



## Short Communication

Catalysts of alkaline nitrates supported on oxides for the diesel soot combustion. Deactivation by hydro-treatment and CO<sub>2</sub>María Lucía Ruiz <sup>a</sup>, Ileana Daniela Lick <sup>b,\*</sup>, Marta Isabel Ponzi <sup>a</sup>, Esther Natalia Ponzi <sup>b</sup><sup>a</sup> INTEQUI (CONICET-UNSL), 25 de Mayo No 384, Villa Mercedes, San Luis, 5730, Argentina<sup>b</sup> CINDECA (CCT-La Plata-CONICET-UNLP), Departamento de Química, Facultad de Ciencias Exactas, calle 47 No 257, La Plata, Buenos Aires, 1900, Argentina

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## ABSTRACT

The deactivation of supported catalysts CsNO<sub>3</sub> and LiNO<sub>3</sub> for diesel soot combustion is studied in this work. The effect of hydro-treatment at high temperature and presence of CO<sub>2</sub> in feed flow were investigated. Catalysts were characterized by means of X ray diffraction, DSC technique and FTIR. A fixed bed reactor was used to measure activity of fresh and deactivated catalysts with NO<sub>2</sub>/O<sub>2</sub> feed. Thermogravimetric system with air/CO<sub>2</sub> feed was used to study the deactivation with CO<sub>2</sub>.

Catalysts with LiNO<sub>3</sub> were the most resistant to deactivation by hydro-treatment, and they are not deactivated by CO<sub>2</sub>. It is postulated that the cesium nitrate solubilizes in water and is eliminated during the hydro-treatment, instead, lithium species interacted more strongly with the support and generate more resistance species.

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## 1. Introduction

The Diesel soot is the solid fraction emitted by exhaust pipes of Diesel engines. Its main component is carbon, which can be eliminated by total oxidation. Filters of catalytic oxidation are a viable technology for elimination of diesel soot by filtering, retention and subsequent oxidation [1]. The catalytic species that covers filters must be active and stable in the severe conditions present in the exhaust pipe given by water vapor presence, high temperature and presence of other contaminants (CO<sub>x</sub>, NO<sub>x</sub>, SO<sub>x</sub>).

There is abundant information about catalysts used for the reaction of diesel soot combustion [2–17]. Carrascull [9] and Ruiz [10] employed catalysts of alkaline metal nitrates supported on oxides. The soot combustion with supported alkaline nitrates catalysts occurs in a temperature range that presents an exhaust pipe. Then, it is interesting to investigate the deactivation of these catalysts.

Alkaline nitrates increase the contact soot-catalyst due to their low melting point [15,18–22] that generates solid–liquid interfaces.

The reaction steps proposed for these catalysts are the following



Oxygen is given by the anion NO<sub>3</sub><sup>−</sup> and taken from the gas phase by the anion in its reduced state (NO<sub>2</sub><sup>−</sup>).

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Nitrogen oxides present in the gaseous phase can be adsorbed to generate continuously species of high reactivity [15–17].

The precursor calcination of the catalyst containing nitrate can give different cation derivatives and this fact depends on the nitrate stability that is a function of the atomic radius of the cation. For cations with larger radii (K, Cs), alkaline nitrates can remain as supported salts (KNO<sub>3</sub>, CsNO<sub>3</sub>) containing free nitrate ions. Nitrates of cations with smaller radii (Li, Na) can generate oxidic species (e.g. Li<sub>2</sub>O, Na<sub>2</sub>O) able to adsorb nitrogen oxides to give surface nitrite/nitrate species [10]. Nitrogen-oxo species (nitrates, nitrites, etc.) are generated “in situ” from oxides of alkaline metals and nitrogen oxides.

One of the main disadvantages that may appear by the use of supported salt catalysts is the deactivation by loss of the active species by “washing” or dissolution in water vapor present in the gas flow. The interaction salt-support is one of the factors that can modify the deactivation by hydro-treatment.

The aim of this work is to investigate the deactivation of cesium nitrate and lithium nitrate catalysts supported on oxides (SiO<sub>2</sub>, ZrO<sub>2</sub>, nH<sub>2</sub>O and ZrO<sub>2</sub>) when catalysts are exposed to hydro-treatments and to the presence of CO<sub>2</sub>. In order to increase the rate of hydro-treatments, very high temperatures are used compared with the temperature in the exhaust pipe of the engine.

## 2. Experimental

## 2.1. Supports

Three supports were used to prepare the catalysts. Silica (SiO<sub>2</sub>, Aerosil 200, Degusa), monoclinic zirconia (ZrO<sub>2</sub>, Anedra) and a hydrated zirconium oxide prepared at the laboratory.

The hydrated zirconium oxide ( $ZrO_2 \cdot nH_2O$ ) used as a support was obtained from the hydrolysis of zirconium oxychloride,  $ZrOCl_2 \cdot 6H_2O$  (Fluka). Aqueous ammonium hydroxide was added to the zirconium salt solution until pH 10 was reached. Mechanical stirring was used to achieve a good homogeneity. The resulting gel was left to rest for 24 h. The formed precipitate was filtered and washed up to non identification of the ion chloride in the washing water, and finally the material was dried at 110 °C for 24 h. The solid obtained was milled in a mortar and sieved to obtain particle sizes between 0.150 and 0.090 mm.

