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DIESEL SOOT COMBUSTION. KNO_3 AND KOH CATALYSTS SUPPORTED ON ZIRCONIA

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Abstract

KNO_3/ZrO_2 and KOH/ZrO_2 catalysts were studied and found active in the catalytic soot combustion. Two equipments were used to carry out the combustion experiments: a thermogravimetric reactor with an O_2/He feed and a fixed bed microreactor with NO/O_2/He feed.

Keywords: Soot, catalytic combustion, NOx

INTRODUCTION

Among several technologies proposed to control emissions of soot, the catalytic combustion of soot is one of the most promising methods [1-2]. Effluent gases of engines have a temperature in the range from 150 to 400ºC, and consequently, it is necessary to develop catalysts active at those temperature levels [1-4]. Catalysts for the combustion of soot are cited in the

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bibliography [5-17]. The activity of catalysts can be attributed to the catalytic effect of potassium [6, 13], to the wetting of the catalytic surface [14-16] and to the presence of redox sites [4, 17].

In this work, the influence of the anion in KNO_3/ZrO_2 and KOH/ZrO_2 catalysts is studied in soot combustion. Besides, the influence of NO is studied on the reaction rate. Thermogravimetric experiments are performed as exploratory measurements due to the versatility of this technique. Experiments with catalysts presenting activity are carried out in a flow microreactor simulating conditions near to the ones found in an exhaust pipe, such as loose contact, NO presence in ppm amounts and O_2 concentration around 10%.

EXPERIMENTAL

Catalyst preparation

The zirconium hydroxide was obtained by the hydrolysis of zirconium oxychloride, $ZrOCl_2.6H_2O$ (Fluka). Necessary amounts of ammonium hydroxide (Tetrahedron 28%) were added to the zirconium oxychloride to reach pH=10. The product obtained by the hydrolysis was filtered and washed to chloride-free state, and finally the material was dried at 110°C for 24 h.

Catalysts containing potassium were prepared by impregnation of the zirconium hydroxide with an aqueous solution of KNO_3 or KOH using the necessary amount of solution to fill the pore volume of the support. In all cases, the impregnated zirconium hydroxide was dried at 110°C for 24 h. To obtain the catalysts, the precursors were calcined at 600°C for 2 h.

Catalysts were prepared with varying potassium contents between 2 and 10%, they will be marked as $KNO_3(n)/ZrO_2$ and $KOH(n)/ZrO_2$, where n is the nominal concentration of potassium (grams of potassium/100 grams of catalyst).

Activity measurements

The soot sample used in this work is a synthetic flame soot named Printex-U manufactured by Degussa. This carbon is commonly used to substitute diesel soot in academic studies.

Two equipments were used to carry out the catalytic experiments: a thermogravimetric reactor with an O_2/He feed and a fixed bed reactor with NO/O_2/He or O_2/He feed.

In the first case, soot combustion was performed in a thermobalance (TGA-50 Shimadzu) with a heating rate of 10°C/min and an O_2/He feed of 2:1. In

order to carry out activity experiments, the soot and the catalyst, (mass: aprox. 3 mg), were milled carefully in a 1/10 ratio 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 values as a function of time, the derivative curve (DTGA) was obtained and from this curve the temperature where the combustion rate is maximum (T_{max}).

In the second case, a quartz microreactor constructed (id = 0.8 cm) was used. The reaction mixture was obtained from three lines controlled individually: NO/He, O_2/He and He to close the balance. The mixture consisted of 8% of O_2 and 1500 ppm of NO (total flow = 50 mL/min). The mass of soot/catalyst (1/10) loaded in the reactor was 33 mg, the temperature range studied between 200-700°C and the heating rate 2ºC/min. Reaction products were analyzed with a Shimadzu model GC-8A gas chromatograph provided with a TCD detector. Separation of the 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 combusted soot was calculated from the chromatographic information on CO_2 and CO.

RESULTS AND DISCUSSION

Thermogravimetric reactor

Figure 1a shows the results of TPO (temperature programmed oxidation) experiments performed in the thermogravimetric reactor with KOH(n)/ZrO_2 catalysts. The TPO experiment carried out without catalyst presents a T_{max} of 665°C and the KOH(2)/ZrO_2 catalyst does not modify significantly the combustion rate. Catalysts containing higher amounts of potassium decrease considerably the combustion temperature. The KOH(5)/ZrO_2 catalyst shows a T_{max} of 445ºC, and the KOH(10)/ZrO_2 catalyst shows a T_{max} of 423ºC.

Figure 1b shows TPO diagrams obtained with the KNO_3(n)/ZrO_2 catalysts. It is observed that all catalysts decrease the soot combustion temperature to 200-250ºC. T_{max} values obtained are 470, 415 and 420ºC for catalysts KNO_3(2)/ZrO_2, KNO_3(5)/ZrO_2 and KNO_3(10)/ZrO_2 respectively.

Results in Figs 1a and 1b show clearly that the catalysts KOH(2)/ZrO_2 and KNO_3(2)/ZrO_2 behave differently. The catalyst prepared from potassium nitrate (T_{max} = 470ºC) is more active than the catalyst prepared from potassium hydroxide (T_{max} = 660ºC). KNO_3 and KOH have low melting points, 334 and 360ºC, respectively. Results show that the catalysts with high potassium concentration (5 and 10%) start the soot combustion at a temperature close to the melting points of KNO_3 and KOH. KOH(5)/ZrO_2 and KOH(10)/ZrO_2 catalysts start the reaction at about 360ºC and KNO_3(5)/ZrO_2 and KNO_3(5)/ZrO_2

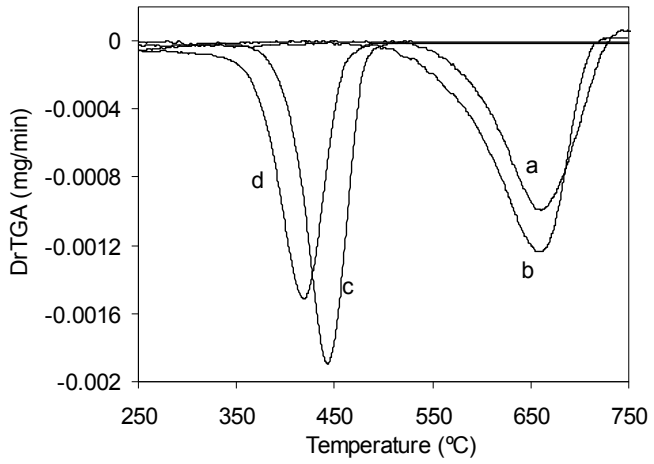

Fig. 1a. TPO thermogravimetric reactor. KOH(n)/ZrO_2 catalysts. a) without catalyst, b) KOH(2)/ZrO_2, c) KOH(5)/ZrO_2 and d)KOH(10)/ZrO_2. O_2/He (2:1), soot/catalyst = 1/10, mass = 3-3.5 mg, heating rate = 10ºC/min

