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Catalytic combustion of particulate matter
Catalysts of alkaline nitrates supported on hydrous zirconium

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Abstract

In order to explore a method to remove particulate matter, catalysts of different alkaline nitrates (Li, K and Cs) supported on hydrous zirconium were prepared by the method of incipient humidity and tested as catalysts for particulate matter combustion. The catalytic activity was determined by using the temperature programmed oxidation technique (TPO), utilizing two equipments, a thermogravimetric reactor and other of fixed bed. In the first case the particulate matter/catalyst mixture was milled carefully in a mortar (tight contact) while in the second case more realistic operative conditions were used, particulate matter/catalyst mixture was made with a spatula (loose contact). All prepared catalysts showed good activity for the particulate matter combustion. The cesium catalyst was the one that presented higher activity, decreasing the combustion temperature between 200 and 250 °C with respect to the combustion without catalyst. The catalyst with lithium nitrate became active at higher temperature than its melting point and the same occurred with the potassium catalyst. This did not occur for the catalyst containing cesium nitrate that melts at 407 °C and became active from 350 °C.

Keywords: Soot; Hydrous zirconium; DSC; TGA; Alkaline metals

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1. Introduction

Diesel engines are used on a large scale for transportation purposes. The particulate matter (soot) amount emitted by diesel engines is much larger than that emitted by otto engines equipped with catalytic converters. This pollutant is hazardous to human health due to its potential mutagenic and carcinogenic activity and to their small size, can penetrate into the lung.

In order to reduce emissions of particulate matter it is possible to use alternative combustibles or special devices to reduce particulate of exhaust gases. Exhaust gases of the engine have a temperature range from 150 to 400 °C. As the particulate matter combustion temperature is much higher than the operational temperature found in the exhaust pipe, the particulate matter combustion temperature must be decreased and consequently active catalysts must be developed in such temperature levels [1,2].

In general, the search for the ideal soot oxidation catalyst is performed by contacting supported active phases (oxides, salts, metals) with particulate matter. Diverse supports have been reported: Al_2O_3, SiO_2, TiO_2 and ZrO_2 [3–5]. The ZrO_2 that presents redox properties has been mentioned as a material moderately active to the particulate matter combustion.

Concerning the active phases, different metal oxides have been proposed, such as Cu, V, Cr, Co, Mn. Also, several catalysts for the combustion of the particulate matter by using alkaline metals as promoter are cited [3,6–12].

In studies presented during last years, the importance of a good contact particulate matter–catalyst is shown [13]. In this sense, molten salt catalysts with compounds that melt at temperatures near to the ones of the soot oxidation, for example, alkaline nitrates were studied [7]. Consequently, it is important to design catalysts of active phases with wetting capacity.

We have previously shown that KNO_3/ZrO_2 catalysts are active for the combustion of diesel soot [7,14]. The aim of

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this work is to analyze the effect of MNO_3 (M = Li, K, Cs) on the rate of particulate matter catalytic combustion.

2. Experimental

2.1. Preparation and characterization of catalysts

The hydrous zirconium was obtained by hydrolysis of zirconium oxychloride, $ZrOCl_2 \cdot 6H_2O$ (Fluka). For this, the necessary amount of ammonium hydroxide solution (tetrahedron 28%) was added to the zirconium oxychloride up to reaching pH = 10. To obtain a higher homogeneity, the solution was stirred with a mechanical stirrer. The precipitate was then filtered and washed until the presence of chloride ions was not observed, thus, verifying the absence with $AgNO_3$, and later on the hydrolysis product was dried at 80 °C for 24 h.

Catalysts containing nitrate of alkaline metals Li, K and Cs were prepared by impregnating the hydrous zirconium with an aqueous solution of the respective nitrates using the necessary amount of solution for the filling of the support pores. In all cases the hydrous zirconium impregnated with the salt was dried at 80 °C for 24 h. These materials were used without subsequent treatment when TPO experiments were performed in the flow reactor, but on the other hand, these materials were dried up to 600 °C before their use in the thermogravimetric reactor to eliminate signals of weight change that may mask the combustion measure of the particulate matter. Catalysts were prepared with a 7.0% content expressed as grams of nitrate ion in 100 g of catalyst.