## 2.2. Preparation of precursors and catalysts

The nominal concentration of nitrate ions in all catalysts was 7.5% w/w (8.34% w/w as lithium nitrate and 23.6% as cesium nitrate).

The support impregnation was carried out with an aqueous solution of alkaline nitrates (4.2% w/v  $LiNO_3$  and 14.1% w/v  $CsNO_3$ ) in a rotovapor equipment operating with a  $T_{bath} = 100$  °C, at a rate of 170 rpm and a vacuum pressure of 500 mm Hg. The aqueous solution used for impregnation was 4.2% w/v for lithium nitrate and 14.1% w/v for cesium nitrate. Precursors were dried at 80 °C for 2 h and subsequently calcined at 600 °C for 1 h. The calcination temperature of precursors was selected approximately 200 °C above the operation temperature of catalysts in an exhaust pipe.

Catalysts are named according to the supported salt and the support used. Z represents the catalyst impregnated on the monoclinic zirconia oxide, Zt the hydrated zirconia oxide and S represents the silica. The nominal concentration of nitrate ions in all catalysts was 7.5% w/w, or 8.34% w/w when expressed as lithium nitrate and 23.6% expressed as cesium nitrate.

## 2.3. Deactivation by hydro-treatments

Hydro-treatments were carried out on samples of fresh catalyst loaded in a quartz reactor fed with an inert (He) gaseous current ( $Q_{Total} = 30$  ml/min) saturated with water vapor (10% vol) for 5 h at 600 °C. In order to name hydro-treated catalysts the letter “h” is used between parentheses at the nomenclature, for example  $CsNO_3Z(h)$  represents the cesium nitrate catalyst supported on monoclinic zirconia hydro-treated.

## 2.4. Stability test

The thermal stability was studied by calcining the catalysts for 10 h at 600 °C. Thermal treatments were carried out on samples of fresh catalyst loaded in a thermogravimetric reactor using a thermobalance (TGA-50 Shimadzu) with an  $O_2/He$  feed ( $60$  cm<sup>3</sup> min<sup>-1</sup>). The mixture composition was: 8%  $O_2$  and helium for balance. In order to name thermal treated catalysts the letter *t* is used between parentheses at the nomenclature, for example  $CsNO_3Zt(t)$ .

## 2.5. Characterization of fresh and hydro-treated catalysts

The lithium or cesium contents in fresh catalysts were determined by atomic absorption spectrometry with an AAnalyst 800 (Perkin-Elmer).

The concentration of nitrates was determined using a colorimetric technique. A sample of 100 mg of catalyst fresh and deactivated was washed several times with tri-distilled water, until nitrate presence was not observed in the washing water and the resulting solution was measured in a colorimeter DR/890 Hach. Results are expressed as % w/w of nitrate ions.

The semi-quantitative analysis of cesium in fresh and hydro-treated catalysts was evaluated by X ray emission spectroscopy (EDAX). Lithium measurements were not performed because the equipment is not sensitive for this element.

Melting points of  $LiNO_3$  and  $CsNO_3$  in precursors and fresh and deactivated catalysts were analyzed by differential scanning calorimetry (Shimadzu DSC-50) calibrated using zinc. The mass used in experiments was 10 mg, nitrogen as carrier gas and the final temperature was 500 °C.

The identification of the crystalline species, in precursors and fresh and deactivated catalysts, was carried out by XRD in Rigaku equipment, model D-Max III C, operating with Cu  $K\alpha$  radiation, Ni filter, 30 KV and 20 mA.

The nitrate anions on precursors and fresh and deactivated catalysts were studied by means of FTIR spectroscopy using a Spectrum RX1 (Perkin-Elmer) equipment. Spectra were recorded at ambient temperature in the 4000–400 cm<sup>-1</sup> range and samples were prepared in form of pills with KBr.

## 2.6. Measurements of catalytic activity

### 2.6.1. Measurements of catalytic activity performed in a fixed bed reactor fed with $NO/O_2$

The soot sample used in this work is synthetic flame soot named Printex-U manufactured by Degussa.

Activity measurements were performed in a fixed bed reactor with  $NO/O_2/He$  feed. A quartz reactor ( $id = 0.8$  cm) was used in simulating conditions near to the ones found in an exhaust pipe (loose contact, NO presence, high space velocity). The mixture composition was 8% v/v of  $O_2$  and 1500 ppm of NO (Total flow = 50 ml/min) and the soot/catalyst sample was mixed with spatula (loose contact). The mass of soot/catalyst (1/10, w/w) loaded in the reactor was 33 mg. The temperature range studied was 200–600 °C and the heating rate 2 °C/min. Reaction products were analyzed with a gas chromatograph Shimadzu model GC-8A equipped with a TCD detector. The separation of products was carried out in a concentric column CTRI of Altech. This system permitted identification and quantification of  $O_2$ ,  $CO_2$  and CO peaks. The amount of oxidized soot was calculated from the chromatographic information of  $CO_2$  and CO. The conversion of soot to COx was 100% in all experiences. The integration of production curves (mmoles de COx vs. temperature) gives similar values of mmoles of carbon burned for all experiments showing that the interval of sample taking used is adequate and the accuracy of  $T_{max}$  informed is estimated about  $\pm 5$  °C.

