

## Catalytic combustion of soot with a O<sub>2</sub>/NO mixture. KNO<sub>3</sub>/ZrO<sub>2</sub> catalysts

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### Abstract

Catalysts containing 0.25–20% KNO<sub>3</sub> supported on ZrO<sub>2</sub> have been studied for diesel soot combustion. The addition of KNO<sub>3</sub> to ZrO<sub>2</sub> support enhances its activity due to the increased contact between soot and catalyst and also because the KNO<sub>3</sub> acts as catalyst. The combustion temperature has been measured for “loose” and “tight” contact, between soot and catalyst, and the difference was 10 K for KNO<sub>3</sub>(20)/ZrO<sub>2</sub> catalyst. This finding is very important because under practical conditions the contact between soot and catalyst is poor and this contact resembles the contact denoted as “loose contact”.

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### 1. Introduction

Emissions of nitrogen oxides (NO<sub>x</sub>) and particulate soot from diesel engines represent a severe environmental problem. The soot and NO<sub>x</sub> contribute to a great extent to the environmental pollution especially in urban areas. Soot emissions can be reduced by placing an oxidation catalyst within the exhaust stream.

The surface mobility of atoms is a key factor in the oxidation of soot with oxygen [1]. Several authors have reported that transition metal oxides

with low melting point are active catalysts in the combustion of diesel soot [2,3]. The performance of CuO-based catalysts in the soot oxidation has been also attributed to the high mobility of the copper ions during burn-off [4].

The beneficial influence of a good contact between the soot and catalyst on the soot oxidation rate has been pointed out by several authors [5–7].

The three-component soot–O<sub>2</sub>–NO reaction over CuFe<sub>2</sub>O<sub>4</sub> catalyst was investigated by Shangguan et al. [8]. Cu containing catalysts have been found active for reduction of nitric oxide by solid carbonaceous materials under lean conditions [9]. Potassium and some first series transition metals (Fe, Cu, Co, Ni) were used as catalysts for

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NO<sub>x</sub> reduction by activated carbons and soot [10,11]. In the first of these tasks the catalyst was impregnated on the activated carbon and in the work of Miró et al. the mixture of catalyst and soot was carefully prepared.

In general the samples which were prepared with spatula have a low activity, while samples prepared with mills and mortars have high activity. Van Setten et al. [12] evaluated different methods for bringing the soot in physical contact with the catalyst to determine which method gives a realistic contact.

In this work catalysts with variable content of potassium nitrate supported on zirconium oxide were studied. In this work samples were prepared in two different ways, by mixing in an agate mortar “tight contact” and by mixing with a spatula “loose contact” and nitrogen oxide was added in the feed.

## 2. Experimental

### 2.1. Catalysts

The zirconium hydroxide was obtained by hydrolysis of zirconium oxychloride, ZrOCl<sub>2</sub> · 6H<sub>2</sub>O (Fluka). The necessary amount of ammonium hydroxide (Tetrahedron 28%) was added to the zirconium oxychloride to reach a pH 10. The product obtained by hydrolysis was filtered and washed up to the nonidentification of the ion chloride in the washing water, and finally the material was dried at 353 K for 24 h.

Catalysts containing potassium nitrate were prepared by impregnation of the zirconium hydroxide with an aqueous solution of KNO<sub>3</sub> using the necessary amount of solution to fill the pore volume of the support. In all cases the zirconium hydroxide impregnated with salt was dried at 353 K for 24 h. To obtain catalysts, precursors were calcined at 873 K for 2 h. Catalysts were prepared with a variable potassium nitrate content between 0.25% and 20% which will be named generically KNO<sub>3</sub>(*n*)ZrO<sub>2</sub>, where *n* is the nominal concentration of potassium nitrate. The potassium nitrate concentration is based on the catalyst (grams of KNO<sub>3</sub>/gram of catalyst).

### 2.2. Catalyst characterization

BET surface area of the catalysts was measured by adsorption of N<sub>2</sub> at 77 K in a Micromeritics Accusorb 2100E equipment. X-ray diffraction (XRD) spectra were recorded on a Rigaku D-Max III equipment with Cu-Kα radiation ( $\lambda = 1.5378$  Å, 40 K, 30 mA). The melting point of the potassium nitrate in the catalysts was studied using a differential scanning calorimetry Shimadzu DSC 50 model.

### 2.3. Activity tests

Catalytic tests were performed in a temperature programmed oxidation (TPO) apparatus, a quartz microreactor with analysis of reaction gases. The feed composition was 1500 ppm of NO and 8% of O<sub>2</sub>. Before the reaction the soot and the catalyst were mixed in two different ways. In the case of “tight contact” the soot was carefully mixed with the catalyst by mechanical mixing in an agate mortar. In the other case, “loose contact”, the soot was mixed with the catalyst with a spatula.

The microreactor is a fixed bed constructed in quartz (i.d. = 0.8 cm), heated electrically and the temperature measured by means of a thermocouple of the K type, in contact with the catalytic bed. The reaction mixture was obtained from three feed lines that are individually controlled: NO/He, O<sub>2</sub>/He and He to close the balance. The microreactor was loaded with 22 mg of the catalyst–soot mixture (10/1) and the oxidation was carried out in the range of 473–973 K in flowing NO/O<sub>2</sub>/He mixture (50 ml/min). A heating rate of 2 K/min was applied in these experiments. Reaction products were monitored with a gas chromatograph Shimadzu Model GC-8A provided with a TCD detector. The separation of products was performed with a concentric column CTRI of Altech. This system permits the identification and quantification of peaks of O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CO. The soot combustion to CO<sub>2</sub> and CO was determined from the area of carbon dioxide and carbon monoxide peaks obtained by chromatographic analysis.

### 3. Results and discussion

The specific surface area of the support and catalysts containing potassium determined by the BET method is shown in Table 1. The support of zirconium oxide ( $\text{ZrO}_2$ ) and catalysts containing potassium nitrate in lower concentration ( $\text{K0.25ZrO}_2$  and  $\text{K1.25ZrO}_2$ ) present the largest surface. The specific surface area of the catalysts shows the minimum value for the 20%  $\text{KNO}_3$  concentration.

TPO diagrams resulting from the soot combustion using the following mixture: 1500 ppm of NO and 8% of  $\text{O}_2$  are shown in Fig. 1. The formation rate of  $\text{CO}_2$  was used as a measure to evaluate the activity of catalysts for the combustion. The  $\text{CO}_2$  evolution is shown in Fig. 1 for the particular case in which the particulate matter and the catalyst were milled in a mortar (“tight con-

tact”). The information of carbon monoxide formed is not presented, the concentration was one order of magnitude lower than that for  $\text{CO}_2$ . Fig. 1 shows that the temperature of maximum combustion rate ( $T_m$ ) for the support promoted with  $\text{KNO}_3$  to 0.25% and 1.25% was around 723 K, while for catalysts containing  $\text{KNO}_3$  in concentrations of 11% and 20% the temperature of maximum combustion rate decreased up to about 648 K approximately.

When the oxidation of particulate matter was performed without addition of catalyst, the amount of carbon monoxide formed was the same as in the case of  $\text{CO}_2$ . The temperature of maximum combustion rate for the system without catalyst is 893 K. The temperature decrease generated by catalysts with a 10–20%  $\text{KNO}_3$  content is around 245 K.

Table 2 shows the temperature of maximum combustion rate for the series prepared by mixing with a spatula, “loose contact”, and by using a catalyst/particulate matter ratio 10/1. It is observed that those catalysts with lower  $\text{KNO}_3$  content present the maximum combustion rate at 823 K, while the ones of higher concentration show a  $T_m$  at 668 K.

To analyze the effect of the mixing type, temperature values at which the combustion rate is maximum are also included ( $T_m$ ) in Table 2 for the series of experiments carried out with mortar milling (“tight contact”). The temperature difference of maximum combustion rate ( $T_m$ ) between “tight contact” and “loose contact” series is high when the potassium nitrate content is low by around 100 degrees when the concentration is 0.25%. This difference is considered as negligible when the potassium nitrate concentration is between 11% and 20%. These results show clearly

Table 1

Specific surface area of the support and catalysts (precursor calcined at 873 K)

Catalyst	$S$ ( $\text{m}^2/\text{g}$ )
$\text{ZrO}_2$	45
$\text{K0.25ZrO}_2$	45
$\text{K1.25ZrO}_2$	52
$\text{K11.5ZrO}_2$	15
$\text{K20.5ZrO}_2$	11

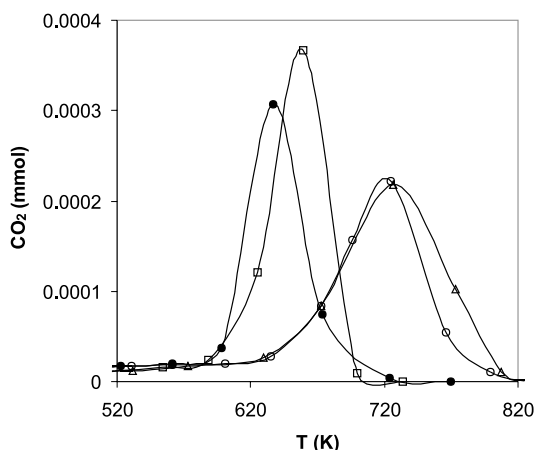


Fig. 1. Influence of the  $\text{KNO}_3$  concentration on the oxidation of particulate matter.  $\circ$ ,  $\text{KNO}_3(0.25)/\text{ZrO}_2$ ;  $\blacktriangle$ ,  $\text{KNO}_3(1.25)/\text{ZrO}_2$ ;  $\square$ ,  $\text{KNO}_3(11)/\text{ZrO}_2$ ;  $\bullet$ ,  $\text{KNO}_3(20)/\text{ZrO}_2$ .

