

SO₂ influence on the K/La₂O₃ soot combustion catalyst deactivation

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Abstract

In the present work, K/La₂O₃ was prepared and tested as a potential catalyst to be used in a diesel engine exhaust. The soot combustion activity was evaluated by temperature-programmed-oxidation (TPO), and the NO_x-catalyst interaction was studied using a microbalance experiment. The SO₂ poisoning process and the regeneration of a poisoned K/La₂O₃ catalyst were analyzed. The fresh catalyst presented a good soot combustion activity. After being treated with a 1000 ppm SO₂ stream, the catalyst was poisoned due to lanthanum sulfate and potassium sulfate formation. The NO_x treatment contributed to the K₂(SO₄) decomposition at the expense of extra La₂(SO₄)₃ formation and the H₂ treatment contributed to the La₂(SO₄)₃ decomposition.

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1. Introduction

The main pollutants emitted for diesel engines are soot particles and nitrogen oxides. Extensive research has been under way in the last several years to find active catalysts for the abatement of diesel exhaust contaminants. The combination of traps and oxidation catalysts appears to be the most plausible after-treatment technique to eliminate soot particles [1] whereas NO_x adsorbers (traps) constitute a technology that is being developed for partial lean-burn gasoline engines and for diesel engines [2]. The adsorbers incorporated into the catalyst washcoat chemically bind nitrogen oxides during the lean engine operation. After the adsorber capacity is saturated, the system is regenerated, and released NO_x is catalytically reduced during a period of rich engine operation [3]. In the case of diesel engines, since a rich operation is not feasible, periodic fuel injections are necessary. This topic has been the object of several studies, most of them performed with Pt, barium-supported catalysts [3,4].

In order to abate soot particles, studies with a large number of catalytic formulations have been reported, including oxide materials and their mixtures [5], perovskite-type oxides [6], spinel-type Cu-chromite [7], Cu/K/Mo/Cl [8], Cu–V–K–Cl/

TiO₂ [9], promoted vanadium oxides [10] and molten salts [8,11].

In previous works [12–17], we reported results on Co and K catalysts supported on MgO, CeO₂ and La₂O₃. We found that K/La₂O₃ is a promising catalyst to be used for the abatement of diesel soot particles. All these catalysts mixed with soot gave maximum combustion rates between 350 and 400 °C in temperature-programmed-oxidation (TPO) experiments, showing good hydrothermal stability. But there are several other characteristics besides being active that a catalyst for diesel exhaust treatment should exhibit. Among them, the catalyst should be stable in the presence of high concentrations of CO₂, water and certain levels of SO₂. Even though these are key issues, only a handful of papers have systematically studied the stability of soot combustion catalysts [18] or catalytic NO_x traps [19]. In recent works [17,20], we studied the effect of temperature, water and sulfur dioxide upon the stability of the Ba, K/CeO₂ catalyst during soot combustion.

Sulfur dioxide is unavoidably present between the combustion products since diesel fuels have sulfur in their chemical composition. It is well known that SO₂ is responsible for the catalyst deactivation of many catalytic formulations. However, few systematic studies have been published about the poisoning of the catalyst with SO₂ [17].

The aim of this work was to study the poisoning of our K/La₂O₃ catalyst with SO₂ after an accelerated deactivation

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process with a 1000 ppm SO₂ stream. The possibility of catalyst regeneration was analyzed.

2. Experimental

2.1. Soot and catalysts 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 m²/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, CO₂ and hydrocarbons was 9.3% of the soot [21].

The K/La₂O₃ catalyst was prepared from a La₂O₃ (Alpha, p.a.) support to which a KOH-containing solution was added in order to obtain a 4.5 wt.% load of K. The suspension was evaporated while being vigorously stirred until achieving a paste, which was dried in a stove for 24 h at 120 °C, and calcined at 400 °C. The K final load was 2.6%, as determined by atomic absorption spectroscopy.