### 2.6.2. Measurements of catalytic activity with $CO_2/air$ mixture

The soot combustion in presence of  $CO_2$  was made in a thermogravimetric reactor using a thermobalance (TGA-50 Shimadzu) with a heating rate of 10 °C/min and an  $O_2/He$  or  $O_2/CO_2/He$  feed ( $60$  cm<sup>3</sup> min<sup>-1</sup>). The mixture composition was: 8%  $O_2$ , 10% of  $CO_2$  and helium for balance. In order to carry out activity experiments, the soot and the catalyst, in a 1/10 ratio, were milled before introduction into the reactor. The soot mass loss and the temperature were recorded as a function of time. The derivative curve (DTG) was obtained from the mass loss information as a function of time.  $T_{max}$  is the temperature value that corresponds to the maximum combustion rate.

## 3. Results and discussion

### 3.1. Activity of catalysts

#### 3.1.1. Effect of hydro-treatments on activity. Catalytic results obtained in a fixed bed reactor with $NO/O_2/He$ mixture

Experiments were performed under experimental conditions observed in the exhaust pipe of a diesel engine. In vehicles using gasoil, the gases produced contains NO which can promote the catalytic soot combustion [10].

Fig. 1A and B show catalytic results obtained with fresh and hydro-treated catalysts in a fixed bed reactor fed with a  $NO/O_2$  mixture.

Curves represent the combustion evolution of soot as function of the temperature.

The curve corresponding to the combustion reaction of soot in absence of catalyst shows that the temperature of the maximum is 580 °C in NO/O<sub>2</sub> presence. All fresh catalysts containing in their composition cesium nitrate present a good activity, with  $T_{max}$  between 360 and 380 °C [22].

Fresh LiNO<sub>3</sub>Z and LiNO<sub>3</sub>Zt catalysts show good activity with  $T_{max}$  of 367 and 355 °C respectively. LiNO<sub>3</sub>S presents poor activity with  $T_{max}$  of 467 °C. The activity of fresh catalysts supported on zirconia is higher than the activity of LiNO<sub>3</sub>S. The zirconia support can participate in the catalytic cycle regenerating nitrate from nitrite formed during combustion [10].

Fig. 1A shows catalytic results for LiNO<sub>3</sub>S, LiNO<sub>3</sub>Z and LiNO<sub>3</sub>Zt fresh and hydro-treated catalysts. Soot combustion curves obtained with hydro-treated catalysts shift toward higher temperatures. The maximum combustion rate for hydro-treated catalysts occurs approximately at 25 °C above the temperature of fresh catalysts. Catalysts supported on zirconia (LiNO<sub>3</sub>Z and LiNO<sub>3</sub>Zt), after being hydro-treated, present an excellent activity from 350 °C.

Fig. 1B shows catalytic results for fresh and hydro-treated CsNO<sub>3</sub>/Support catalysts and Table 1 shows the temperature value for the maximum combustion rate ( $T_{max}$ ) of all catalysts studied.  $T_{max}$  increase approximately 25 °C when hydro-treated lithium nitrate catalysts are used. Instead  $T_{max}$  increase between 40 and 100 °C for hydro-treated cesium nitrate catalysts.

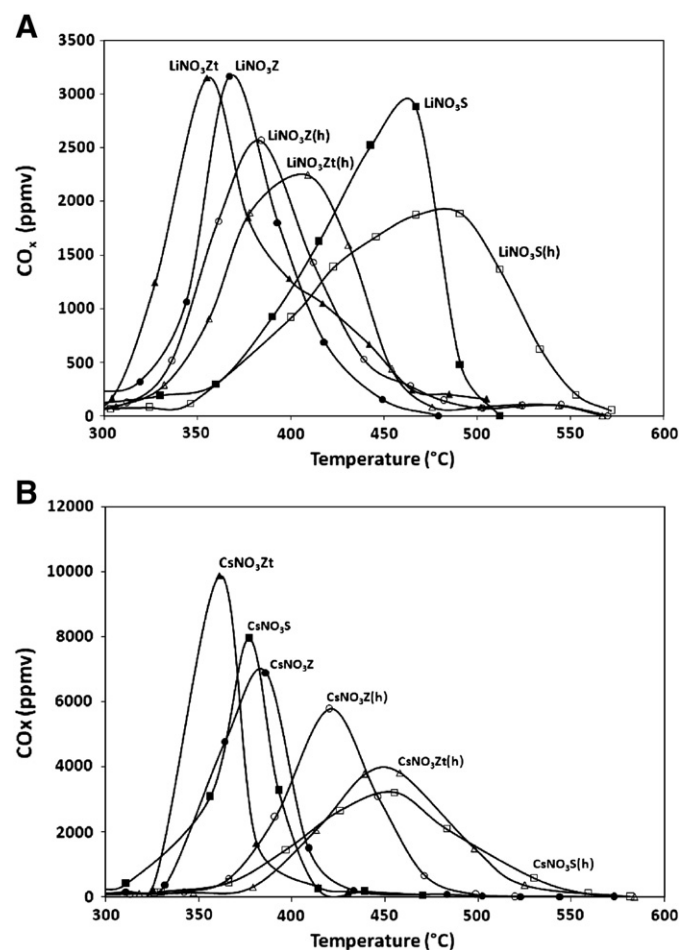


Fig. 1. Activity of fresh and hydro-treated catalysts A) LiNO<sub>3</sub> catalysts and B) CsNO<sub>3</sub> catalysts.