Table 2

Effect of the mixing method on the temperature of maximum combustion rate of the particulate matter

Catalysts	“loose contact”	“tight contact”	$\Delta T$
	$T$ (K)	$T$ (K)	
$\text{KNO}_3(0.25)/\text{ZrO}_2$	823	728	95
$\text{KNO}_3(1.25)/\text{ZrO}_2$	813	728	85
$\text{KNO}_3(11)/\text{ZrO}_2$	673	638	35
$\text{KNO}_3(20)/\text{ZrO}_2$	668	658	10

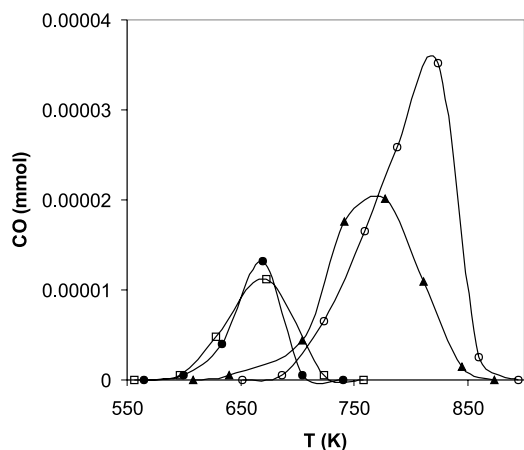


Fig. 2. Influence of  $\text{KNO}_3$  concentration on CO generation, 22 mg of the catalyst-soot (10/1) mixture, “loose contact”.  $\circ$ ,  $\text{KNO}_3(0.25)/\text{ZrO}_2$ ;  $\blacktriangle$ ,  $\text{KNO}_3(1.25)/\text{ZrO}_2$ ;  $\square$ ,  $\text{KNO}_3(11)/\text{ZrO}_2$ ;  $\bullet$ ,  $\text{KNO}_3(20)/\text{ZrO}_2$ .

that the molten potassium nitrate makes it possible to obtain good contact between the catalyst and the particulate matter without the need to use a milling process with an agate mortar.

The CO amount generated during the combustion with “loose contact” is shown in Fig. 2. The amount of carbon monoxide is 10 times lower than the generated amount of carbon dioxide. It is observed that the area below the curve decreases as the potassium nitrate content increases. These results show that although the zirconium oxide as support is active for the soot combustion, the potassium nitrate favors the total combustion.

Experiments using the support alone in one case and only the potassium nitrate in the other case were carried out to discern the contribution made to the combustion by both components of the catalyst, the potassium nitrate and the zirconium oxide. For the series of mortar milling (“tight contact”) the temperatures of maximum combustion rate were 760 K for the support and 636 K for the potassium nitrate. This last value coincides with the temperature of maximum combustion rate for catalysts with 11% and 20% potassium nitrate content.

It is evident from previous results that the potassium nitrate has a greater effect than the support to catalyze the combustion. The temperature difference of maximum combustion rate between

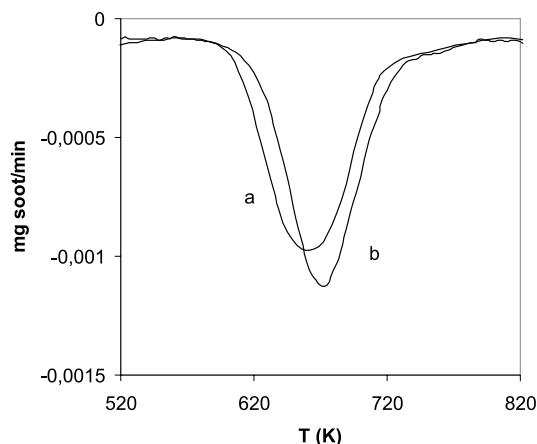
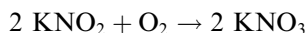
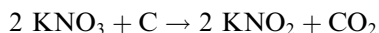


Fig. 3. Catalyst-soot (100/1) mixture, “loose contact”, air/He: 2/1; (a)  $\text{KNO}_2/\text{ZrO}_2$ ; (b)  $\text{KNO}_3/\text{ZrO}_2$ .

the soot oxidation without using catalyst ( $T_m = 893$  K) and using catalysts with high potassium nitrate concentration ( $T_m = 668$  K) is 225 K. A probable mechanism is that one in which the nitrate is reduced to nitrite by the reaction with carbon and that the oxygen or the nitrogen oxide oxidize the nitrite again to nitrate.



To discern whether the proposed mechanism was sustainable two complementary experiments were carried out. One of them was performed by using catalyst with potassium nitrate and the other one using catalyst with potassium nitrite. These experiments were made in a thermobalance Shimadzu, TGA50 model with air/He mixture utilizing the “loose contact” method to prepare the soot/catalyst mixture. Results of these experiments are shown in Fig. 3. The catalyst containing potassium nitrite presents the temperature of maximum combustion rate at 658 K, 20 degrees below the potassium nitrate catalyst. These results corroborate the mechanism proposed above.

#### 4. Conclusions

Catalysts of supported potassium nitrate are active for the combustion reaction of particulate

matter. When the concentration is high they possess practically the same activity if they are mixed or milled with the particulate matter. It is very important to denote the temperature decrease of maximum combustion rate that they generate even when they are only mixed with the particulate matter. This decrease reaches up to 225 K for the catalyst with 20%  $\text{KNO}_3$ .

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