2.2. Activity test

The catalytic activity of K/La₂O₃ for the combustion of soot was determined by TPO. The soot and the catalysts were mechanically mixed in an agate mortar so as to obtain a soot/catalyst ratio = 1/20 (w/w). A gaseous flow (40 cm³/min) with 6% oxygen in nitrogen was used and the temperature was increased at a rate of 12 °C/min, using a 10 mg of the catalyst + soot mixture. A modified TPO technique [22] was employed which consisted in passing the gases coming from the reactor through a methanation reactor, where CO and CO₂ were converted into CH₄. Afterwards, methane was continuously measured with a FID detector. The methanation reactor contained a nickel catalyst and operated at 400 °C.

2.3. NO_x adsorption studies

The NO_x adsorption studies were performed in a Cahn 2000 Microbalance in order to study the interaction of the catalyst with NO + O₂. The catalyst was submitted to a mixture of NO (4%) + O₂ (18%) (He balance) at 70 °C and under these conditions the formation of NO₂ took place, the NO₂/NO ratio being 1300 (as determined by FTIR downstream the reactor) [23]. Then, the catalyst was heated up to 490 °C at 5 °C/min. Afterwards, it was maintained at this temperature for 10 min and then cooled down to 70 °C. At this temperature, the feeding mixture was changed to He and then the procedure was repeated with the He feed.

The purpose of using this much higher than real NO concentration was to study the eventual NO catalyst deactivation in short times.

2.4. Temperature-programmed reduction (TPR)

Temperature-programmed reduction experiments were performed to regenerate the catalyst. A 5% H₂ in Ar at a flow rate of 40 cm³/min was used in the TPR experiments. The heating rate was 10 °C/min and the final temperature was either 600 or 900 °C.

2.5. Catalysts characterization

2.5.1. X-ray diffraction (XRD)

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

2.5.2. IR spectroscopy (FTIR)

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 4 cm⁻¹ resolution.

2.6. Stability tests

In order to study the effect of SO₂ on the stability, catalysts were pre-treated before the TPO experiments as follows: air containing 1000 ppm of SO₂ was flowed for different times through the catalyst bed, which is at 400 °C. After this treatment, the catalyst was purged with air for 2 h at the same temperature. Similar concentrations of SO₂ in air have been previously used by other research groups; for example Neri et al. [24] used 1000 ppm SO₂ at 300 °C.

3. Results and discussion

3.1. Fresh catalyst activity

Fig. 1a shows the TPO profile of the K(4.5)/La₂O₃ fresh catalyst mixed with soot. As it was previously described [25],

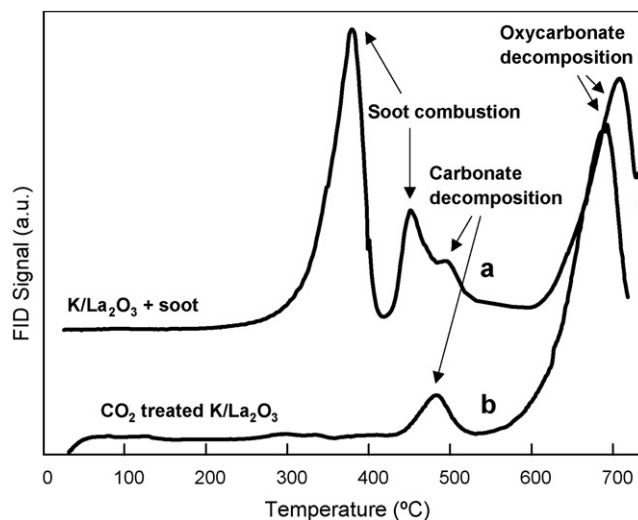


Fig. 1. TPO profile corresponding to the K/La₂O₃ + soot mixture (a) and TPD profile corresponding to K/La₂O₃ treated with CO₂ (b).