Table 1

Activity of fresh and hydro-treated catalysts. Maximum temperatures obtained in presence of NO/O<sub>2</sub>.

Catalysts	Fresh catalysts	Hydro-treated catalysts	$\Delta T$
	Maximum temperature (°C)		
Printex U	585	–	
LiNO <sub>3</sub> S	467	480	13
LiNO <sub>3</sub> Zt	355	380	25
LiNO <sub>3</sub> Z	367	384	17
CsNO <sub>3</sub> S	377	455	78
CsNO <sub>3</sub> Zt	361	458	97
CsNO <sub>3</sub> Z	380	420	40

### 3.1.2. Catalytic results obtained in a thermogravimetric reactor

3.1.2.1. Effect of CO<sub>2</sub> (10%) on activity. Carbon dioxide is one of the principal components of the gaseous flow in soot combustion. The soot combustion is an irreversible reaction, so it is not expected that carbon dioxide generates reversibility in the combustion reaction, but it can generate any transformation of species present on the catalytic surface. For this reason, combustion experiments with and without CO<sub>2</sub> were carried out using a thermobalance following the weight loss.

Table 2 shows the combustion temperature range of fresh catalysts with and without carbon dioxide in the feed flow.  $T_{max}$  (temperature of maximum combustion rate) is also indicated in each experiment. The CO<sub>2</sub> presence in the feed flow does not affect substantially the activity of cesium nitrate catalysts. The CO<sub>2</sub> increases the activity of all lithium nitrate catalysts with  $T_{max}$  decrease around 30 °C for catalysts supported on zirconia. This effect is attributed to the formation of carbonate-type intermediate with the partially oxidized soot, which then decomposes and releases the CO<sub>2</sub> [23–25].

3.1.2.2. Thermal stability of catalysts. To demonstrate that the same samples can repetitively promote the soot oxidation, fresh CsNO<sub>3</sub>Zt and LiNO<sub>3</sub>Zt catalysts were used in three successive catalytic cycles. Table 3 presents temperatures ( $T_{ini}$ ,  $T_{max}$  and  $T_f$ ) obtained when performing TPO tests in presence of catalysts. In all cases the combustion of soot occurs at much lower temperatures than that of the pure soot ( $T_{max} = 625$  °C).

CsNO<sub>3</sub>Zt and LiNO<sub>3</sub>Zt catalysts show activity after being used three times in reaction evidencing the stability of catalysts during cyclic soot oxidation.

The catalysts calcined at 600 °C for 10 h do not lose their activity.

### 3.2. Characterization of fresh and hydro-treated catalysts

#### 3.2.1. Chemical analyses of fresh catalysts

Table 4 shows the concentration of alkaline ions (lithium or cesium) in fresh catalysts obtained by AAS. In addition, the soluble nitrate concentration obtained by the colorimetric technique (UV–vis) is shown.

The concentration values of alkaline metals (lithium and cesium) determined by AAS are similar to the nominal values, 0.84% w/w in lithium and 16.1% w/w in cesium.

Otherwise, the soluble nitrate concentration in fresh catalysts (7.5% w/w) is markedly lower than the nominal one in the three catalysts LiNO<sub>3</sub>/Support. Since the lithium concentration is similar to the nominal one, it is postulated that part of lithium nitrate has been transformed in lithium oxide, Li<sub>2</sub>O, during the catalyst calcination stage [10]. This decomposition is not complete, part of lithium nitrate remains in the catalyst as lithium nitrate.

The concentration of soluble nitrate ions for cesium catalysts supported on zirconium oxide, CsNO<sub>3</sub>Z and CsNO<sub>3</sub>Zt is similar to the value of the total nominal concentration (7.5% w/w).

**Table 2**  
Catalysts deactivation by CO<sub>2</sub>.

Catalysts	Air/CO <sub>2</sub> /He Flow				Air/He Flow			
	T <sub>ini</sub>	T <sub>max</sub>	T <sub>f</sub>	ΔT <sub>f</sub> -T <sub>ini</sub>	T <sub>ini</sub>	T <sub>max</sub>	T <sub>f</sub>	ΔT <sub>f</sub> -T <sub>ini</sub>
LiNO <sub>3</sub> S	386	493	534	148	407	510	578	171
LiNO <sub>3</sub> Zt	370	420	466	96	361	449	504	143
LiNO <sub>3</sub> Z	351	429	466	115	347	445	489	142
CsNO <sub>3</sub> S	287	410	464	177	295	394	441	146
CsNO <sub>3</sub> Zt	284	385	420	136	295	392	430	135
CsNO <sub>3</sub> Z	273	391	433	160	280	383	426	146

The concentration of the soluble nitrate ion for CsNO<sub>3</sub>S catalyst is lower than the nominal concentration. Two causes can originate a lower concentration of soluble nitrates compared with the total nominal concentration of nitrates. One possibility is the nitrate decomposition of the alkaline metal and the second one is that the nitrate is not in free state but interacted with the support as coordinated species and insoluble nitrates. Since the nitrate concentration is markedly lower than the nominal one, a cesium salt decomposition is suggested giving oxidic species that remain in the catalyst, which explains why the cesium content is similar to the nominal one.

