Effect of Potassium on Sol-Gel Cerium and Lanthanum Oxide Catalysis for Soot Combustion

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Abstract

The catalytic activity in the soot combustion is reported for a series of potassium-promoter alumina supported catalysts prepared by the sol-gel method to be used in the catalytic combustion of soot. The studied systems correspond to CeO₂-Al₂O₃ and La₂O₃-Al₂O₃ with charges of 3 and 5 wt% of CeO₂ and La₂O₃. Potassium impregnation is performed to reach 3 atoms of K per nm² of the mixed oxide. The effect of the potassium incorporation increases its reducibility, decreases the surface area and forms a new type of oxygen that is stronger than the oxygen in mixed oxides with similar chemical nature. The existence of potassium oxides, K₂O and oxygen responsible for the vacancies and/or lattice defects (O²⁻) are related to good catalytic activity. Additionally, the presence of alkali affects the structural and textural characteristics of the catalyst, promoting the catalytic activity in soot combustion.

Keywords
Sol-Gel, Potassium, Cerium, Lanthanum, Soot Combustion

1. Introduction

It is generally known that in the oxidation of hydrocarbons, the volatile organic compounds (VOCs), the particulate matter such as soot, and the emission of NOₓ species into the atmosphere are harmful to people and environment [1]. An alternative for the control of these species is catalytic combustion [2]-[8]. The stabilization of the emission levels of these materials is increasingly strict, and new catalysts have been developed to meet the requirements of these new technologies. Soot is a particulate material resulting from the incomplete combustion...
of diesel fuel that remains in the filters of vehicle engines, causing serious health problems [9]. An alternative is to burn this particulate material [7] [9]. The catalyst deposited in the ceramic filters could oxidize the soot, reducing its emission into the atmosphere. However, the temperatures at which the gases emitted into the atmosphere are cooled between 300˚C and 400˚C, coal is burned at temperatures that range between 500˚C and 600˚C. Therefore, the catalysts used in the catalytic combustion of soot must be capable of presenting catalyst activity at low temperatures [10].

An important number of catalytic formulations have been developed in this field, including oxides [11]-[14], perovskites [9] [15]-[17], spinels [18] and metals [19]. The range of metals refers to the use of noble metals [20] which are not favorable for commercial use due to their high cost. However, metallic oxides [21]-[23] used as catalysts are more favorable as the atomic number of the metal increases because of the promotion effect with alkali materials [24]. Additionally, K⁺ could lower the unsaturation of oxide anion coordination and the mobility of atoms. It is well known that the catalytic combustion of soot is favored by basic catalysts [24]; thus, to enhance the catalytic properties of K-supported catalysts, the addition of CeO₂ and La₂O₃ is proposed to improve and enhance the catalytic activity of the support metal oxides.

The catalysts in this study have been impregnated with potassium. Additionally, the thermal stability, redox properties and wide application of metallic oxides are widely recognized. The incorporation of two metals into the oxide allows materials to be generated with different structural and electronic properties [25]. Within these properties, the morphological and valence changes are highlighted, as well as possible vacancies that originate in the material or the change in the chemical nature of the elements. CeO₂ has been considered because of its redox properties and its great affinity for the adsorption of oxygen [26]-[28], which could favor the basic characteristics of the catalyst. Furthermore, the great capacity of the cerium to admit modifications in both the surface and in the bulk of the material is also highlighted. La₂O₃ has been chosen because of its recognized thermal stability, and the presence of La³⁺ confers a basic character to the catalyst. The aim of this work is to study the different effects produced when K is supported on two different mixed oxides: CeO₂/Al₂O₃ and La₂O₃/Al₂O₃. The samples are prepared by the co-gelation of the catalyst precursors to avoid sintering and the induction of a stronger interaction between the oxides.

2. Experimental Analysis

2.1. Preparation

The sol-gel La₂O₃-Al₂O₃ and CeO₂-Al₂O₃ mixed oxides were prepared using tri-sec-aluminum butoxide and the corresponding acetylacetonates of cerium and lanthanum to achieve 3 and 5 wt% of CeO₂ and La₂O₃. The gelation reaction was accomplished in 1 h under reflux at 70˚C and in presence of distilled water and 2-buthanol, maintaining water to 2-buthanol molar ratio of 1:4. The obtained gels were dried in air at 110˚C and calcined at 600˚C for 6 h. The potassium was impregnated with an aqueous KNO₃ and dissolution dried at 100˚C; it was again calcined at 600˚C for 4 h. The potassium content was fixed in three K atoms per nm² of support. Considering the similar specific area values of the mixed oxides, the K content was around to 9 wt% in the prepared catalysts.

2.2. Characterization

The calcined sol-gel mixed oxides and K-supported catalysts were characterized by means of AAS in a Perkin Elmer 3100 absorption spectrometer and N₂ adsorption isotherms at 77 K using Micromeritics ASAP 2010 equipment. XRD was performed in a Rigaku diffractometer, using CuKα (λ = 0.15406 nm) as a radiation source and an Ni filter. For the TPR experiments, 0.500 g of the sample was reduced under an H₂ flow up to 700˚C in a Micromeritics TPR/TPD 2900 system equipped with a thermal-conductivity detector. Programmed thermal desorption profiles of O₂ and NH₃ were performed prior to cleaning the samples in He to a flow of O₂ for 1 h at 700˚C and then cooled at room temperature. After reaching room temperature, the desorption profile was detected at a heating rate of 10˚C·min⁻¹. The XPS measurements were performed in a VG Thermo Escalab 200R spectrometer equipped with an MgKα radiation source. Prior to the analysis, the samples were degasified at 300˚C for 1 h in the spectrometer chamber. As reference, the peak of C1s occurred at 284.8 eV.

2.3. Catalytic Activity

The evaluation of the catalytic activity for soot combustion was studied using carbon black (CB) as the soot
model. The catalyst and CB mixture for the assessment of the catalytic activity was prepared by mixing 4 mg of CB and 16 mg of catalyst in tight contact. The catalytic oxidation of the soot was conducted in a thermogravimetric apparatus (Netzsch 409 PC) with 7.5 mg of the mixture heated in a 180 mL·min⁻¹ flow of 12%O₂/He at 10°C·min⁻¹ up to 800°C. The temperature at which combustion occurs at the maximum rate, denoted as Tₚ, was used as the measure of the catalytic activity. The stationary point method was used to calculate the apparent activation energy. Typically, samples of the catalysts and CB mixtures in tight contact were heated at four different heating rates in 180 mL·min⁻¹ of 12%O₂/He in a thermogravimetric equipment.

3. Results and Discussion

3.1. Specific Area

The specific BET areas are summarized in Table 1. As expected, the sol-gel method generated materials with high surface area, which decreased when the alkali metal was added [24] [29]. Although the impregnation of 10 wt% of a metal could decrease the surface area of the support, the larger decreases illustrated in Table 1 were a consequence of the chemical behavior of potassium. Previous studies of this behavior indicate that, independent of the nature of support, the impregnation of potassium decreases the surface area over 50% of its total extent [24] [30]. The results of Table 1, corresponding to the reported effect, greatly decrease the S_BET values for the K₅%La₂O₃-Al₂O₃ catalyst, in which the area decreases to a value as low as 35 m²·g⁻¹, corresponding to 90% of the mixed oxide. In the other catalysts the decreases were approximately 85%.

3.2. XRD Diffraction

The diffraction profiles of the mixed oxides and the K-supported catalysts are shown in Figure 1. At the top of Figure 1, the diffractograms correspond to the K-supported catalysts, and the bottom diffractograms correspond to the mixed oxides. It is seen that the addition of cerium or lanthanum precursor to the aluminum alkoxide during the gelation step leads to rather amorphous solids. Regarding to the CeO₂-Al₂O₃ mixed oxides, the CeO₂ (JPDF: 43-1002) phase is clearly identified, increasing with CeO₂ loading. A different behavior is observed in the La₂O₃-Al₂O₃ counterparts, in which no diffraction peaks attributed to La₂O₃ (JPDF: 22-0369) are detected. The explanation relates to the previous reports where lanthanum species are inserted into the pore alumina or no diffraction is detected because the lanthanum species are highly dispersed in the amorphous phases [2]. Thus, the observed trend indicates that the lanthanum species inserted into the alumina lattice and the cerium is deposited as surface patches on the alumina. However, only for the 5 wt% La₂O₃-Al₂O₃ is it possible to detect a diffraction line of La₂O₃, indicative that for 5 wt% of La₂O₃, the lanthanum species are well-dispersed and could form agglomerates. Table 1 displays the detected phases for the mixed oxides and the K-supported catalysts. Moreover, the similar diffractograms of the mixed oxides and the K-supported catalysts indicate a high thermal stability of the sol-gel mixed oxides. With regard to the K-supported catalysts, the K content of ~9 wt% allows crystalline K species to be detected if they are in a low dispersion degree. No diffraction lines attributed to the K

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_BET, m²·g⁻¹</th>
<th>V_pore, cm³·g⁻¹</th>
<th>K, wt%</th>
<th>Detected XRD phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%CeO₂-Al₂O₃</td>
<td>502</td>
<td>0.26</td>
<td>-</td>
<td>CeO₂</td>
</tr>
<tr>
<td>5%CeO₂-Al₂O₃</td>
<td>475</td>
<td>0.40</td>
<td>-</td>
<td>CeO₂</td>
</tr>
<tr>
<td>3%La₂O₃-Al₂O₃</td>
<td>486</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5%La₂O₃-Al₂O₃</td>
<td>490</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K/3%CeO₂-Al₂O₃</td>
<td>69</td>
<td>0.17</td>
<td>9.2</td>
<td>CeO₂</td>
</tr>
<tr>
<td>K/5%CeO₂-Al₂O₃</td>
<td>156</td>
<td>0.26</td>
<td>9.1</td>
<td>CeO₂</td>
</tr>
<tr>
<td>K/3%La₂O₃-Al₂O₃</td>
<td>116</td>
<td>0.35</td>
<td>9.2</td>
<td>-</td>
</tr>
<tr>
<td>K/5%La₂O₃-Al₂O₃</td>
<td>35</td>
<td>0.04</td>
<td>9.0</td>
<td>-</td>
</tr>
</tbody>
</table>

(–) indicates nothing was detected.
species are detected, except for the larger La$_2$O$_3$ content in which only one diffraction line for a potassium species of K$_2$O (JPDF:77-2151) is detected. This diffraction peak of K$_2$O indicates lower potassium dispersion in this K/5% La$_2$O$_3$-Al$_2$O$_3$ catalyst.

3.3. Temperature Programmed Reduction (TPR)

Temperature-programmed reduction (TPR) profiles up to 700$^\circ$C are shown in Figure 2. The similarity of the reduction profiles of each series is noticeable. The absence of the well-defined reduction peak of the mixed oxides indicates practically irreducible solids.

The non-reducible behavior of the mixed oxides used as support, attributable to the reduction peak at $\sim$500$^\circ$C, appear for the K-supported catalysts to the potassium species. Moreover, the large reduction peak of the K-supported catalysts confirms the presence of potassium; although its presence was not detected by XRD because of its high dispersion degree. For better insight into the reduction behavior, the total H consumption in the TPR profiles between 400$^\circ$C and 500$^\circ$C, which is a measure of the amount of K$^+$ species, is evaluated by deconvolution of the area under the curve using a Lorentzian peak, as shown in Table 2. The similar H consumption that corresponds to a $\sim$25% reduction indicates a similar amount of reduced potassium. It is proposed that the lower the reduction temperature, the lowest the K-mixed oxide interaction. Thus, for the CeO$_2$-Al$_2$O$_3$ mixed oxides, the larger extent of cerium oxide as patches in 5%CeO$_2$-Al$_2$O$_3$ facilitate the alkali reduction at lower temperatures. The opposite effect is observed for the catalysts with lanthanum oxide, in which the reduction profiles indicate a reduction of the alkaline metal of the catalyst K/3%La$_2$O$_3$-Al$_2$O$_3$ at 511$^\circ$C, shifted towards higher temperatures; for K/5%La$_2$O$_3$-Al$_2$O$_3$, the catalyst presents the highest temperature of reduction.

3.4. O$_2$-Desorption Profile (O$_2$-DTP)

Figure 3 displays the evolution of oxygen during the temperature-programmed desorption (O$_2$-TPD) experiments, which is also closely related to the redox properties of the catalysts. The O$_2$-TPD profiles of the mixed oxides are similar, indicating the large extent of desorbed oxygen, as expected because of their large number of hydroxyl groups. With regard to the K-supported catalysts, both series display similar desorption profiles, attributed to the alkali presence, and confirm the presence of highly dispersed K species. The TPD-MS experiments confirm that the evolved gas and the He flow only contain oxygen; therefore, the deconvolution of the oxygen desorption curves using the Lorentzian peak shapes allow the amount of the different desorbed oxygen species to be calculated. In Table 2, the amount of desorbed oxygen for the desorbed temperature is displayed. For the La$_2$O$_3$-Al$_2$O$_3$ series, there are clear larger increases of desorbed oxygen in the K-supported catalysts compared to the mixed oxides. This behavior indicates that potassium allows oxygen to be withheld and contributes to the formation of surface oxygen with deeper interactions with K. For lower contents of La$_2$O$_3$, the oxygen is desorbed over 250$^\circ$C; however, for higher La$_2$O$_3$ content, the desorption temperature is displaced over 350$^\circ$C. This is in agreement with the results of TPR because at lower contents of La$_2$O$_3$, the potassium interacts with the support that allows for more oxygen desorption when compared to cerium catalysts. This corroborates the ease of CeO$_2$ to retain oxygen. Previous works have established that the desorption peak lower 400$^\circ$C are associated oxygen that is weakly bonded to the solid network [31]. Likewise, desorption at temperatures close to 500$^\circ$C is
attributed to the strong oxygen bonds to the network [32]-[35]. Clearly, the incorporation of potassium allows oxygen to have more force than in solids without alkali. According to Table 2, the amount of desorbed oxygen is lower for the K-cerium catalysts.

### 3.5. XPS analysis

Table 3 compiles the respective binding energies (BE) of the core electrons of the elements. The C1s, O1s, Ce3d5/2, La3d5/2 and K 2p3/2 core-level spectra were recorded for the K-supported catalysts. The C1s, O1s, Ce3d5/2, La3d5/2 and K 2p3/2 core-level spectra were recorded for the K-supported catalysts. Figure 4 shows the spectra for one representative catalyst, the K/5%La2O3-Al2O3. The C1s emission was used as reference. According to Praveen et al. [36] and Fleming et al. [37], the BE range of Ce between 875 eV and 925 eV indicates a mixture of surface Ce3+ and Ce4+. The obtained BE values of Table 3 of Ce 3d5/2 at 883.0 eV and Ce 3d3/2 at 900 eV have a relationship with 13% and 12% of Ce3+ for the K3%CeO2-Al2O3 and K5%CeO2-Al2O3 catalysts, respectively. The presence of Ce3+, poorly appreciated, associated with the surface anion vacancies could be a consequence of the removal of oxygen during the sample pretreatment.

The reported BE of La 3d between 830 eV and 870 eV [36] and La 3d5/2 at 834.9 eV for surface La3+ indicates that the obtained values of 835.1 and 835.4 eV shifted towards higher BE, indicating the presence of only La3+.
Table 3. Binding energies (eV) of the core levels for the K-supported catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ce 3d$_{5/2}$</th>
<th>La 3d$_{5/2}$</th>
<th>O 1s</th>
<th>K 2p$_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/3%CeO$_2$-Al$_2$O$_3$</td>
<td>883.0 (13)</td>
<td>------</td>
<td>531.6</td>
<td>293.6</td>
</tr>
<tr>
<td>K/5%CeO$_2$-Al$_2$O$_3$</td>
<td>883.1(12)</td>
<td>------</td>
<td>531.7</td>
<td>293.8</td>
</tr>
<tr>
<td>K/3%La$_2$O$_3$-Al$_2$O$_3$</td>
<td>------</td>
<td>835.1</td>
<td>531.5</td>
<td>292.8</td>
</tr>
</tbody>
</table>

(*) mean percentage of Ce$^{3+}$ over the surface catalyst

This is the expected result considering no other stable oxidation state of lanthanum occurs when combined with oxygen. Thus, the corresponding BE of lanthanum in the La$_2$O$_3$-Al$_2$O$_3$ mixed oxides indicates a La$^{3+}$ cation is partially inserted into the alumina lattice leading to a strong La-O interaction [39]. The O1s BE at 531.5 to 531.7 eV is associated with the weakly bonded surface species [32]. With regard to the surface K species, the BE at 293.4 to 293.8 eV is indicative of potassium in a cationic chemical environment (K δ$^+$) [30], present in 3 wt% La$_2$O$_3$, 3 wt% CeO$_2$ and 5 wt% CeO$_2$ content of the K catalysts. A different behavior is detected for the...
K/5%La₂O₃-Al₂O₃, in which the BE decreases to 292.8 eV. This shift towards higher BE indicates more oxidized species, whereas the shifts towards lower BE are related with the surface deficit electronic density potassium species. According to the XRD spectra, the K₂O detected appears as a cationic chemical environment (K⁰⁺) when the potassium is similar to the K₂O species [28].

Figure 5 and Figure 6 show the bulk and surface Ce/Al, La/Al and K/Al atomic ratios. It can be seen for both of the studied series that the higher surface values are indicative of the surface enrichment of Ce and La. Although, in the K-supported on the CeO₂-Al₂O₃ catalysts, the lower difference between the surface and bulk Ce/Al indicates a lower dispersion of CeO₂ on the Al₂O₃, easily detected by XRD. With regard to the La/Al, the larger differences between the surface and bulk values as well as the shifted of surface La³⁺ species support the hypothesis that surface K/5%La₂O₃-Al₂O₃ catalysts becomes La-enriched. Surface K/Al ratios are lower than the bulk ratios for both series with similar values for each series. The higher surface K/Al ratios for the K/CeO₂-Al₂O₃ catalyst indicate highly dispersed K species, in agreement with XRD. With regard to the La₂O₃-Al₂O₃ catalysts, the surface La-enrichment in the K/5% La₂O₃-Al₂O₃ catalyst by the larger inclusion of La³⁺ in the Al₂O₃ lattice may be the responsible for the presence of the K₂O phase, detected by XRD, and the large K dispersion compared to the K/3%La₂O₃-Al₂O₃.

3.6. Catalytic Activity

Figure 7 shows the DTG curves for the CB combustion of the K-supported catalysts. The catalytic activity is related to the temperature corresponding to the maximum of the DTG curve (Tₘ). Higher values of Tₘ indicate lower catalytic activity. The Tₘ values and the apparent activation energy (Eₗₐₜ) of the mixed oxides and the K-supported catalysts are summarized in Table 4. The Tₘ value for the uncatalyzed CB combustion was found to be 650°C (not shown), relatively the same value as the corresponding mixed oxides without the alkali active phase (not shown). Thus, the decreases at approximately 200°C in the Tₘ values for the K-supported catalysts indicate the catalytic effect of the alkali. Although Figure 7 shows that there are no large differences in the K-supported catalysts, the 10°C temperature decreases of the maximum reaction rate for the K/5%La₂O₃-Al₂O₃ catalysts can be explained considering the characterization results. Moreover, the apparent activation energy supports this feature. The apparent activation energies of the uncatalyzed reaction is 170 kJ∙mol⁻¹, and Eₗₐₜ values from 108 to 81 kJ∙mol⁻¹ have been reported for soot combustion with potassium-lanthanum cobaltite catalysts [40]. The Eₗₐₜ of the mixed oxides is on the order of 137 to 145 kJ∙mol⁻¹, so it decreases to 92 and 81 kJ∙mol⁻¹.


for the K-supported catalysts; the larger decreases can be related to the redox and basic properties, favoring the oxygen activation on the catalyst surface.

4. Conclusion

The sol-gel method allows solids of high surface area to be obtained, thereby decreasing the area with the addition of potassium, which covers the pores of the material. The drastic effect is the most evident for the K/5%La2O3-Al2O3 catalyst. The effect of the incorporation of potassium increases its reducibility, decreases the surface area and allows having stronger oxygen in mixed oxides of a similar chemical nature. For K-La2O3 catalysts, La2O3 enters into the alumina and promotes the availability of K2O in K/5%La2O3-Al2O3 with a chemical environment that favors its catalytic activity. However, for K-CeO2 catalysts, the oxygen vacancies and mobility of these oxygen species for the catalytic activity in soot combustion reaction are crucial because the cerium oxide cannot enter the network. The characterization of the mixed oxides and K-supported catalysts confirms the importance of the use of potassium active phases as catalysts in soot combustion.

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