the composition of this catalyst is very complex since it depends on its exposure to the amounts of CO_2 and water in the atmosphere. As shown below, soot combustion takes place with simultaneous phase transformations. The main phases present in the catalyst calcined at 400°C are $\text{La}(\text{OH})_3$ and $\text{La}_2\text{O}_2\text{CO}_3$, as seen by XRD and FTIR techniques [25]. There is also some $\text{La}_2(\text{CO}_3)_3$. The TPO profile shows four maxima (Fig. 1a). In order to determine whether those maxima correspond to the soot combustion or to phase transformations (such as carbonate decomposition), a temperature-programmed desorption (TPD) experiment of the catalyst was performed. The experimental conditions used in this experiment were the same as those in the TPO experiment. Previously, a CO_2 stream passed through the catalyst bed at 450°C during 30 min. The aim of this experiment was to determine which maxima of the TPO profile correspond to the decomposition of a carbonate-like compound, formed in the catalyst due to the CO_2 treatment. This experiment is shown in Fig. 1b. Both maxima are compared with the DSC and TGA results obtained with the same catalyst and in similar conditions [25]. With these results, it could be assumed that the third maximum observed in Fig. 1a corresponds to the $\text{La}_2(\text{CO}_3)_3$ to $\text{La}_2\text{O}_2\text{CO}_3$ phase transformation, the fourth maximum corresponds to the $\text{La}_2\text{O}_2\text{CO}_3$ to La_2O_3 phase transformation, and the other two maxima would correspond to soot combustion. Although it may seem trivial, evidence of the catalytic burning of soot can be found in the color of the catalyst–soot mixture after a TPO experiment. The catalyst is white but the color of the catalyst–soot mixture before a TPO experiment is black due to the soot. After the TPO, the color of the mixture becomes white again, since the soot has been burnt. When the TPO experiment is detained after the first maximum and before the second one, i.e. at 420°C , the color of the mixture is gray. This means that not all the soot has been burnt at this point, and it could be shown that the second maximum in the TPO experiment is due to soot combustion. The reasons for the appearance of two soot combustion maxima will be the object of further research.

3.2. SO_2 poisoned catalyst activity

In order to study the SO_2 stability, the catalyst was treated with a 1000 ppm SO_2 stream at 400°C for 8, 32 and 62 h. Fig. 2 shows the corresponding TPO profiles. From the comparison of the different treatments, it can be observed that, as time in SO_2 increases, both soot combustion maxima shift to higher temperatures. Moreover, the 62-h treated catalyst profile is similar to the non-catalytic soot combustion profile. It can also be seen that the ratio between the intensities of the second and the first maximum changes, increasing as time in SO_2 increases.

In order to try to regenerate the catalyst, a TPR experiment was performed with the catalyst treated in SO_2 for 62 h. After that, the catalysts with different treatments (TPR up to 600°C and up to 900°C) were mixed with soot and the TPO of the mixtures were performed. Fig. 2 shows the TPO performed after using 600°C as the TPR final

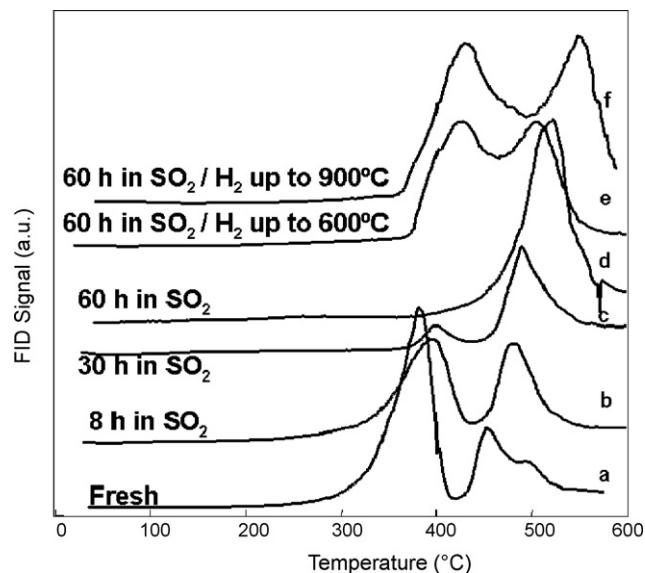


Fig. 2. TPO profiles corresponding to the following mixtures with soot: fresh $\text{K/La}_2\text{O}_3$, $\text{K/La}_2\text{O}_3$ treated in SO_2 for 8, 32 and 62 h and $\text{K/La}_2\text{O}_3$ treated in SO_2 for 62 h + TPR.

temperature. Although the activity is not so good as the one corresponding to the fresh catalyst, it can be seen that the catalyst recovers some activity. When the TPO is performed after using 900°C as the TPR final temperature, a similar profile is obtained (not shown) except that the higher temperature maximum shifts to a higher temperature. Thus, a higher reduction temperature does not improve the catalyst activity. Moreover, the activity decreases.

3.3. NO_x treated catalyst activity

Microbalance experiments were performed in order to get some insight into the interaction between the catalyst and NO_x . The fresh catalysts, the SO_2 treated one and the (SO_2 + TPR) treated one were submitted to the NO_x adsorption described in Section 2. After that, each catalyst was mixed with soot and a TPO experiment was performed. Surprising results were obtained. Fig. 3 shows the activity of the SO_2 treated catalyst after NO_x adsorption. It can be seen that the catalyst recovers activity. Moreover, taking into account that the TPO profile

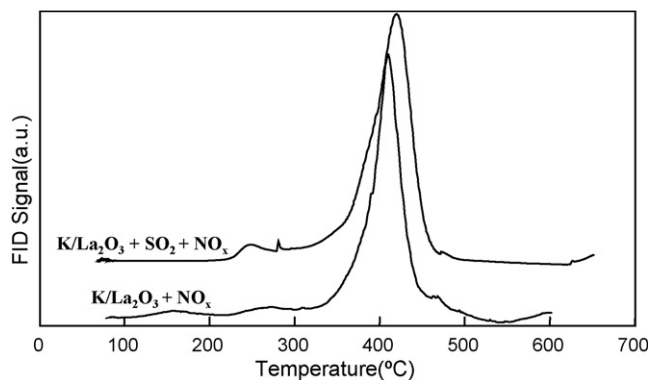


Fig. 3. TPO profiles corresponding to the following mixtures with soot: $\text{K/La}_2\text{O}_3$ treated in NO_x and $\text{K/La}_2\text{O}_3$ treated in SO_2 for 62 h + NO_x .

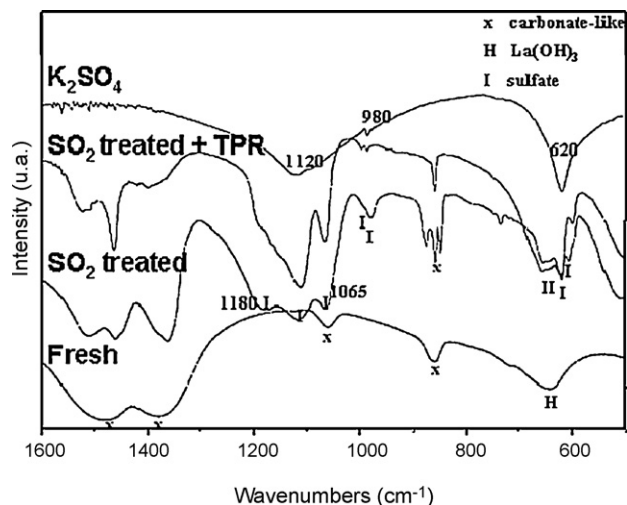


Fig. 4. IR spectra of: fresh K/La₂O₃, K/La₂O₃ treated in SO₂ for 62 h, K/La₂O₃ treated in SO₂ for 62 h + TPR and K₂SO₄.

presents only one maximum corresponding to soot combustion, and that this maximum appears at almost the same temperature as in the fresh catalyst first maximum, it could be said that the activity improves with respect to that of the fresh catalyst without any further treatment. Besides, the activity of the SO₂ treated catalyst after being in NO_x flow is practically the same as the activity of the fresh catalyst after the same treatment (Fig. 3).

