$_2$ are shown for comparison. Symbols: ▲ Ba(NO$_3$)$_2$, ★ BaSO$_4$, ● BaCO$_3$, ◯ KNO$_3$, □ K$_2$SO$_4$, ⊙ free NO$_3^-$.

definition of the BaSO$_4$ peaks. Fig. 3d depicts that the sulfated K/CeO$_2$ solid after the NO + O$_2$ treatment only shows the presence of surface free NO$_3^-$ species and K$_2$SO$_4$, which indicates that in the absence of barium, K$_2$SO$_4$ is not transformed into KNO$_3$. Moreover, the IR spectrum of the mechanical mixture of sulfated K/CeO$_2$ and sulfated Ba/CeO$_2$ after the nitration process (not shown) indicated that K$_2$SO$_4$ remained on the surface and new bands around 1400–1260 cm^{-1} (attributed to sulfated species) were observed.

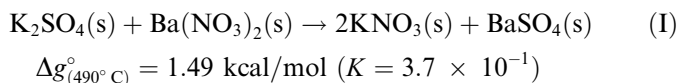## 4. Discussion

In previous papers [5,7] we showed that both Ba/CeO$_2$ and Ba,K/CeO$_2$ can effectively work as NO$_x$ catalytic traps when NO + O$_2$ is fed, while in the absence of oxygen, NO adsorption is negligible. Thus, NO$_2$ formation is necessary and it really takes place under the conditions used in our experiments. In order to discuss the results, let us first analyze the NO$_x$ adsorption process. In the fresh Ba/CeO$_2$ solid, Ba is mainly under the form of carbonate. After contact with NO + O$_2$ during the microbalance experiments, nitrates are formed but a considerable fraction of Ba remains as carbonate. In fact, ca. 64% of the NO$_x$ storage capacity of the solid has been used to store NO$_x$ after the complete treatment in the microbalance (Table 1).
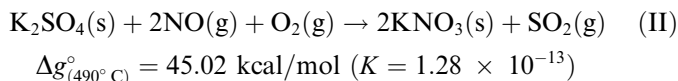
When the Ba/CeO$_2$ solid is sulfated, a portion of BaCO$_3$ is converted into BaSO$_4$. The remaining BaCO$_3$ is still capable of retaining NO$_x$, but of course, the overall capacity of the trap decreases to about one third of its original value (see Fig. 1 and Table 1). Catalytic NO$_x$ traps should

be regenerated when the sulfation degree is high and the trapping capacity is too low [9]. IR spectra of the Ba/CeO$_2$ catalyst after subsequent treatments with SO$_2$ and NO$_x$ show the characteristic bands of carbonates, sulfates and nitrates. Nevertheless, the signal of carbonates significantly decreases, meaning that nitrates are formed from carbonates as stated above. In fact, it is known that BaSO$_4$ is stable in the presence of NO$_2$, and the reaction between them is not thermodynamically favored [10].

The IR spectrum of the Ba,K/CeO$_2$ solid treated first with SO$_2$ and then with NO + O$_2$ shows the presence of BaSO$_4$, Ba(NO$_3$)$_2$, KNO$_3$ and traces of BaCO$_3$. No K$_2$SO$_4$ signals are observed. However, when the sulfated K/CeO$_2$ solid is treated with NO$_2$, no KNO$_3$ is formed (i.e., K$_2$SO$_4$ does not react with NO + O$_2$). Thermodynamic considerations indicate that the equilibrium constant at 490 °C of the reaction

$$K_2SO_4(s) + Ba(NO_3)_2(s) \rightarrow 2KNO_3(s) + BaSO_4(s) \qquad (I)$$
$$\Delta g^\circ_{(490°C)} = 1.49 \text{ kcal/mol} \ (K = 3.7 \times 10^{-1})$$

is 12 orders of magnitude higher than the equilibrium constant at the same temperature of the reaction

$$K_2SO_4(s) + 2NO(g) + O_2(g) \rightarrow 2KNO_3(s) + SO_2(g) \qquad (II)$$
$$\Delta g^\circ_{(490°C)} = 45.02 \text{ kcal/mol} \ (K = 1.28 \times 10^{-13})$$