### 3.2.2. X-ray diffraction (XRD) of fresh and hydro-treated catalysts

Fig. 2A shows XRD diagrams of fresh cesium nitrate catalysts on the three supports.

All diagrams of CsNO<sub>3</sub>/support catalyst present diffraction lines of cesium nitrate (2θ = 28.28°; 19.8°). The commercial zirconia used for the preparation of catalysts is of pre-established and monoclinic crystalline structure (2θ = 28.2°; 31.5° and 34.5°). XRD diagrams of CsNO<sub>3</sub>Zt catalyst show diffraction lines of metastable tetragonal zirconia (2θ = 30.5°, 35.2° and 50.7°) and diffraction lines of the monoclinic phase (2θ = 28.2°; 31.5° and 34.5°).

The presence of crystalline cesium nitrate in catalysts is attributed to the high concentration of supported salt and to the absence of chemical transformations of alkaline nitrate during calcination. Diffraction lines of CsNO<sub>3</sub> are more intense in the diagram of CsNO<sub>3</sub>Z catalyst than in diagrams of catalysts CsNO<sub>3</sub>Zt and CsNO<sub>3</sub>S. The CsNO<sub>3</sub>Z catalyst was prepared on a support of low area (8 m<sup>2</sup>/g) leading to a low nitrate dispersion on the surface.

An important decrease of the cesium nitrate signal is observed in XRD diagrams (Fig. 2B) of hydro-treated catalysts.

### 3.2.3. Analysis of differential scanning calorimetry (DSC) in fresh and hydro-treated catalysts

Ruiz et al. [22] reported that DSC diagrams of catalysts CsNO<sub>3</sub>Zt and CsNO<sub>3</sub>Z show an endothermic signal at 414 °C attributed to the melt of supported salt, while in the CsNO<sub>3</sub>S catalyst, the signal is not observed. Fig. 3 shows DSC diagrams of fresh and hydro-treated catalysts, the endothermic signal is not observed in hydro-treated catalyst.

The signal absence can be originated by cesium nitrate loss during the hydrothermal treatment or by a higher interaction of salt with the

**Table 3**  
Thermal stability of catalysts.

Catalysts	Cycles	Air/He flow		
		T <sub>ini</sub>	T <sub>max</sub>	T <sub>f</sub>
LiNO <sub>3</sub> Zt	First cycle	361	449	504
	Second cycle	355	440	503
	Third cycle	362	450	510
CsNO <sub>3</sub> Zt	First cycle	295	392	430
	Second cycle	275	367	398
	Third cycle	277	368	403
LiNO <sub>3</sub> Zt(t)	First cycle	345	437	470
	First cycle	270	395	412

**Table 4**  
Results of chemical analyses of fresh catalysts.

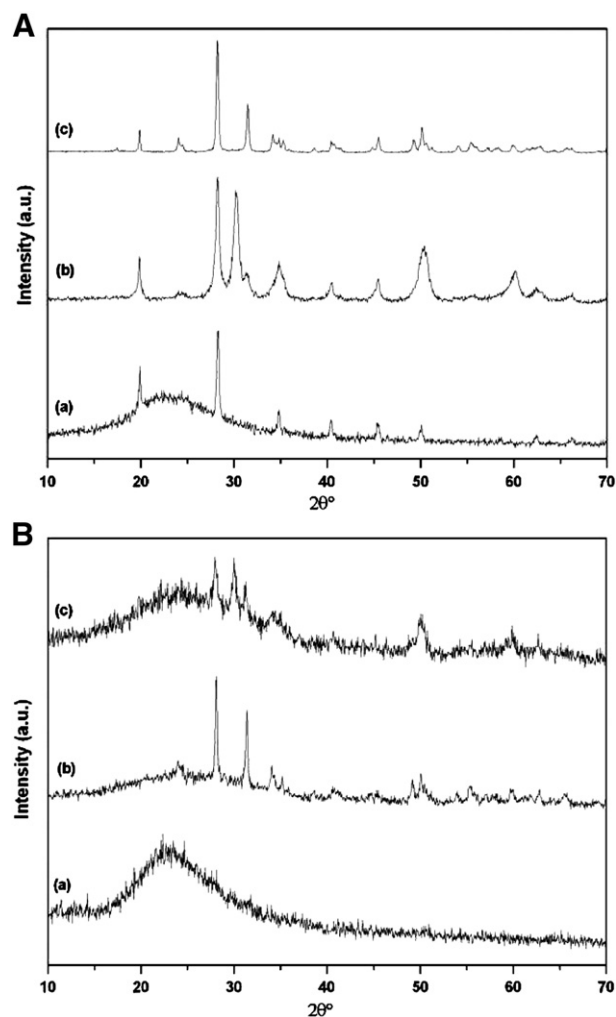
	% alkaline cation	% NO <sub>3</sub> <sup>-</sup>
LiNO <sub>3</sub> S	0.74	0.75
LiNO <sub>3</sub> Z	0.80	0.62
LiNO <sub>3</sub> Zt	0.76	0.45
CsNO <sub>3</sub> S	13.80	1.30
CsNO <sub>3</sub> Z	16.00	7.50
CsNO <sub>3</sub> Zt	14.80	7.90

support. If the salt interacts with the support, free salt properties are lost, and there are no melting peaks. These results agree with the decrease of the cesium nitrate signal in hydro-treated catalysts observed in XRD experiments.

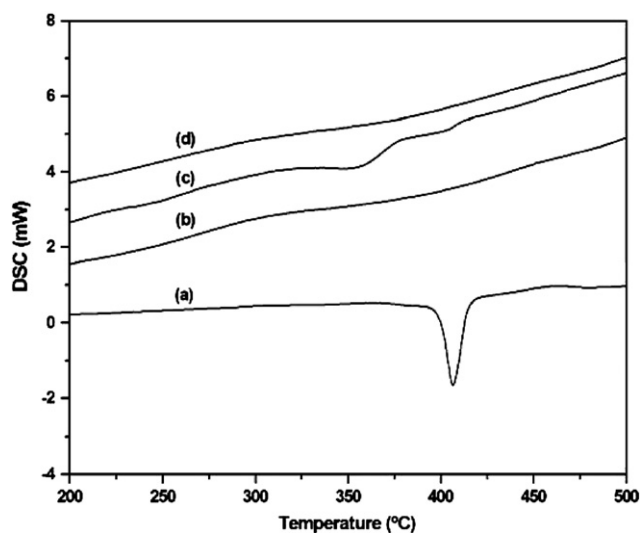
DSC of fresh catalysts LiNO<sub>3</sub>/support does not present the melting signal of LiNO<sub>3</sub> salt. This is attributed to the fact that part of lithium nitrate is transformed during the calcination process into Li<sub>2</sub>O [10] and the rest is not sufficient to present a bulk type behavior.

### 3.2.4. FTIR spectroscopy in fresh and hydro-treated catalysts

The activity of catalysts of alkaline nitrates can be assigned to the presence of nitrate species. The presence and nature of nitrate ions in fresh and hydro-treated catalysts is performed by IR spectroscopy and spectra attained are presented in Fig. 4A and B.



**Fig. 2.** X ray diffraction diagrams. A) Fresh CsNO<sub>3</sub> catalysts: (a) CsNO<sub>3</sub>S, (b) CsNO<sub>3</sub>Z, (c) CsNO<sub>3</sub>Zt. B) Hydro-treated CsNO<sub>3</sub> catalysts: (a) CsNO<sub>3</sub>S(h), (b) CsNO<sub>3</sub>Z(h), (c) CsNO<sub>3</sub>Zt(h).



**Fig. 3.** DSC diagram of catalysts  $\text{CsNO}_3/\text{supports}$  fresh and hydro-treated. (a)  $\text{CsNO}_3\text{Z}$ , (b)  $\text{CsNO}_3\text{Z}(\text{h})$ , (c)  $\text{CsNO}_3\text{Zt}$ , (d)  $\text{CsNO}_3\text{Zt}(\text{h})$ .

Catalysts containing lithium nitrate,  $\text{LiNO}_3\text{Z}$ ,  $\text{LiNO}_3\text{Zt}$  and  $\text{LiNO}_3\text{S}$ , present weak energy absorption bands associated to the antisymmetric N-O vibration of free nitrate ions at  $1385\text{ cm}^{-1}$  and of nitrate ions coordinated with the support ( $1410$  and  $1480\text{ cm}^{-1}$ ) [10].

Spectra of hydro-treated catalysts  $\text{LiNO}_3\text{S}(\text{h})$ ,  $\text{LiNO}_3\text{Z}(\text{h})$  and  $\text{LiNO}_3\text{Zt}(\text{h})$  show only bands associated to the presence of coordinated nitrate ions at  $1410$  and  $1480\text{ cm}^{-1}$ . Absorption bands of free nitrate species disappear. These results suggest that free nitrate ions are eliminated in the hydro-treatment process, while nitrate ions coordinated with the support remain in the catalyst.

Spectra of fresh catalysts  $\text{CsNO}_3\text{Zt}$ ,  $\text{CsNO}_3\text{Z}$  and  $\text{CsNO}_3\text{S}$  show only the presence of free nitrate ions ( $1385\text{ cm}^{-1}$ ). Neither the typical signals of coordinated nitrate species ( $1410$  and  $1480\text{ cm}^{-1}$ ) nor the signal of free nitrite ions ( $1360\text{ cm}^{-1}$ ) are observed in spectra.

Spectra of hydro-treated catalysts  $\text{CsNO}_3\text{S}(\text{h})$ ,  $\text{CsNO}_3\text{Z}(\text{h})$  and  $\text{CsNO}_3\text{Zt}(\text{h})$  show remaining bands of very weak free nitrate ions at  $1385\text{ cm}^{-1}$  and they do not present absorption bands of species coordinated with the support.

These observations show that nitrate species of catalysts prepared with  $\text{LiNO}_3$  result more stable with respect to the hydro-treatment than species present in catalysts containing  $\text{CsNO}_3$ .

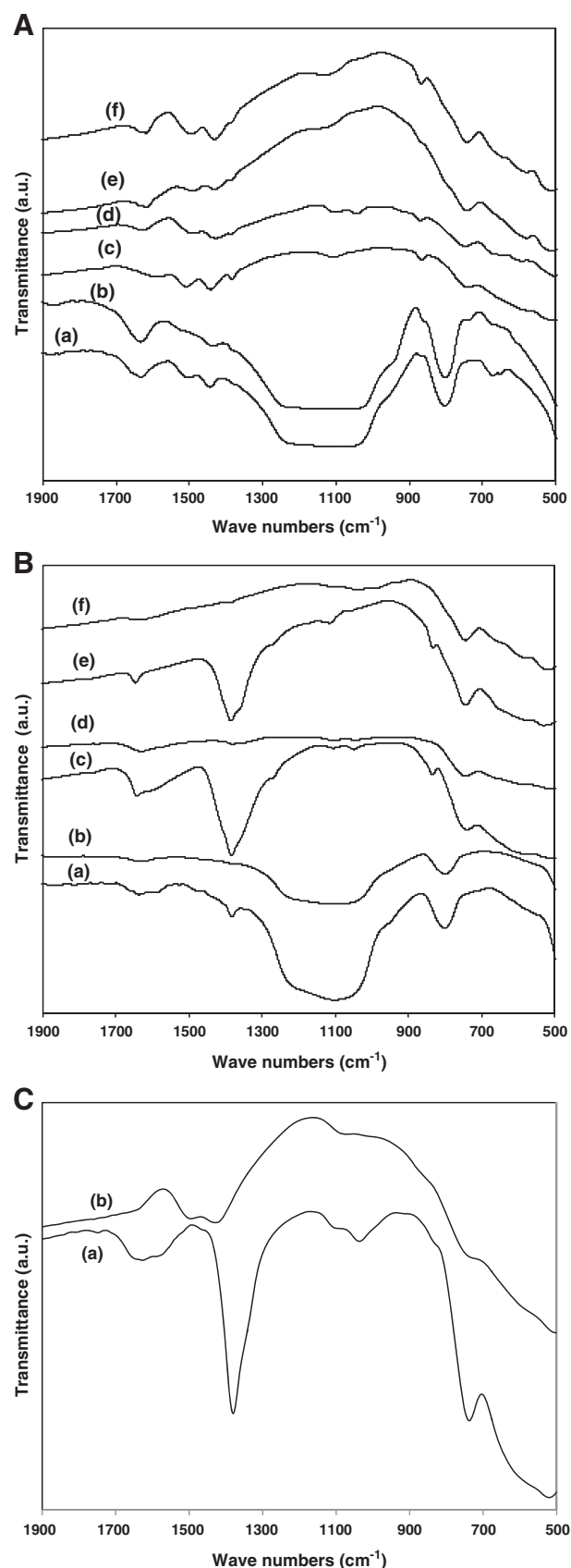
Spectra of thermal treated catalysts,  $\text{LiNO}_3\text{Zt}(\text{t})$  and  $\text{CsNO}_3\text{Zt}(\text{t})$ , are similar to those of fresh catalysts. The  $\text{LiNO}_3\text{Zt}(\text{t})$  catalyst spectrum (Fig. 4C) shows only bands associated to the presence of coordinated nitrate ions. The  $\text{CsNO}_3\text{Zt}(\text{t})$  catalyst spectrum shows bands associated to the presence of free nitrate species. These results suggest that the nitrates species are thermally stable. It to be noted that during the hydro-treatment of catalysts prepared with  $\text{CsNO}_3$  the nitrate species loss should be produced by the presence of water steam in the feed.

### 3.2.5. SEM-EDAX spectroscopy in fresh and hydro-treated catalysts

Table 5 shows atomic ratios Cs/Zr and Cs/Si obtained with fresh and hydro-treated catalysts by means of surface analysis with SEM-EDAX. Results achieved indicate a decrease of the cesium surface concentration after the hydro treatment in catalysts supported on zirconia.

### 3.3. General discussion

The soot combustion without catalyst presents the maximum reaction rate at  $585\text{ °C}$  in  $\text{NO}/\text{O}_2$  presence.



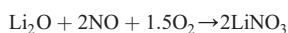
**Fig. 4.** FTIR spectrum of catalysts. A) Fresh and hydro-treated  $\text{LiNO}_3/\text{Support}$  catalysts: (a)  $\text{LiNO}_3\text{S}$ ; (b)  $\text{LiNO}_3\text{S}(\text{h})$ ; (c)  $\text{LiNO}_3\text{Zt}$ ; (d)  $\text{LiNO}_3\text{Zt}(\text{h})$ ; (e)  $\text{LiNO}_3\text{Z}$ ; (f)  $\text{LiNO}_3\text{Z}(\text{h})$ . B) Fresh and hydro-treated  $\text{CsNO}_3/\text{Support}$  catalysts. (a)  $\text{CsNO}_3\text{S}$ ; (b)  $\text{CsNO}_3\text{S}(\text{h})$ ; (c)  $\text{CsNO}_3\text{Zt}$ ; (d)  $\text{CsNO}_3\text{Zt}(\text{h})$ ; (e)  $\text{CsNO}_3\text{Z}$ ; (f)  $\text{CsNO}_3\text{Z}(\text{h})$ . C) Thermal treated catalysts: (a)  $\text{CsNO}_3\text{Zt}(\text{t})$ , (b)  $\text{LiNO}_3\text{Zt}(\text{t})$ .

**Table 5**  
Surface atomic ratios Cs/Zr, Cs/Si, for the series of fresh catalysts Cs/supports.

	Cs/Zr	Cs/Si
CsNO <sub>3</sub> S	–	0.08
CsNO <sub>3</sub> Zt	0.21	–
CsNO <sub>3</sub> Z	0.33	–
CsNO <sub>3</sub> S (h)	–	0.07
CsNO <sub>3</sub> Zt (h)	0.05	–
CsNO <sub>3</sub> Z (h)	0.03	–

All catalysts were prepared with a concentration 7.5% w/w nitrate ion, which corresponds to 0.12 mole of ion (NO<sub>3</sub><sup>-</sup>, Li<sup>+</sup>, Cs<sup>+</sup>) per 100 g catalyst (Table 6).

All fresh catalysts supported on zirconia present the maximum combustion rate between 355 and 380 °C. The activity does not depend on the cation used because NO/O<sub>2</sub> present in the feed flow of reactor can regenerate “in situ” nitrate anions.



The NO<sub>x</sub> adsorption on catalysts with alkali species was also observed by other authors [8,17,26,27].

IR spectrum of LiNO<sub>3</sub>Zt extracted from the reactor after being used in reaction with NO/O<sub>2</sub> shows the formation of nitrate species (Fig. 5). The spectrum of sample extracted from the reactor shows a very intense free nitrate signal, while this signal is weak in the spectrum of the fresh catalyst. Free nitrate bands are also increasing in spectra of catalysts LiNO<sub>3</sub>Z and LiNO<sub>3</sub>S used in reaction with NO/O<sub>2</sub>.

The activity of hydro-treated catalysts depends on alkaline cation (Li or Cs) and the activity decreases in all samples. Hydro-treated LiNO<sub>3</sub>/support catalysts show an increase of maximum combustion rate ( $T_{\text{max}}$ ) lower than 25 °C.  $T_{\text{max}}$  increase is much higher for catalysts prepared with cesium nitrate (CsNO<sub>3</sub>/support), the values are in the range 40 to 100 °C.

In order to explain this behavior, the solubility of different lithium and cesium species is analyzed. Table 6 shows the solubility of lithium and cesium species at two temperatures 0 and 100 °C.

The solubility of cesium nitrate at 100 °C is 10 times higher than the solubility of lithium species. This property of cesium nitrate explains the decrease of Cs/Zr ratio observed in hydro-treated catalysts (Table 4).

During the hydro-treatment, part of cesium nitrate (CsNO<sub>3</sub>) can be solubilized and thus it may be eliminated. Instead, lithium catalysts have species that present lower solubility and they are more stable during the hydro-treatment.

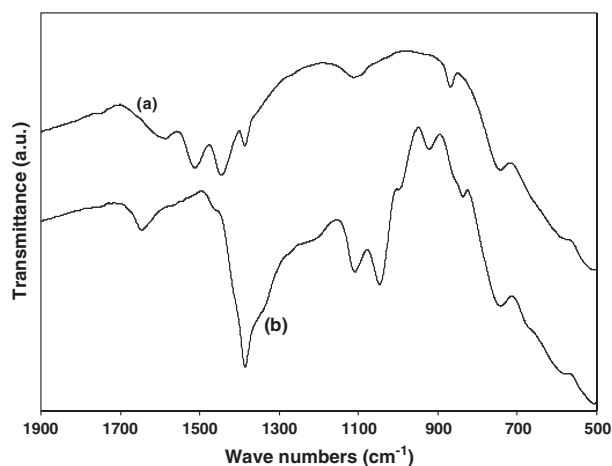
#### 4. Conclusions

Catalysts presented in this work are very efficient in the soot combustion with NO/O<sub>2</sub> mixture. Catalysts supported on zirconia are the most active ones. In these catalysts, in addition to the oxygen in the gas phase, oxygen of zirconium oxide may participate [10] in the reoxidation of nitrite ion ( $2\text{NO}_2^- + \text{O}_2 \rightleftharpoons 2\text{NO}_3^-$ ).

The hydro-treatment process with water vapor and high temperature causes a great deactivation of catalysts prepared with cesium nitrate. The

**Table 6**  
Solubility of lithium and cesium compounds.

Compound	Solubility 0 °C (g/100 ml)	Solubility 100 °C (g/100 ml)
LiO <sub>2</sub>	6.67	10.02
LiOH	12.7	17.5
CsNO <sub>3</sub>	9.16	196.8



**Fig. 5.** Spectrum of fresh and used catalysts LiNO<sub>3</sub>Zt. a) Fresh catalyst and b) sample extracted from the reactor.

same behavior does not happen with those catalysts prepared from lithium nitrate that show high resistance to hydro-treatment.

The hydro-treatment with water vapor does not affect substantially the activity of catalysts that contain lithium nitrate. Surface lithium species can generate (in-situ) nitrate anions from nitrogen oxides (NO<sub>x</sub>). Catalysts with lithium supported on zirconia, independently of its structure, have activity in the temperature range of exhaust pipe (Temperatures lower than 450 °C).

CsNO<sub>3</sub>/support hydro-treated catalysts, CsNO<sub>3</sub>Zt(h), CsNO<sub>3</sub>Z(h) and CsNO<sub>3</sub>S(h), present the  $T_{\text{max}}$  shifted toward higher temperature. The series prepared with the cesium cation results less resistant to hydro-treatment than the series prepared with the lithium cation. This phenomenon is attributed to the high solubility of cesium nitrate that at 100 °C is 10 times higher than the solubility of lithium species.

The CO<sub>2</sub> presence in the feed does not modify substantially the activity of catalysts for the combustion.

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