3.4. IR and DRX characterization

Fig. 4 shows the IR spectrum of the fresh catalyst, the SO₂ treated one and the (SO₂ + TPR) treated one. The SO₂ treated La₂O₃ (Fig. 5) and the K₂SO₄ (Fig. 4) spectra are also shown as reference. The fresh catalyst presents signals corresponding to lanthanum carbonate, oxycarbonate and hydroxide. The signals at 645 and 3620 cm⁻¹ correspond to La(OH)₃. The signals at about 1480, 1380, 1060 and 860 cm⁻¹ correspond to carbonate-

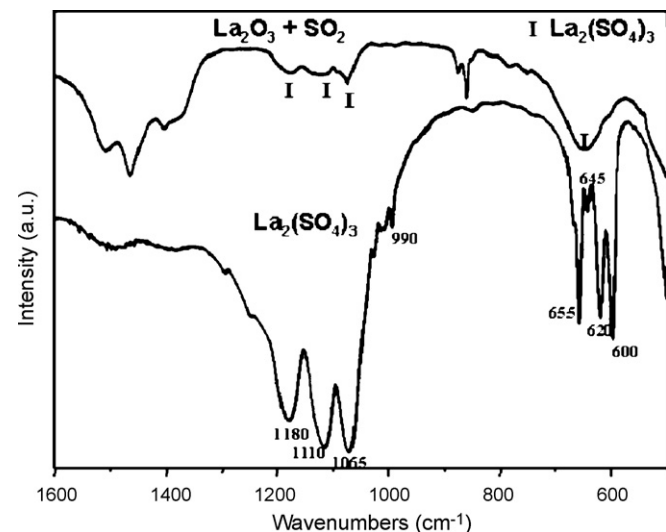


Fig. 5. IR spectra of La₂(SO₄)₃ and La₂O₃ treated in SO₂ for 8 h.

like compounds. There is some discrepancy in the literature regarding the signal assignments to lanthanum carbonate, type I oxycarbonate and type II oxycarbonate.

The K₂SO₄ spectrum presents three signals at 620, 980 and a broad one at 1120 cm⁻¹. These signals appear in the SO₂ treated K/La₂O₃ catalyst. The SO₂ treated lanthanum oxide spectrum (Fig. 5) presents three signals in the 1000–1250 cm⁻¹ region, which coincide with those corresponding to the SO₂ treated K/La₂O₃ in the same range. The three signals mentioned above are: 1180, 1110 and 1065 cm⁻¹. The signals in this region are characteristic of the sulfate group [26–28] as can be seen from the La₂(SO₄)₃ spectrum, which has been added to Fig. 5 as reference. The signals that appear at about 655, 645, 620 and 600 cm⁻¹ and the signal that appears at 990 cm⁻¹ in the SO₂ treated K/La₂O₃ spectrum are not present in the fresh catalyst and could correspond to La₂(SO₄)₃, as can be seen if compared to the La₂(SO₄)₃ spectrum. Then, the signals at about 1180, 1110, 1065, 990, 655, 645, 620 and 600 cm⁻¹ would correspond to La₂(SO₄)₃. Thus, both La₂(SO₄)₃ and K₂SO₄ would be formed in the SO₂ treated K/La₂O₃ catalyst. In the TPR treated catalysts, the signals corresponding to K₂SO₄ are still present. After the TPR experiment, the 1000–1250 cm⁻¹ region takes a shape similar to the corresponding shape of K₂SO₄. Apparently, this treatment would decompose only La₂(SO₄)₃ but not the K₂SO₄, higher temperatures being needed to decompose K₂SO₄.

Fig. 6 shows the DRX diffractograms of the fresh catalyst, the SO₂ treated one and the (SO₂ + TPR) treated one. The fresh catalyst presents the signals corresponding to lanthanum hydroxide and oxycarbonate. The SO₂ treated catalyst

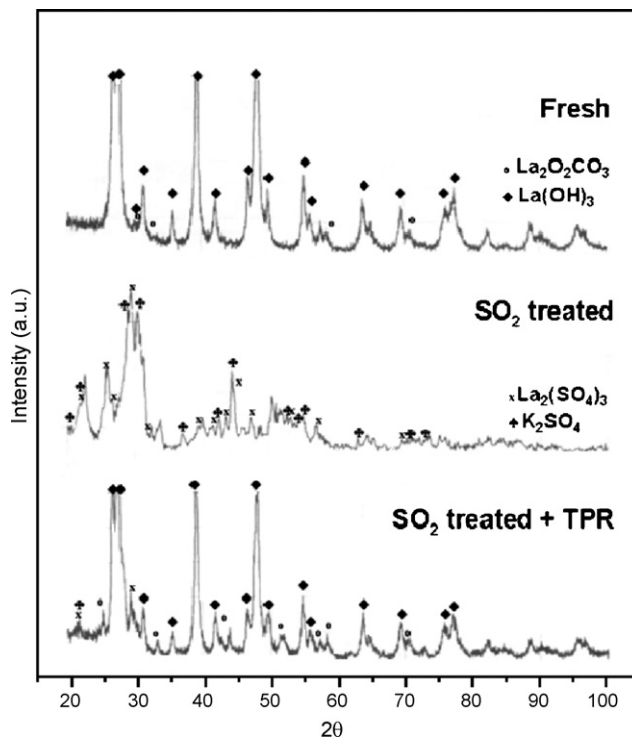


Fig. 6. DRX patterns of fresh K/La₂O₃, K/La₂O₃ treated in SO₂ for 62 h and K/La₂O₃ treated in SO₂ for 62 h + TPR.

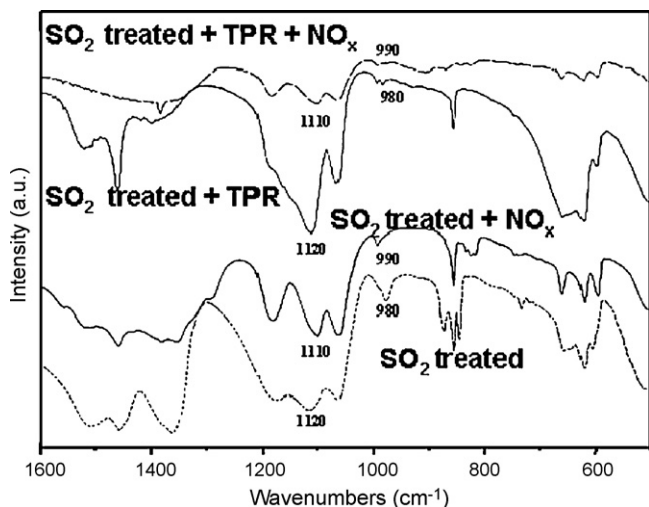
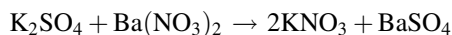
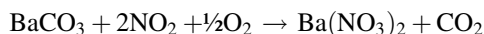


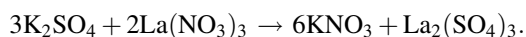
Fig. 7. IR spectra of: K/La₂O₃ treated in SO₂ for 62 h, K/La₂O₃ treated in SO₂ for 62 h + NO_x, K/La₂O₃ treated in SO₂ for 62 h + TPR and K/La₂O₃ treated in SO₂ for 62 h + TPR + NO_x.

presents signals that possibly correspond to La₂(SO₄)₃ (JCPDS#: 3-74) and K₂SO₄ (JCPDS#: 25-681). The (SO₂ + TPR) treated catalyst diffractogram is very similar to the fresh catalyst one.

Fig. 7 shows the IR spectrum of the SO₂ treated catalyst before and after being treated in NO_x flow. The K₂SO₄ signals at 1120 and 980 cm⁻¹ which are present in the poisoned catalyst are absent in the catalyst after being treated with NO_x. Besides, the spectrum shape in the 1000–1250 cm⁻¹ range, and in the 600–700 cm⁻¹ range, becomes similar to the La₂(SO₄)₃ one. The same result is observed comparing the (SO₂ + TPR) treated catalyst before and after being treated with NO_x. Thus, during the treatment with NO_x, K₂SO₄ decomposes and KNO₃ is formed. In a previous work [4], we reported similar results. In that case, the catalyst used was Ba, K/CeO₂. After the SO₂ treatment, K₂SO₄ and BaSO₄ were formed on that catalyst. However, part of the Ba remained as BaCO₃ [17]. Besides, recent studies of this sulfated catalyst after being treated in NO_x atmosphere showed that the main species on the support surface were Ba(NO₃)₂, KNO₃ and BaSO₄. Therefore, during the NO_x treatment the following reactions took place [4]:

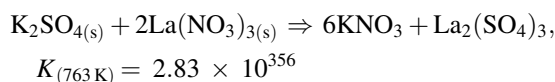
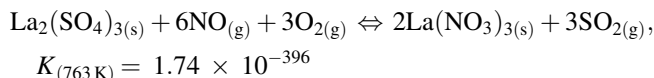
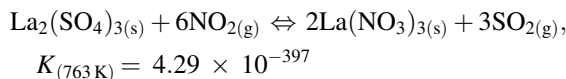
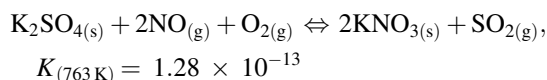
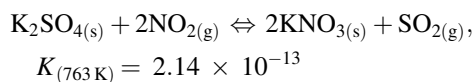


In the present work, it could be assumed that a similar process is taking place in the SO₂ treated K/La₂O₃ catalyst. After the treatment with NO_x, K₂SO₄ decomposes at the expense of an extra La₂(SO₄)₃ formation:



Similarly, lanthanum nitrate would be formed during the NO_x experiment. In order to have a more precise idea of what is happening during the treatment with NO_x, the following

equilibrium constants were calculated:



From the calculated values we can say that the decomposition of the K₂SO₄ is favored by the presence of La(NO₃)₃. On the other hand, decomposition of both K₂SO₄ and La₂(SO₄)₃ due to the individual reactions with NO_x are not favored. This fact is consistent with IR results, in which, after the NO_x treatment, the spectrum takes the shape of the La₂(SO₄)₃ spectrum.

3.5. Both NO_x + TPR treated catalyst activity

A TPR was performed on the (SO₂ + NO_x) treated catalyst. In the previous sections, it was suggested that NO_x treatment decomposes K₂SO₄ at the expense of extra La₂(SO₄)₃ formation; and it was also seen that the TPR experiment contributes to La₂(SO₄)₃ decomposition. Then, it could be thought that the combination of both successive treatments would constitute a promissory after-treatment procedure. Thus, a regeneration including first the NO_x treatment and then the TPR treatment was carried out. However, after performing TPO to the poisoned catalyst, which had been previously submitted first to NO_x and then to TPR treatments, it can be seen (results not shown) that the activity does not improve if compared to the activity of the (SO₂ + NO_x) treated catalyst. This could have been expected since the active element for soot combustion is potassium. The NO_x treatment recovers potassium as an active element while the TPR treatment recovers part of lanthanum. The role of lanthanum in oxidation reactions is not very clear. La₂O₃ vacancies could induce oxygen diffusion from the bulk to the surface [29]. In this catalytic system, potassium would be playing a more important role. The role of potassium is related to potassium wetting properties and mobility, which improve the catalyst–soot contact, this contact being a very important requisite for the catalytic soot combustion. Thus, recovering potassium as an active element would be more important than recovering lanthanum, at least, in this catalytic system.

4. Conclusions

The K/La₂O₃ catalyst used in this work presents a good soot combustion activity. The catalyst is deactivated after being

exposed to a 1000 ppm SO₂ stream at 400 °C. Both K₂SO₄ and La₂(SO₄)₃ are formed in the catalyst after this treatment. After being exposed to a NO_x stream, in the temperature range corresponding to soot combustion, the catalyst undergoes K₂(SO₄) decomposition. The K₂(SO₄) decomposition occurs at the expense of extra La₂(SO₄)₃ formation. A TPO performed after this NO_x treatment shows that the catalytic activity is not only recovered but also improved, since the TPO profile shows a single soot combustion maximum instead of the two maxima present in the fresh catalyst. On the other hand, the H₂ treatment (TPR) would contribute to the La₂(SO₄)₃ decomposition.

Since potassium sulfate is not an active component for soot combustion, the NO_x treatment alone (in which potassium is recovered as an active species (KNO₃)) is enough not only to recover but also to improve the catalytic activity. However, the treatment with H₂, or some other reductant, is necessary in order to keep the catalytic system working. Otherwise, the lanthanum would eventually be completely poisoned with SO₂. Then, K₂SO₄ would no longer be able to decompose at the expense of La₂(SO₄)₃ formation, since lanthanum would be saturated in SO₂.

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