Therefore, in the K/CeO$_2$ solid where K is as KNO$_3$ the treatment with SO$_2$ leads to K$_2$SO$_4$ formation, and this K$_2$SO$_4$ does not react with NO + O$_2$, as seen by IR (Fig. 3) and confirmed by the thermodynamic calculations. In the case of the sulfated Ba,K/CeO$_2$ solid (which contains BaSO$_4$, K$_2$SO$_4$ and BaCO$_3$), the treatment with NO$_2$ produces Ba(NO$_3$)$_2$ and decomposes the K$_2$SO$_4$ through the formation of KNO$_3$. Also, more BaSO$_4$ is formed by the reaction between the liberated SO$_2$ and the Ba(NO$_3$)$_2$. This means that reaction I takes place and all the K$_2$SO$_4$ is transformed to KNO$_3$. This indicates that K is not poisoned by SO$_2$ when BaCO$_3$ is present during the working period of the trap so that the properties of K towards soot combustion are preserved during the same period. Once Ba is saturated with sulfur, K will be also sulfated and the trap should be regenerated. It has been recently reported that the role of alkali promoters is not only that of favoring the soot-catalyst contact but also that of enhancing the participation of active oxygen species from the catalyst to soot particles [11].

On the other hand, the IR spectrum of the mechanical mixture of sulfated K/CeO$_2$ and sulfated Ba/CeO$_2$ after the nitration procedure showed that K$_2$SO$_4$ remained on the surface and new bands around 1400 – 1260 cm^{-1} associated to covalent sulfates appeared. Therefore, a close contact between K$_2$SO$_4$ and Ba(NO$_3$)$_2$ favored reaction I.

It should be remarked that potassium has also been reported as an efficient NO$_x$ adsorber. In fact, there exists a commercial process called SCONO$_x$ for the simultaneous removing of CO, VOC's and NO$_x$ [12]. The commercial catalyst is a ceramic monolith design, with a platinum-based catalyst and a potassium carbonate coating, thus
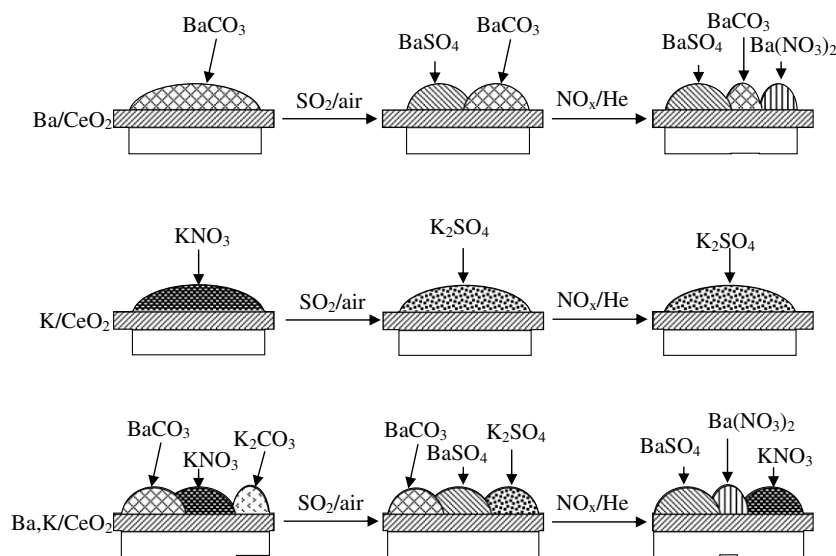
Fig. 4. Scheme of species formed during sulfation and nitration processes according to the IR results.

acting as a CO and VOC's combustion while adsorbing NO_x in effluents from stationary sources. The main finding of this work is that potassium, in spite of its being sulfated, can adsorb NO_x during the working period of the catalytic trap thanks to reaction I.

In order to illustrate the species formed after both the sulfation and nitration processes, Fig. 4 was drawn.

Two remarkable issues stand out from this figure:

- $BaCO_3$ is still present in the sulfated and nitrated Ba/CeO_2 solid, whereas no $BaCO_3$ is found after the same treatments in the Ba,K/CeO_2 catalyst,
- KNO_3 is quantitatively transformed into K_2SO_4 in the K/CeO_2 solid while in the case of the Ba-containing solid (Ba,K/CeO_2), the K_2SO_4 formed after the sulfation process is completely transformed back into KNO_3.

5. Conclusions

The interaction between Ba and K in the Ba,K/CeO_2 catalysts preserves potassium from sulfur poisoning when NO_x is present in the feed. This phenomenon is due to the $K_2SO_4(s) + Ba(NO_3)_2(s) \rightarrow 2KNO_3(s) + BaSO_4(s)$ reaction that is thermodynamically favored. In the absence of NO_x, the soot combustion reaction is strongly depressed by SO_2, showing a TPO peak at 550 °C, which is close to the non-catalyzed soot combustion. When NO is present in the feed, both the sulfated and the non-sulfated catalysts present similar TPO patterns.

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