The differential scanning calorimetry (DSC) was carried out in a Shimadzu equipment, model DSC-50 and was used to study the melting of the respective nitrates of alkaline metals in catalysts, utilizing an inert gas flow (N_2). Studies of weight loss as a function of time were performed in a thermobalance Shimadzu model TGA-50H, in helium current.

2.2. Activity measurements

Two equipments were used to carry out catalytic experiments. A thermogravimetric reactor [15] with an air and inert feed and a reactor of fixed bed utilizing a feed of oxygen, nitric oxide (NO) and He.

In the first case, the particulate matter combustion was performed in a thermobalance with a heating rate of 10 °C/min and an air/He current (2:1). In order to carry out the activity experiments, the particulate matter (Printex-U) and the catalyst, in a 1/100 ratio, were milled carefully in an agate mortar before introduction into the reactor. The weight loss and the temperature were recorded as a function of time. From the weight loss information as a function of time, the derivative curve (DTGA) was obtained and from it the temperature at which the combustion starts, as well as the temperature where the combustion rate is maximum. The following method was used to avoid the overlapping of the weight loss generated by catalyst transformations during TPO experiment with the signal of particulate matter burning. First, the catalyst was calcined in the thermobalance with a heating rate of 10 °C/min an air/He current (2:1). Then, the catalyst was cooled in the same current, it was removed from the thermobalance and milled with the particulate matter to perform the TPO experiment.

In the second case, a microreactor constructed in quartz (i.d. = 0.8 cm) was used, electrically heated and the temperature measured by a thermocouple of K type, in contact with the catalytic bed. The reaction mixture was obtained from three lines controlled individually: NO/He, O_2/He and He to close the balance. The mixture composition was 1500 ppm of NO and 8% of O_2 and the volume 50 ml/min. The mass of particulate matter/catalyst (1/10) loaded in the reactor was 33 mg, the temperature range studied between 200 and 700 °C and the heating rate 2 °C/min. Reaction products were analyzed with a gas chromatograph Shimadzu model GC-8A provided with a detector TCD. The separation of products was carried out in a concentric column CTRI of Altech. This system allowed to identify and quantify O_2, N_2, CO_2 and CO peaks. The amount of burnt particulate matter was calculated from the chromatographic information of CO_2 and CO.

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 shows DSC curves of the ($ZrO_2 \cdot nH_2O$) support and of catalysts. In the support, two signals are observed (400 and 440 °C) attributed to the transformation of the amorphous zirconium oxide to the crystalline phases tetragonal and monoclinic. In the three catalysts, a well-defined signal is

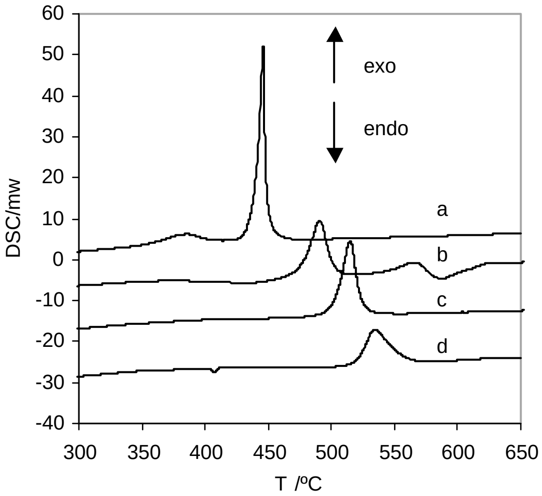

Fig. 1. DSC of catalysts, mass 10 mg, N_2 20 ml/min, ΔT 20°/min: (a) $ZrO_2 \cdot nH_2O$; (b) $LiNO_3/ZrO_2 \cdot nH_2O$; (c) $KNO_3/ZrO_2 \cdot nH_2O$; (d) $CsNO_3/ZrO_2 \cdot nH_2O$.

Table 1
Melting point of different nitrates of alkaline metals

Catalyst	Nitrate ion (%)	MNO_3 (%)	Melting point MNO_3[a]	Experimental melting point
$LiNO_3/ZrO_2{\cdot}nH_2O$	7.0	7.78	264	–
$KNO_3/ZrO_2{\cdot}nH_2O$	7.0	11.4	334	–
$CsNO_3/ZrO_2{\cdot}nH_2O$	7.0	22.1	414	406

[a] CRC Handbook of Chemistry and Physics, 58th ed., CRC Press Inc.

observed that may be attributed to the amorphous–crystalline transformation of the zirconium oxide, this transformation occurs at higher temperature as the atomic number of metal increases (490, 520 and 540 °C).