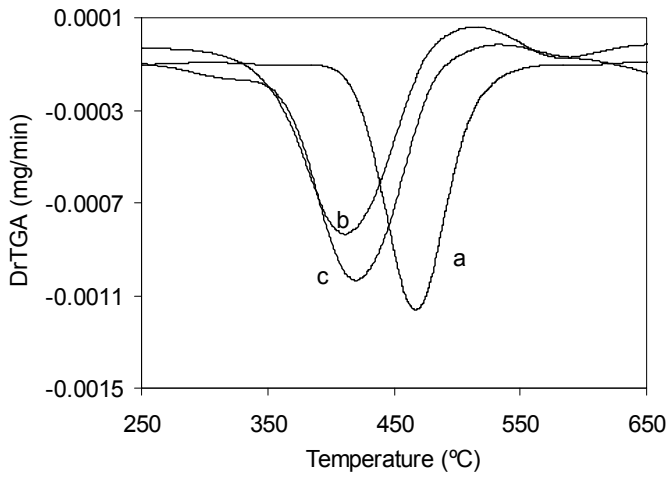

Fig. 1b. TPO thermogravimetric reactor. KNO_3(n)/ZrO_2 catalysts. a) KNO_3(2)/ZrO_2, b) KNO_3(5)/ZrO_2 and c) KNO_3(10)/ZrO_2. O_2/He (2:1), soot/catalyst = 1/10, mass = 2.5-3 mg, heating rate = 10ºC/min

catalysts at 330ºC. This phenomenon can be assigned to the presence of KOH and KNO_3 not interacting with the support, retaining their bulk properties. Catalysts with low potassium concentration start the combustion at a higher temperature than the melting point of the precursor and in this case, the different behavior among them is noticeable. The $KNO_3(2)/ZrO_2$ catalyst presents higher activity than the $KOH(2)/ZrO_2$ catalyst and this fact can be ascribed to the contribution of the reaction between the nitrate anion and soot [4, 17].

$$2KNO_3 + C \leftrightarrow 2KNO_2 + CO_2$$

$$2KNO_2 + O_2 \leftrightarrow 2KNO_3$$

The series of the $KNO_3(n)/ZrO_2$ catalysts presents, in general, higher activity than the series of the $KOH(n)/ZrO_2$ catalysts. Although the activity of catalysts of both series with 5 and 10% potassium starts at temperatures near to the melting point, the higher activity of the series with KNO_3 can also be attributed to the contribution of the redox cycle NO_3^-/ NO_2^-.

These preliminary experiments performed in the thermogravimetric reactor show that all catalysts are active below 400ºC. Therefore, measurements in realistic conditions will be made; for this, the reactions were carried out in a NO/O_2 flow and "loose contact" between the catalyst and the soot.

Catalytic results obtained in the fixed bed reactor

Figure 2 shows results obtained from programmed temperature oxidation experiments of the series $KOH(n)/ZrO_2$ in the presence of NO/O_2. The temperature at which the combustion rate is maximum (T_{max}) for the combustion without catalyst is around 590ºC, while when catalysts $KOH(5)/ZrO_2$ and $KOH(10)/ZrO_2$ are used that temperature decreases considerably, the T_{max} values found are 355 and 330ºC respectively.

The series of catalysts $KNO_3(n)/ZrO_2$ obtained by using potassium nitrate as precursor salt was studied in the same way. Values of Tmax are summarized in Table 1. All catalysts of this series present high activity decreasing the T_{max} by 200°C. It is important to remark that the catalyst $KNO_3(2)/ZrO_2$ (T_{max} = 395°C) is much more active than the homologous one prepared from KOH (T_{max} = 540°C).

Results obtained with a mixture containing only 8% O_2 and He are shown in the same table. The NO affects the activity of the series of catalysts in a different way. The NO increases the activity of $KOH(n)/ZrO_2$ catalysts and this increase is attributed to the formation of potassium nitrite or potassium nitrate on the catalytic surface.

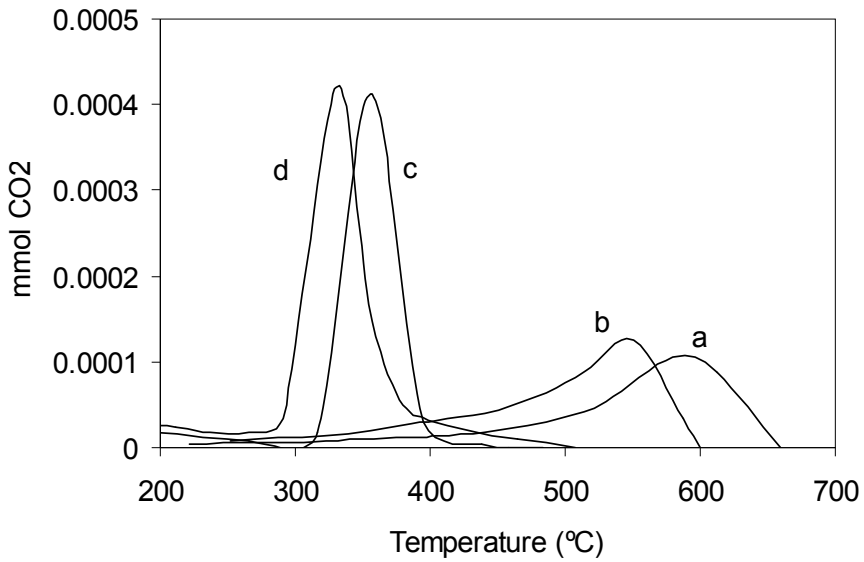

Fig. 2. TPO in a fixed bed reactor with catalysts KOH(n)/ZrO_2. (a) without catalyst, b) KOH(2)/ZrO_2, c) KOH(5)/ZrO_2 and d) KOH(10)/ZrO_2. 8% O_2 and 1500 ppm NO (50 mL/min), mass = 33 mg, heating rate 2°C/min

Table 1

Temperature of the maximum combustion rate in the fixed bed reactor

Catalyst	T_{max} (°C)	
	NO/O_2*	O_2
Without catalyst	590	562
KOH(2)/ZrO_2	540	538
KOH(5)/ZrO_2	355	400
KOH(10)/ZrO_2	330	400
KNO_3(2)/ZrO_2	395	360
KNO_3(5)/ZrO_2	378	350
KNO_3(10)/ZrO_2	395	340

* Concentration of reagents: 8% O_2, 1500 ppm NO. Heating rate 2°C/min

$$2KOH + 2NO + 0.5O_2 \rightarrow 2KNO_2 + H_2O \text{ and/or } K_2O + 2NO + 0.5O_2 \rightarrow 2\ KNO_2$$

$$2KOH + 2NO + 1.5O_2 \rightarrow 2KNO_3 + H_2O \text{ and/or } K_2O + 2NO + 1.5O_2 \rightarrow 2\ KNO_3$$

Taking into account the previous studies, it was possible to observe that potassium nitrite has the same behavior as that of potassium nitrate [4]. However, it is the NO which decreases the activity of $KNO_3(n)/ZrO_2$ catalysts. The activity decrease observed with the NO addition when using potassium nitrate catalysts could be associated with an effect of competitive adsorption of NO and O_2, or with some reversibility of the redox cycle.

$$2KNO_3 + C \Leftrightarrow K_2O + NO + NO_2 + CO_2$$

$$K_2O + NO_2 + 1.5O_2 \Leftrightarrow 2KNO_3$$

Thermodynamic calculations show that the proposed reaction occurs and it is irreversible in the range of temperatures studied, consequently, the activity decrease is attributed to the competitive adsorption of reagents.

CONCLUSIONS

Catalysts prepared from potassium nitrate and potassium hydroxide proved to be active for the reaction of catalytic oxidation of soot, particularly those of higher potassium concentration (5 and 10%).

The presence of NO increases the activity of catalysts prepared from KOH, and this fact can be associated with the nitrite/nitrate formation on the catalytic surface.

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REFERENCES

1. A. Setiabudi, M. Makkee, J. Moulijn: *Appl. Catal., B* **42,** 35 (2003).
2. A.A. Barry, A.L. van Setten, M. Makke and J.A. Moulijn: *Catal. Rev.,* **43,** 489 (2001).
3. R. Farrauto and K.E. Voss: *Appl. Catal., B* **10**, 29 (1996).
4. A. Carrascull, I. D. Lick, E. N. Ponzi, M. I. Ponzi: *Catal. