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Dra. Maria Silvia Leguizamón

Nos dirigimos a Ud. para informarle que el trabajo denominado "*Particulate matter combustion. Cordierite-supported potassium nitrate catalysts modified with transition metal oxides*" cuyos autores son María S. Leguizamón Aparicio, Maia Montaña, María L. Ruiz, Sandra M. Mosconi, Juan J. Musci, Marco A. Ocsachoque, Mónica L. Casella y Ileana D. Lick, ha sido aceptado para su publicación en la edición especial del Journal of the Argentine Chemical Society (Anales de la Asociación Química Argentina) en virtud de las IV Jornadas en Ciencias Aplicadas "Dr. Jorge J. Ronco".

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PARTICULATE MATTER COMBUSTION. CORDIERITE-SUPPORTED POTASSIUM NITRATE CATALYSTS MODIFIED WITH TRANSITION METAL OXIDES

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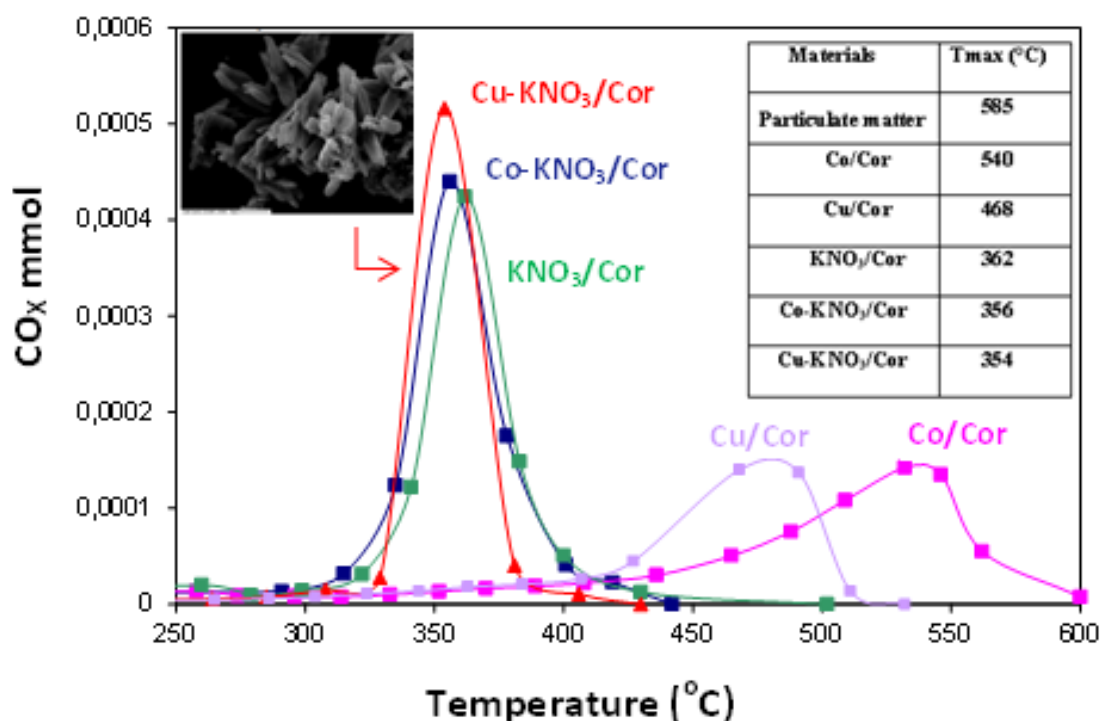
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Resumen Gráfico



Resumen

En este trabajo se estudian catalizadores de nitrato de potasio modificados con óxidos de metales de transición soportados sobre cordierita como catalizadores para la combustión de material particulado proveniente de emisiones de motores Diesel. Los catalizadores se prepararon mediante el método de humedad incipiente utilizando los respectivos nitratos. Estos catalizadores se caracterizaron mediante difracción de rayos X (DRX), calorimetría diferencial de barrido (DSC), reducción a temperatura programada (TPR), espectroscopía FTIR y microscopía de barrido provista con analizador EDS.

Los catalizadores que contienen KNO_3 presentan alta actividad en presencia de O_2/NO . La temperatura de la máxima velocidad de quemado disminuye más de $200\text{ }^\circ\text{C}$ con respecto al proceso sin catalizador. La actividad se puede asociar con la presencia del KNO_3 y la contribución del par redox $\text{NO}^3/\text{NO}^{2-}$ y al efecto de mojado de la superficie que aporta la sal soportada.

Abstract

In this work, cordierite-supported potassium nitrate catalysts modified with transition metal oxides are studied as catalysts for the particulate matter combustion from diesel engine emissions. The catalysts were prepared by nitrate solutions. The catalysts were characterized by XRD, differential scanning calorimetry (DSC), thermal programmed reduction (TPR), vibrational spectroscopy (FTIR) and Scanning microscopy provided with EDS analyzer.

KNO_3 containing catalysts present high activity in the presence of O_2/NO . The T_{max} obtained with these catalysts decreases more than $200\text{ }^\circ\text{C}$ with respect to the temperature of the non-catalyzed process. The activity is associated with the presence of KNO_3 and the role of this salt can be attributed to the $\text{NO}^3/\text{NO}^{2-}$ redox cycle contribution and to the surface wetting effect.

Palabras clave: material particulado; oxidación, aniones nitrato, cordierita.

Keywords: particulate matter; oxidation, nitrate anions, cordierite.

1. Introduction

The gaseous emissions of diesel engines contain, among other components, water, volatile organic compounds (VOCs), carbon oxides, sulphur oxides, nitrogen oxides and particulate matter (PM). Some of these compounds are considered pollutants that put both the environment and human health at risk [1-3].

The particulate material consists of small particles ($0.1\text{-}10\text{ }\mu\text{m}$) whose main component is carbon, and is commonly designated PM-10. These particles can enter the lungs and increase the chances of getting respiratory diseases. Hydrocarbon molecules and other organic and inorganic compounds can be adsorbed on PM particles, which are also considered mutagenic species. Besides, these particles are also harmful to the environment and to the historical heritage [4].

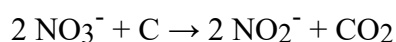
On the last few decades, global regulations tend to lower the permitted emission limits of most pollutants. The decrease in carbon monoxide (CO) and hydrocarbons or residual VOCs emissions are achieved adding oxidation catalysts in the exhaust pipe. In order to reduce PM emissions filters and catalysts can be used. The filters consist of metallic or ceramic substrates in the shape of monoliths that retain the particulate matter these filters must be regenerated periodically to eliminate the accumulated PM and avoid an obstruction in the exit gases [5].

Active regeneration is the process of heating a filter at high temperature (approximately $600\text{-}650\text{ }^\circ\text{C}$) to burn the retained material. On the other hand, passive regeneration is the process of oxidizing the retained PM to CO_2 , at the temperature range at which the cars exhaust

operates (150-450 °C). To achieve this, filters must contain catalysts that accelerate the combustion reaction [6].

Several catalytic active phases have been reported for PM combustion. Among the most active are those based on noble metals such as platinum, gold, palladium, silver, ruthenium and rhodium [7-9]. Also, catalysts based on perovskites [10], oxides and mixed oxides, some of them derived from hydrotalcites [11-14], ceria [15] and many salts (chlorides and molten salts) [16] have been studied. Oxidic phases of the transition metal oxides such as: CoOx, CuO and Fe₂O₃ were active for this reaction, but it has been observed that the burning temperature is high. The modification of these catalysts with alkali metals is a subject of great interest since these species increase the activity of the catalysts [17-22].

Cs, K, Na and Li nitrates are among the salts that have the best activity this fact is assigned to their low temperature melting point and adequate redox characteristics [6,23-27]. A mechanistic hypothesis has been proposed, which has been supported by numerous bibliographic reports [28], in which a nitrite/nitrate redox cycle that can intervene in the PM combustion reaction, according to the following equation:



This reaction is thermodynamically spontaneous and feasible in the operation range of an exhaust pipe. The generated nitrite is then oxidized to nitrate with the O₂ of the gas stream. However, catalysts containing only alkaline nitrates present the disadvantage, that they are not completely selective towards CO₂ formation and this can be improved by adding metal oxides to the catalyst formulation [29,30]. Based on previous knowledge, this paper proposes the study of potassium nitrate catalysts (KNO₃) promoted with transition metal oxides (CuO or Co₃O₄) supported on cordierite powder and test them in the PM combustion reaction in the presence of NO/O₂/He oxidant mixture.

The interest in using transition metal oxides, is due to their ability to originate a M^{m+}/ Mⁿ⁺ redox pair capable of oxidizing CO to CO₂ and generating adsorbed oxo-nitrogenous species (NO_x ads) when the catalysts work in an atmosphere of nitrogen oxides (NO_x), which are another pollutants present in emission currents [31-33].

The choice of cordierite powder (2MgO.2Al₂O₃.5SiO₂) as support for active species is based on the market availability of this ceramic material in the form of monoliths or structured filters at low cost [34]. Direct impregnation method of active phases over cordierite has been chosen in order to simplify the preparation of the catalytic materials.

2. Experimental

2.1 Catalyst preparation

The catalysts were prepared in powder form using cordierite as support. Cordierite powder was obtained by grinding a honeycomb type monolith of commercial cordierite, (Corning), followed by a sieving step to retain the portion of the selected granulometry, smaller than 60 mesh.

Supported potassium nitrate (KNO_3) catalyst was prepared by impregnation of the cordierite powder with aqueous KNO_3 nitrate solution using the incipient wetness technique. Catalysts modified with transition metal oxides were prepared by co-impregnation of KNO_3 and the corresponding transition metal nitrate ($\text{Co}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$). In addition, supported metal oxide catalysts were prepared. The materials obtained by impregnation of the support and subsequent drying in an oven at 100°C are called precursors. To obtain the catalysts, the precursors were calcined at 600°C for 2 h.

The KNO_3 catalyst was prepared with a potassium nominal concentration of 10 wt.% (12.5% w/w nitrate ion) and is called $\text{KNO}_3/\text{cordierite}$. In the modified catalysts the concentration of the transition metal (copper or cobalt) is 5 wt%.

2.2. Characterization of catalysts.

The semiquantitative chemical analysis of the catalysts was performed with a scanning electronic microscope (SEM) Philips 505 attached to an energy dispersive spectrometer (EDAX DX PRIME 10).

Crystalline phases present in the catalysts were identified by powder X-ray diffraction (XRD) analysis using a Philips Pw 1732/10 diffractometer equipped with $\text{CuK}\alpha$ radiation, and operated at 40 kV and 20 mA. The scan range was $2\theta = 10\text{--}70^\circ$ and the scan speed was 1°min^{-1} .

The melting point of the catalysts containing KNO_3 was analysed by differential scanning calorimetry (DSC) using a Shimadzu DSC 50 equipment. The experiments were carried out in a nitrogen inert atmosphere, from room temperature up to 500°C , with a temperature ramp of $10^\circ\text{C}/\text{min}$. For the experiments, sealed aluminium pans and 10 mg of sample were used.

The presence of nitrate anions on fresh and used catalysts was studied by means of FTIR spectroscopy using a Perkin-Elmer Spectrum RX1 equipment. Spectra were recorded at room temperature in the $4000\text{--}400 \text{ cm}^{-1}$ range and the samples were prepared in form of pills with KBr. The sample concentration in the pills was 3 wt%.

TPR (temperature programmed reduction) experiments were carried out with a laboratory-made conventional equipment. The TPR was performed using 10% hydrogen in nitrogen (flow rate $20 \text{ cm}^3 \cdot \text{min}^{-1}$) with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ from 50 up to $800 \text{ }^\circ\text{C}$. The sample loaded was 30 mg.

2.3. Catalytic activity

To perform the experiences of burning the particulate matter, a fixed bed quartz microreactor was used analysing the reaction gases. The microreactor (id = 0.8 cm) was electrically heated with a heating rate of $2 \text{ }^\circ\text{C}/\text{min}$. The reaction mixture was obtained from three feed lines individually controlled: NO/He, O₂/He, and He to close the balance. The reactor was fed with the following mixture: 2000 ppm of NO and 8% of O₂ ($Q_{\text{total}} = 50 \text{ mL}/\text{min}$). The microreactor was loaded with 30 mg of catalyst and 3 mg of soot (Printex-U) and the combustion was carried out in the range of 200–650 °C. Before the reaction, the soot was mixed with the catalyst, with a spatula (loose contact). Reaction products were monitored with a Shimadzu GC2014 gas chromatograph, equipped with a TCD detector. The amount of burned particulate matter is calculated from the chromatographic information of CO₂ and CO.

3. Results and discussion

The catalyst samples were analysed with various physicochemical techniques in order to obtain information about the supported active phases. Table 1 shows the results of the semiquantitative chemical analysis of the surface contents of the catalysts. These results were obtained with a scanning electron microscope (SEM) provided with EDS analyser. Besides, the micrographs of the catalysts are shown in Figure 1. The EDS results indicate that the atomic superficial concentration of potassium, cobalt and copper are superior to the nominal ones (0.2 %, 0.09 % and 0.08 % respectively). It can be suggested that the supported species are segregated on the surface. The atomic content of potassium is similar for the three catalysts containing this element and in contrast, the surface content of cobalt is substantially greater than that found for copper. Moreover, specific analysis of the atomic content of cobalt, in areas where the mapping showed a higher concentration of this metal, reveal a high atomic concentration indicating the formation of segregated structures that decrease the exposed concentration of the other elements of the formulation.

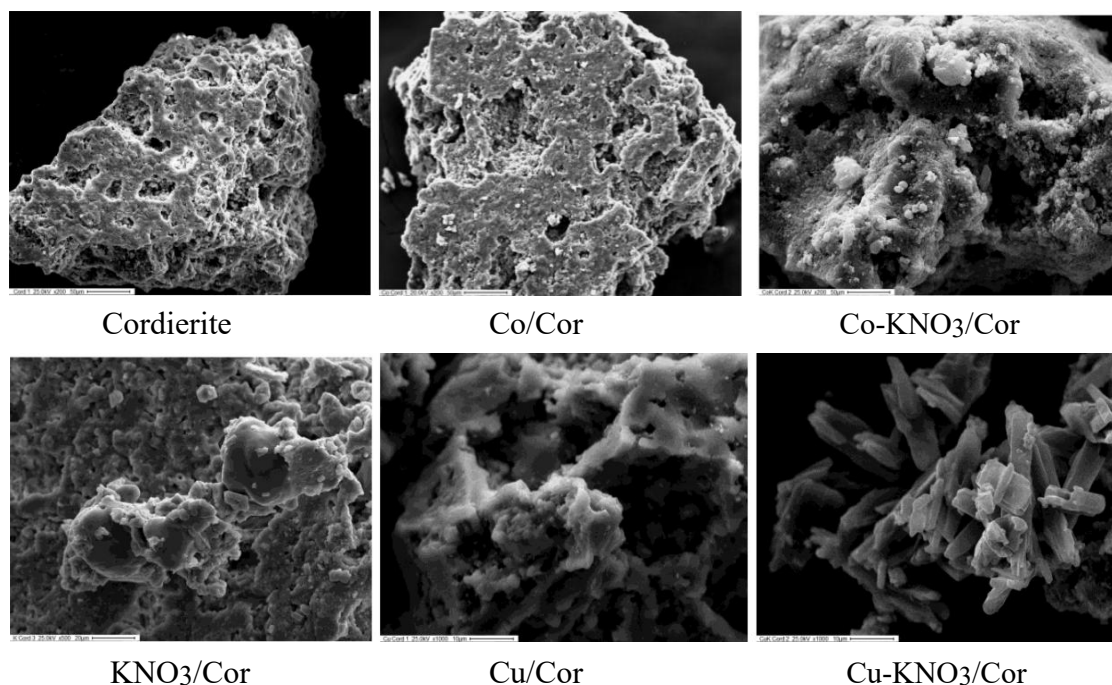


Figure 1. SEM micrographs of the catalysts.

Table 1. Semiquantitative chemical analysis of the surface atomic contents of the catalysts measured by SEM-EDS.

	Cu/Cor	Co/Cor	KNO ₃ /Cor	Cu-KNO ₃ /Cor	Co-KNO ₃ /Cor
O	49.8	41.25	53.61	49.26	44.46
Mg	7.71	7.89	7.07	7.23	6.61
Al	17.05	18.02	14.91	16.12	14.87
Si	24.15	24.51	20.6	23.18	19.14
Co	-	8.33	-	-	10.08
Cu	1.29	-	-	1.15	-
K	-	-	3.82	3.06	3.83

KNO₃ is a melting substance that can modify the crystalline structure of the support, therefore XR diffraction tests were carried out on the original support and on catalysts. The cordierite XRD diagram (Figure 2, curve a) shows the typical diffraction lines of cordierite, located at $2\theta = 10.43^\circ$; 21.73° ; 26.38° , 28.43° , 29.46° and 33.93° (JCPDS-ICDD 01-084-1222). These same lines are observed in the diffractogram of catalysts, indicating that the presence of supported species do not modified the crystal structure of the support.

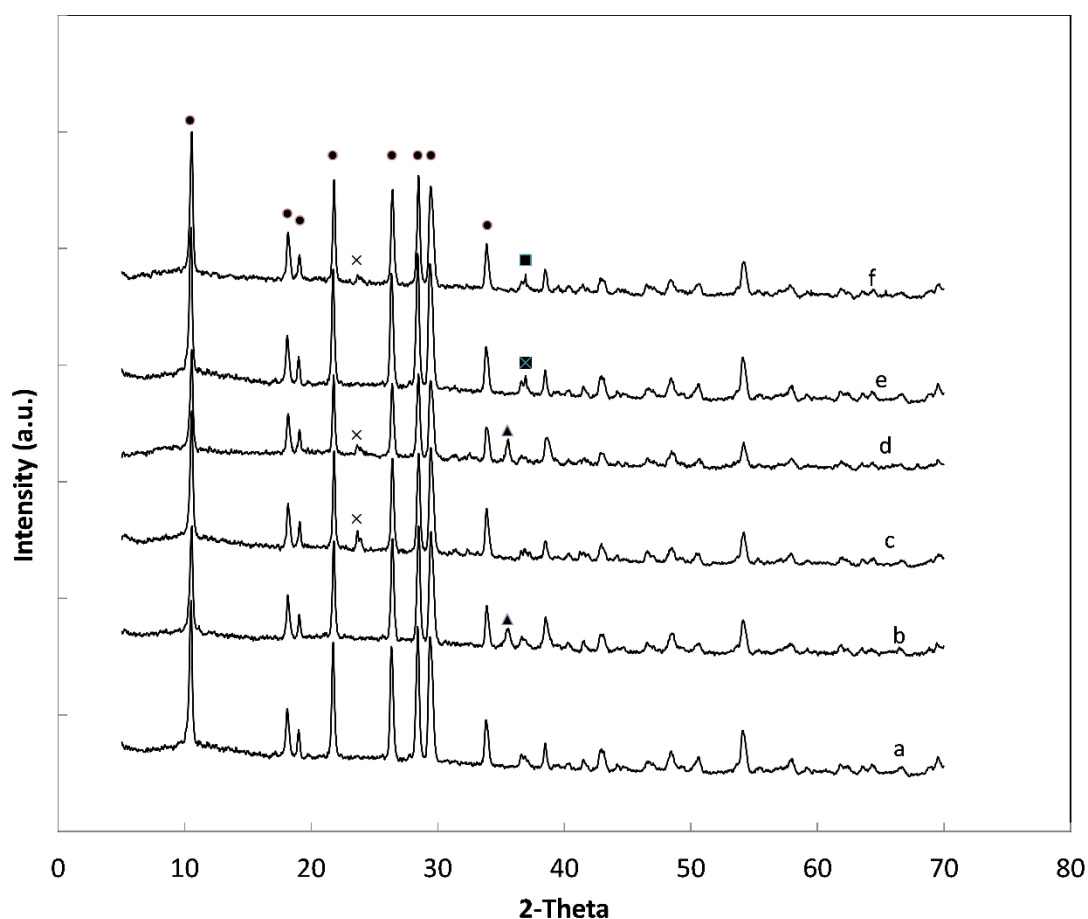


Figure 2. XRD diagrams of original cordierite and catalysts: a) Cordierite, b) Cu/Cor, c) KNO_3 /Cor, d) Cu- KNO_3 /Cor, e) Co/Cor and f) Co- KNO_3 /Cor.
 (●) Cordierite, (▲) CuO, (■) Co_3O_4 , (X) KNO_3 .

Both in the Cu/Cor and Cu- KNO_3 /Cor catalyst XRD diagrams (Figure 2, curve b and curve d), the principal diffraction line of crystalline CuO species (JCPDS-ICDD 03-065-2309), located at 35.69° can be observed. This result indicates that part of the copper is supported as crystalline oxidic phases.

The Co_3O_4 spinel is present in the Co/Cor and Co- KNO_3 /Cor catalysts (Figure 2, curve e and curve f), as can be inferred from the fact that the XRD diagrams show the main diffraction line of this compound, located at 36.9° (JCPDS-ICDD 01-076-1802).

A similar result was observed for the KNO_3 containing catalysts: in their XRD diagrams signals located at $2\theta = 23.52^\circ$, 23.79° , 32.34° and 33.62° (JCPDS-ICDD 01-074-2055) can be observed, which are associated to the presence of supported crystalline KNO_3 . The line located at 29.4° overlaps with signals from the cordierite.

The presence of melted phases in KNO_3 containing catalysts was analysed by differential scanning calorimetry (DSC) and the results are shown in Figures 3A and 3B. The DSC diagram of KNO_3 shows the endothermic signals assigned to the crystalline structure change and fusion of the salt at 137 and 335 °C, respectively [35]. In the DSC diagrams of the KNO_3/Cor , $\text{Cu-KNO}_3/\text{Cor}$ and $\text{Co-KNO}_3/\text{Cor}$ catalysts, several endothermic signals can be observed. These signals located at temperatures below 250°C are associated with the loss of water molecules and the change in the crystalline structure of potassium nitrate. The endothermic signals that are between 325 and 350 °C are associated with the fusion of supported KNO_3 . This fusion is corroborated by an exothermic signal that is attributed to the liquid-solid state change when a cooling step, with a gradient of -10 °C/min, follows the heating stage. Both signals of change in the crystal structure and the signals that show the change of state of potassium nitrate are present in the DSC diagrams. The presence of the potassium nitrate salt on the catalytic surface of KNO_3/Cor , $\text{Cu-KNO}_3/\text{Cor}$ and $\text{Co-KNO}_3/\text{Cor}$ catalysts is evident.

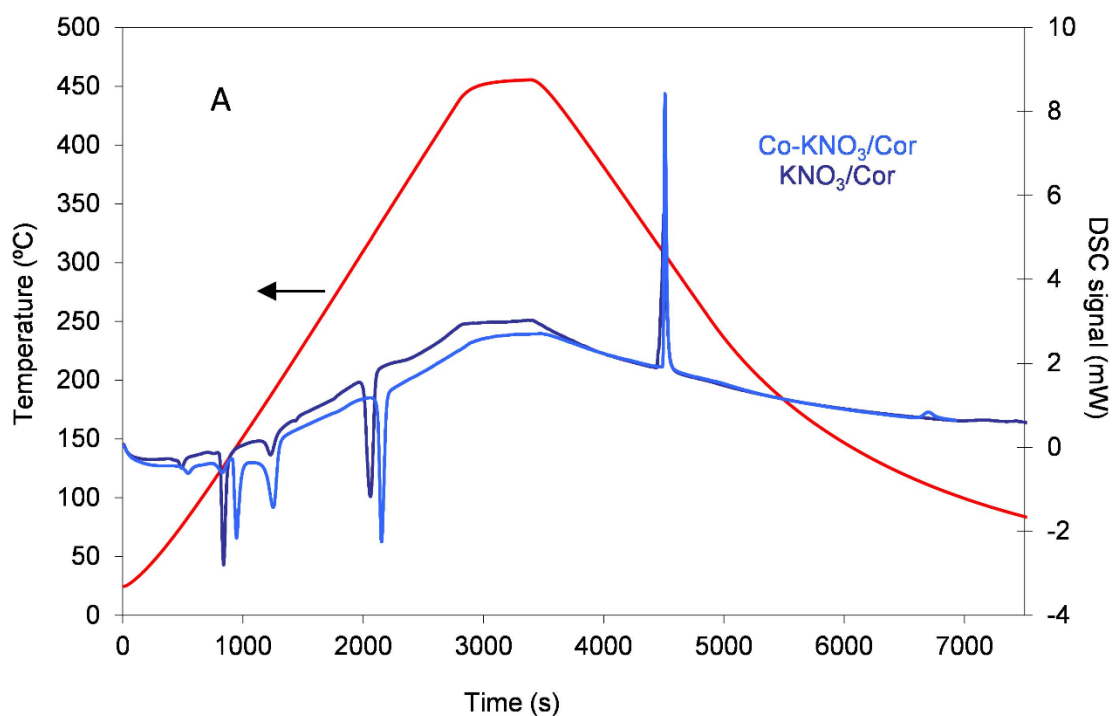


Figure 3A. DSC diagrams of: KNO_3/Cor y $\text{Co-KNO}_3/\text{Cor}$ catalysts.

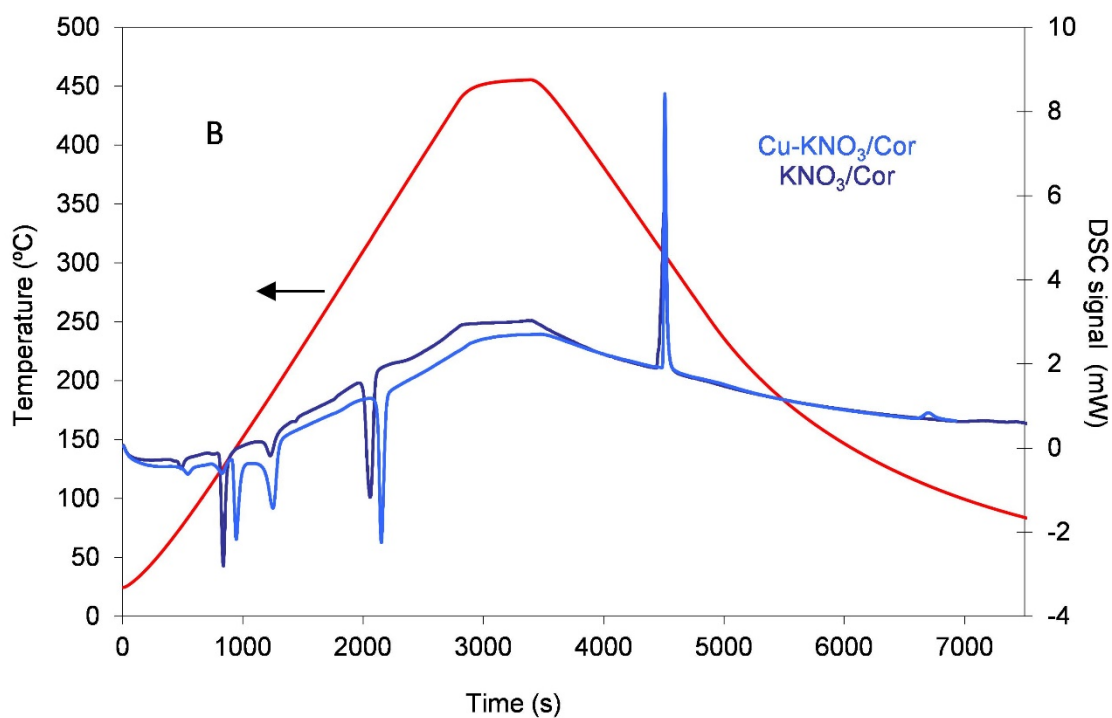


Figure 3B. DSC diagrams of: KNO₃/Cor y Cu-KNO₃/Cor catalysts.

Analyses by FTIR were performed in order to study the presence of nitrogen oxo-species (nitrate ions, nitrite ions) in the catalysts. Figure 4 shows the FTIR spectra of the catalysts and of the cordierite support. In the spectrum of the KNO₃/Cor catalysts (curve b) an absorption band at 1385 cm⁻¹ assigned to antisymmetric N–O stretching of free nitrate species is observed [36]. This band is also observed in the spectra of the catalysts modified with transition metal oxides, Cu-KNO₃/Cor (curve d) and Co-KNO₃/Cor (curve c).

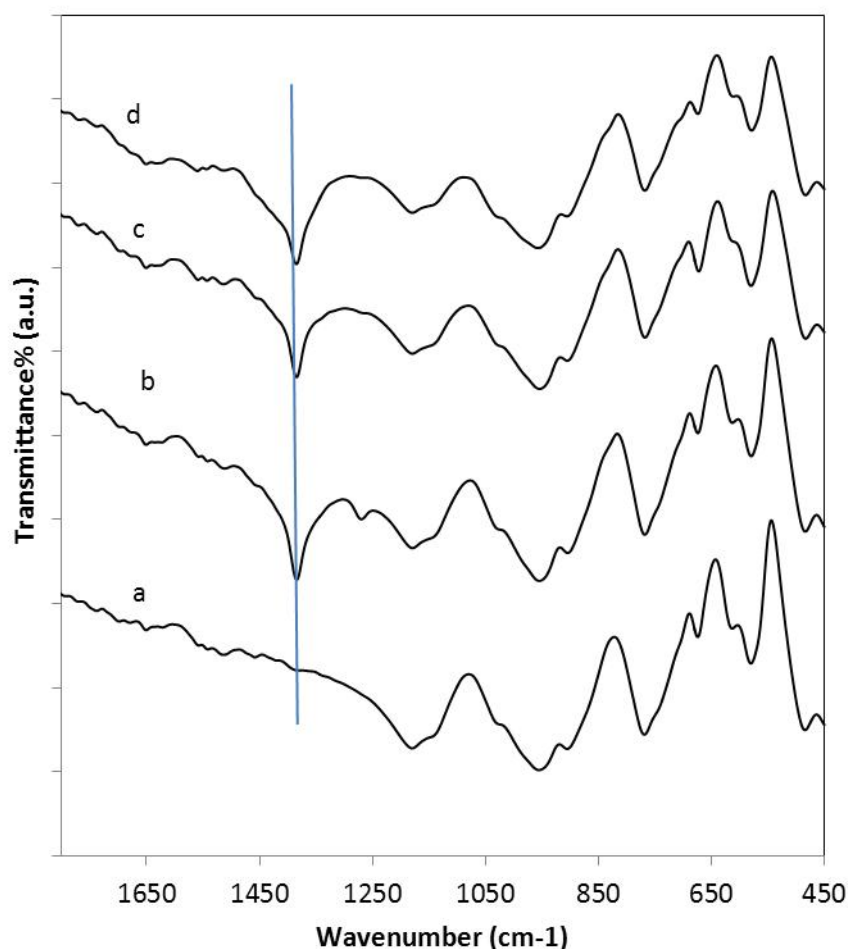


Figure 4. FTIR spectra of catalysts: a) Cordierite, b) KNO_3/Cor , c) $\text{Co-KNO}_3/\text{Cor}$, and d) $\text{Cu-KNO}_3/\text{Cor}$.

The reducibility of the species present in the catalysts was evaluated by means of the hydrogen temperature programmed reduction technique. Figure 5 shows the diagrams of the studied catalysts. The TPR diagram of the unmodified cordierite support (not shown) does not show any signal, which indicates the absence of reducible phases in the studied temperature range. The Cu/Cor catalyst presents a reduction signal between 300 and 360 °C, attributed to the reduction of CuO , since this pure mass oxide reduces between 270 and 380 °C. The reduction profile of Co/Cor catalyst presents a single signal between 330 and 415 °C which is attributed to the reduction Co_3O_4 spinel. This oxide has a reduction profile characterized by two signals, the first one is assigned to the reduction of Co(III) to Co(II) and the second one is assigned to the reduction of Co(II) to Co° (with maxima located at 324 and 397 °C respectively). If the cobalt spinel is supported, the two reduction stages are not resolved in the TPR diagram, as is shown in Figure 5 for the Co/Cor catalyst. The TPR diagram of KNO_3/Cor catalyst presents an important reduction signal between 550 °C and 630 °C, assigned to the potassium nitrate reduction. The potassium nitrate can be reduced with H_2 generating nitrites, nitric oxide or ammonia [27, 35].

The reduction diagram of Cu-KNO₃/Cor catalyst presents a single signal between 515 and 570°C which is attributed to the simultaneous reduction of copper oxide and nitrate ions reduction. It should be noted that the CuO reduction process is not observed as a separate signal and that the nitrate ions reduction occurs at a lower temperature than that observed for KNO₃/Cor catalyst. This behaviour has been reported for other systems containing alkali nitrates and transition metal oxides with a high interaction between both species [37-38]. The Co-KNO₃/Cor catalyst shows a similar behaviour.

In terms of reducibility, copper containing catalysts exhibit lower reduction temperatures than those containing cobalt.

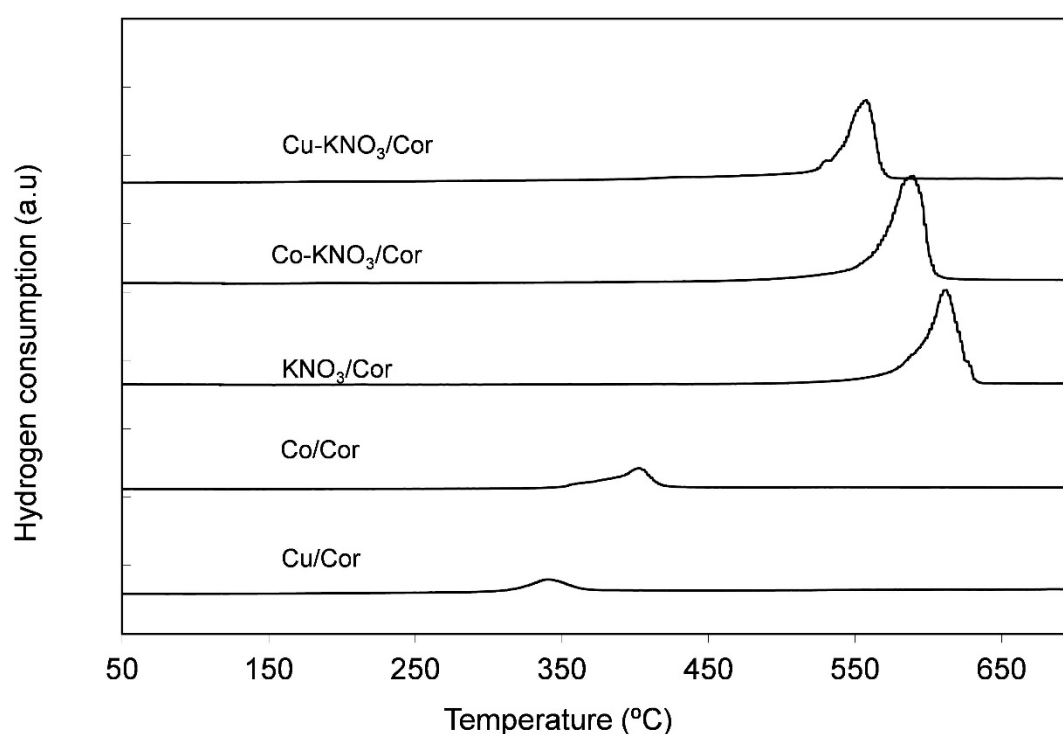


Figure 5. TPR patterns of catalysts.

The results of SEM-EDS microscopy support the idea that the alkaline salt interacts strongly with the oxide. Figure 6 shows an electron scanning micrograph of the Co-KNO₃/Cor catalyst surface with a high magnification. The supported particles correspond to potassium species, fundamentally KNO₃, as corroborated by the semiquantitative analysis of these particles that shows a high concentration of potassium. Besides, the analysis of the particles surrounding the structures containing potassium shows a high concentration of cobalt, and this concentration is considerably higher than the nominal concentration of cobalt (Figure 6A, curve c).

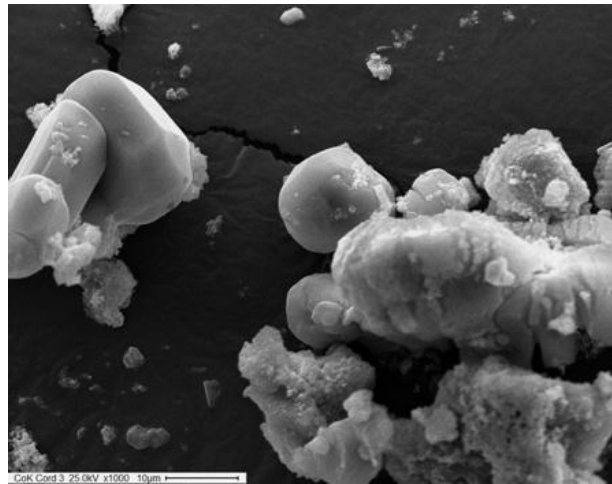


Figure 6A. SEM micrographs. Micrograph of a supported particle on Co- KNO₃/Cor catalyst (x1000).

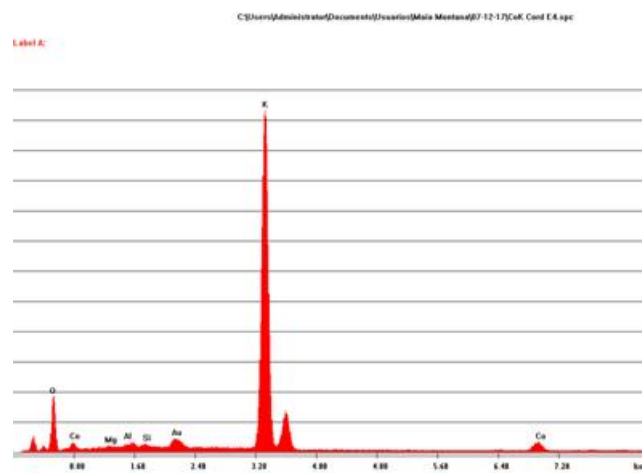


Figure 6B. EDS spectrum of a K rich particle.

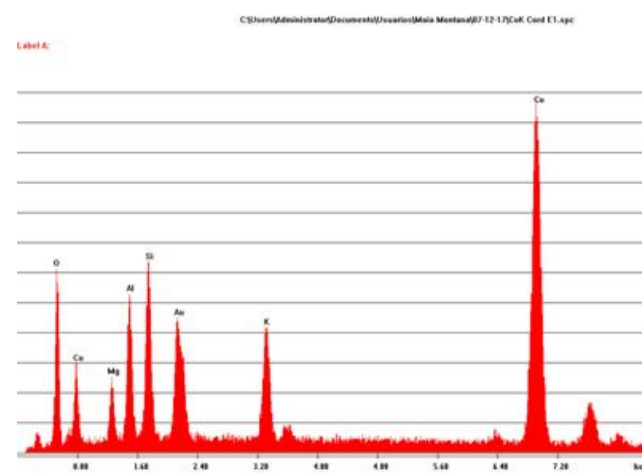


Figure 6C. EDS spectrum of particle surrounding area.

The catalysts were tested in the particulate matter combustion reaction in a fixed-bed reactor. Figure 7 shows the catalytic results obtained using a NO/O₂/He oxidant mixture. Particularly, the mmol of carbon oxides (CO₂ + CO) generated as a function of temperature are shown. From these curves, information about the temperature range at which the catalysts present activity is obtained, as well as the temperature at which the burning speed is maximum (T_{max}), that corresponds to the temperature where CO_x generation presents a maximum. The curve representing mmol CO_x evolution in the absence of a catalyst has a T_{max} around 585 °C (not shown), this temperature decreases considerably (Table 2) when a catalyst is used.

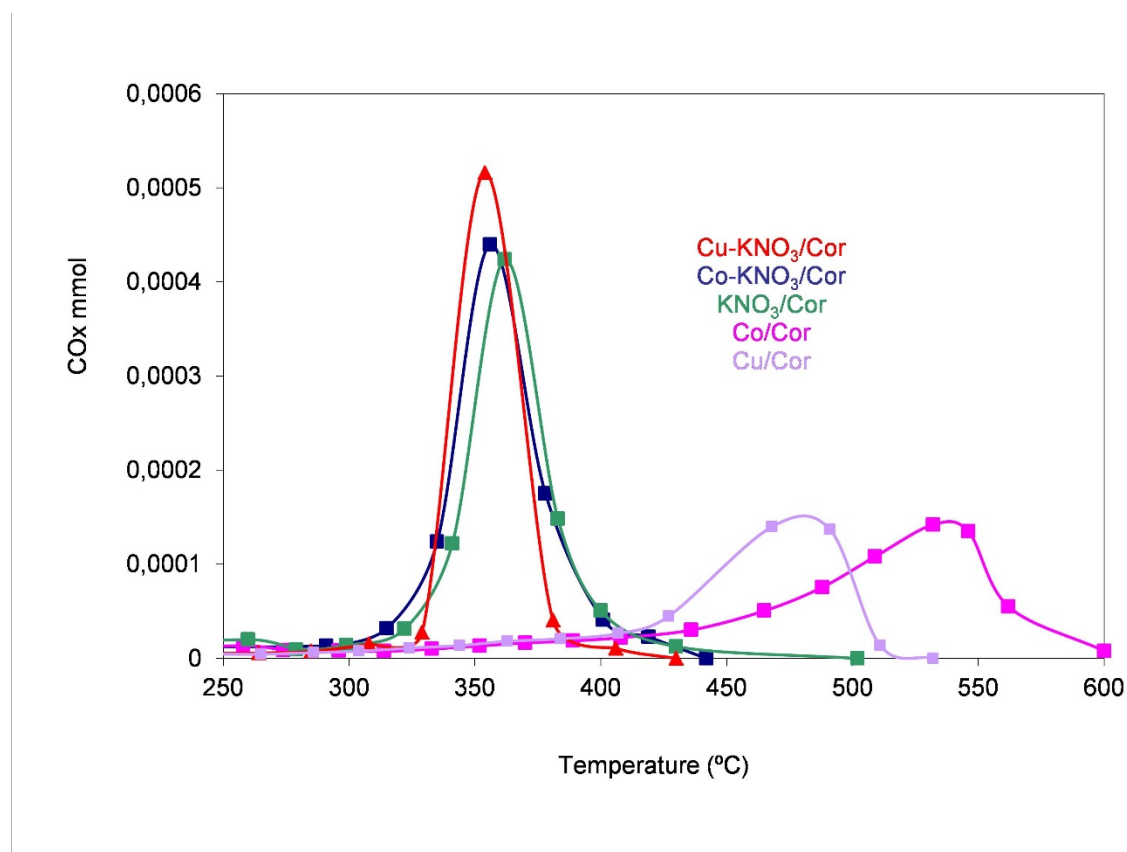


Figure 7. PM combustion curves obtained with the catalysts using a NO/O₂ mixture as an oxidant.

Table 2. T_{max} obtained for particulate matter combustion reactions in NO/O₂ presence.

Materials	T _{max} (°C)
Particulate matter	585
Co/Cor	540
Cu/Cor	468
KNO ₃ /Cor	362
Co-KNO ₃ /Cor	356
Cu-KNO ₃ /Cor	354

The Cu/Cor and Co/Cor catalysts show low activity, having with their T_{max} at 468 °C and 540 °C, respectively. The higher activity of Cu/Cor catalyst can be attributed to its greater reducibility, since, according to the results of TPR, Cu/Cor catalyst presented a signal at a lower temperature than that of Co/Cor catalyst. As previously mentioned, these signals are associated with reduction of supported oxidic species. These oxidic species are capable of absorb oxygen from the gas phase in a reversible surface oxidation process. So, it could be said that the higher catalytic activity obtained with Cu/Cor catalyst is assigned to the presence of species having higher redox capacity in spite of their lower superficial concentration. In addition, both transition elements can provide additional adsorption sites to generate adsorbed NO_x species. These could generate NO_2 , which is more oxidant than oxygen. This type of mechanism has also been proposed for other oxidic systems [12].

The potassium nitrate containing catalysts, KNO_3/Cor , $Co-KNO_3/Cor$ and $Cu-KNO_3/Cor$ present very good activity. With these catalysts, it is possible to reduce considerably the T_{max} (approximately 230 °C) in comparison to that obtained in the reaction without catalyst. Based on these results, the catalysts are active in a temperature range at which the automobiles exhaust pipe operates (150-450 °C).

The addition of transition metals (Cu or Co) does not generate a significant increase in the activity of nitrate containing catalysts. However, its presence is important to improve the selectivity of the materials towards complete combustion. The non-catalyzed reaction shows a selectivity of 57% [27]. This selectivity increases in the presence of the catalysts with potassium nitrate, for example the KNO_3/Cor catalyst shows a 92% selectivity while the $Cu-KNO_3/Cor$ catalyst shows 100% selectivity. A similar result was obtained with $Co-KNO_3/Cor$ catalyst.

Has been reported that potassium superficial species increase the ability of the catalysts to adsorb oxygen and then the reaction proceeds via an oxygen spillover mechanism. This alkali specie also can form compounds with low melting point, which increase the contact between soot and catalyst [27, 29, 39-40].

The activity of the nitrate-containing catalysts is associated with the presence of nitrate ions capable of generating catalytic nitrite-nitrate redox cycles and also to the presence of phases that can melt. Potassium nitrate can provide what is called the catalytic surface wetting effect, due to the low temperature melting point of this salt (335 °C). In the differential scanning calorimetry (DSC) diagrams of KNO_3 -containing catalysts, signals associated with alkali salt fusion could be observed. Catalysts containing salts that can melt close to combustion temperature have a matter particulate-liquid-gas-oxidizing beneficial interface for the

combustion reaction, because the contact between the particulate matter and the catalyst increases [12,13,39].

4. Conclusions

A series of supported potassium nitrate catalysts modified with transition metal oxides were prepared using cordierite as supports. All of them were tested in the particulate matter combustion reaction. These catalysts were characterized by several physicochemical techniques.

Co/Cor and Cu/Cor catalysts present low activity for the catalytic soot combustion reaction. The catalytic activity obtained with these catalysts is assigned to the presence of oxidic species having redox capacity. In addition, Co_3O_4 and CuO supported species can provide additional adsorption sites to generate adsorbed NO_x species and generate NO_2 , which is more oxidant than oxygen.

The high catalytic activity obtained with KNO_3 containing catalysts is assigned to the presence of nitrate ions capable of generating catalytic nitrite-nitrate redox cycles. These catalysts also show the presence of phases that can melt, generate the surface wetting effect and increase the possible effective collisions between soot and catalyst. KNO_3 melting is observed by means of the DSC technique. Temperatures corresponding to the maximum combustion rate (T_{max}) are 362, 356 and 354 °C for KNO_3/Cor , Co- KNO_3/Cor and Cu- KNO_3/Cor catalysts respectively. The T_{max} values decrease more than 200 °C with respect to the temperature of the process without catalyst.

Systems containing KNO_3 and transition metal oxides present a high interaction between both species. However, the addition of CuO or Co_3O_4 does not generate a significant increase in the activity, the copper and cobalt contributions are associated with the reaction selectivity toward the total CO_2 formation. The results obtained are promising due to the low difficulty of the catalysts preparation method and also due to the availability of cordierite in the monoliths form, which can lead to the preparation of structured catalysts.

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