Table 1 shows values found in the bibliography of the melting point of each of the nitrates used in the preparation of catalysts and the experimental value. The melting is only observed clearly in the $CsNO_3/ZrO_2{\cdot}nH_2O$ catalyst. Since all catalysts were prepared with the same nitrate ion concentration, the cesium catalyst is the one with higher salt percentage (22%). The signal absence in the other two catalysts can be attributed to several causes, one of them is that the salt mass present in the sample used for the DSC experiment is insufficient to detect the melting. Other possibility is that the salt is very dispersed on the support or interacted with the support and that these facts impede the salt melting.

Fig. 2 shows diagrams of thermogravimetric experiments performed with the support and MNO_3. In Table 2, weight losses are indicated up to 650 and 750 °C for components of catalysts in individual form, support ($ZrO_2{\cdot}nH_2O$) and salts ($LiNO_3$ and $CsNO_3$) as well as for catalysts ($LiNO_3/ZrO_2{\cdot}nH_2O$ and $CsNO_3/ZrO_2{\cdot}nH_2O$). The weight loss for catalysts is estimated supposing that the support and the salt behave as independent entities.

The prediction of percentage weight loss of the catalyst corresponding to the support was calculated as follows:

$$\%\ \text{weight loss of support} \times \%\ \text{of support in the catalyst}$$

For example, for the $LiNO_3/ZrO_2{\cdot}nH_2O$ catalyst and for the experiment up to 650 °C, the prediction of percentage weight loss of the catalyst corresponding to the support was calculated as

$$26.9 \times \frac{100 - 7.78}{100} = 24.8$$

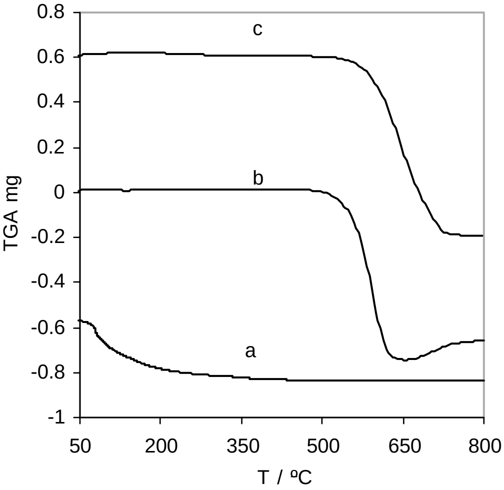

Fig. 2. TGA of MNO_3 and support, mass 1 mg, He 20 ml/min, ΔT 20°/min: (a) $ZrO_2{\cdot}nH_2O$; (b) $LiNO_3$; (c) $CsNO_3$.

The prediction of percentage weight loss of the catalyst was calculated as follows:

$$\%\ \text{weight loss } MNO_3 \times \%\ MNO_3 + \%\ \text{weight loss of support} \times \%\ \text{support}$$

For example, for the $LiNO_3/ZrO_2{\cdot}nH_2O$ catalyst and for the experiment up to 650 °C the prediction of percentage weight loss of the catalyst was calculated as

$$\frac{75.0 \times 7.78}{100} + 26.9 \times \frac{100 - 7.78}{100}$$

When the calcination is carried out up to 650 °C, the weight loss of both catalysts coincides with the weight loss corresponding to the support. This would indicate that in both cases the salt does not decompose up to that temperature. However, when the calcination is made up to 750 °C, the situation is different for the two catalysts. The lithium catalyst presents again a weight loss equivalent to the support, which would indicate that even at this temperature the lithium salt does not decompose. Instead, in the cesium catalyst, a weight loss is already observed (29.8%) that overcomes to the one corresponding only to the support (21%) but it is lower than the value corresponding to the salt decomposition (bulk) up to that temperature (38.6%). Salt decomposition up to 650 °C

Table 2
Transformations of support, of MNO_3 and of catalysts containing lithium and cesium

Catalyst	MNO_3 (%)	Percentage weight loss (experimental)		Percentage weight loss of the catalyst corresponding to the support (prediction)		Percentage weight loss of the catalyst (prediction)	
		650 °C	750 °C	650 °C	750 °C	650 °C	750 °C
$ZrO_2{\cdot}nH_2O$	–	26.9	27.0				
$LiNO_3$	100	75.0	68.2				
$CsNO_3$	100	44.7	79.5				
$LiNO_3/ZrO_2{\cdot}nH_2O$	7.78	24.9	25.1	24.8	24.9	30.6	30.2
$CsNO_3/ZrO_2{\cdot}nH_2O$	22.1	20.1	29.8	20.9	21	30.8	38.6

Catalyst mass: 10 mg.

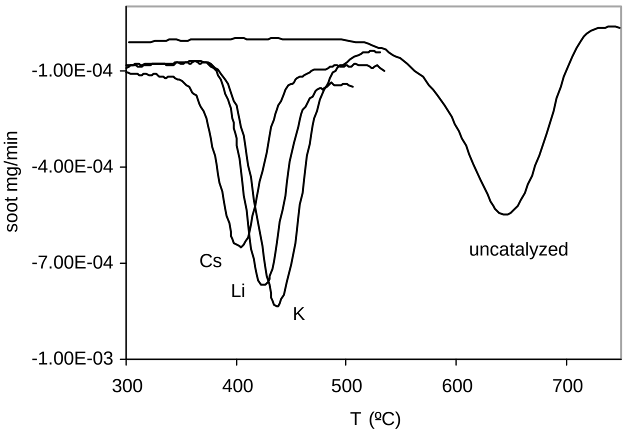

Fig. 3. TPO of soot/catalyst (1/100) carried out in thermogravimetric reactor: (Li) $LiNO_3/ZrO_2 \cdot nH_2O$; (K) $KNO_3/ZrO_2 \cdot nH_2O$; (Cs) $CsNO_3/ZrO_2 \cdot nH_2O$.

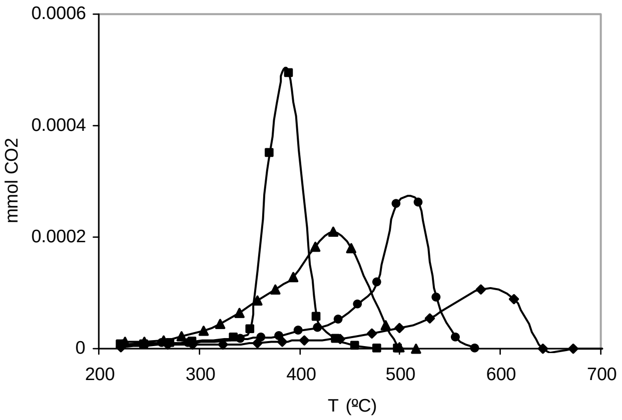

Fig. 4. TPO of soot/catalyst (1/10) carried out in reactor of fixed bed, catalyst mass and soot 33 mg, gaseous feed (NO) 1500 ppm, O_2 8%: (◆) uncatalyzed; (●) $LiNO_3/ZrO_2 \cdot nH_2O$; (▲) $KNO_3/ZrO_2 \cdot nH_2O$; (■) $CsNO_3/ZrO_2 \cdot nH_2O$.

is not observed for the cesium catalyst, while for the lithium catalyst, the decomposition is not observed up to 750 °C.

The higher lithium catalyst stability can be originated in the smaller size of lithium ion allowing to diffuse into the hydrous zirconium support. The cesium may be difficult to diffuse by its larger size and remains as cesium nitrate salt, that at high temperature could be volatilized.

3.2. *Activity measurements*

Fig. 3 presents TPO results performed in the thermogravimetric reactor. In this experiment, a low soot/catalyst ratio was used and the soot/catalyst mixture was carefully milled in mortar (tight contact). With TPO information, the initial combustion temperature as well as the temperature, where the combustion is maximum were calculated.

All catalysts increase considerably the activity for the combustion of particulate matter, in the case of the catalyst containing cesium, the maximum rate temperature decreases around 250 °C if it is compared with the combustion without catalyst. For the other two catalysts the temperature decrease is lower (210–220 °C). Results show that the initial combustion temperature registers the lowest value (364 °C) for the $CsNO_3/ZrO_2 \cdot nH_2O$ catalyst.

Under these experimental conditions (tight contact), the initial combustion temperature is the same for catalysts containing lithium and potassium and lower for the catalyst containing cesium. The higher activity of catalyst containing cesium can be attributed to its higher electropositive character. In catalysts containing lithium and potassium opposed effects can appear, on one hand, potassium is more electropositive than lithium and increases the combustion rate, but the potassium nitrate melts at higher temperature than the lithium nitrate. The intimate contact between the particulate matter and the catalyst would be more important for the catalyst with lithium nitrate.

As previous TPO experiments in the thermogravimetric reactor were very far from conditions of soot burning of a diesel engine in a filter with catalyst, the study was complemented with TPO experiments under experimental conditions nearer to the real ones. The soot/catalyst ratio was increased, the mixing was made with spatula (loose contact) and besides in the gaseous current one of the present contaminants in the exhaust gases was added, the nitrogen oxide. All these factors make slower the reaction rate of soot burning, the catalyst amount decreases, the contact is deteriorated and a contaminant is added affecting the combustion rate.

Setiabudi et al. [16] studied the NO influence using catalysts containing metal (Pt/γ-alumina) and molten salts ($Cs_2SO_4 \cdot V_2O_5$). When they used the Pt/γ-alumina catalyst, the NO presence increased the activity and the mechanism proposed was the NO oxidation with oxygen in presence of metal to give NO_2. Instead, the NO presence decreased the catalyst activity with molten salts although the activity decrease was slight. With the catalysts of molten salts used by authors the reaction between NO and oxygen did not occur to give NO_2 considered as an oxidant agent of soot stronger than oxygen.

Fig. 4 shows results of the soot combustion performed in the flow reactor with operative conditions nearer to the ones found in the exhaust gases of a diesel engine. The formation rate of CO_2 was used as a measure to evaluate the activity of catalysts. TPO diagrams are shown and result from the particulate matter combustion utilizing a soot/catalyst ratio 1/10, loose contact and a gaseous feed containing nitrogen oxide (1500 ppm of NO and 8% of O_2).

Results show that the temperature at which the combustion rate is maximum (T_{max}) for the combustion without catalyst is around 600 °C, while when catalysts are used that temperature decreases between 100 and 200 °C.

The soot combustion using the $CsNO_3/ZrO_2 \cdot nH_2O$ catalyst occurs in the temperature range between 350 and 450 °C. For this temperature range the support is found in amorphous form and from 400 °C the salt is molten. The soot combustion with the $KNO_3/ZrO_2 \cdot nH_2O$ catalyst occurs in the temperature range between 300 and 500 °C. The only visible transformation in DSC in this temperature range is the amorphous crystalline transformation that occurs from 400 °C and ends at 525 °C. Finally, the combustion with the $LiNO_3/ZrO_2{\cdot}nH_2O$ catalyst is carried out between 350 and 570 °C. When the combustion starts with this catalyst, the support is found even in amorphous form and when it ends (570 °C) the support is already crystallized.

In the bibliography, the activity increase of the particulate matter combustion by catalysts containing alkaline metals is attributed to the electropositive character. Catalysts used in operative conditions similar to the one of a diesel engine exhaust present higher activity when the electropositive character of the metal is higher, and the most active is the catalyst containing cesium nitrate.

4. Conclusions

Catalysts of nitrates of alkaline metals supported on hydrous zirconium are active for the combustion reaction of the particulate matter. Under operative conditions similar to the catalyst behavior in the engine (loose contact) and in presence of nitrogen oxide, the activity correlates with the electropositive character of the metal. The cesium nitrate catalyst presents a combustion temperature of 364 °C within the values required for the catalyst to operate in the real case of an automobile. Besides, it does not present salt loss in dry calcination treatments up to 650 °C.

Catalysts studied are thermally stable up to 650 °C. When the lithium catalyst is calcined up to 750 °C the weight loss coincides with the weight loss corresponding to the support, which indicates that the support has stabilized in some way to the lithium salt and impedes its decomposition or volatilization. The same occurs for the precursor that contains $CsNO_3$, but the stability in this case is only verified up to 650 °C.

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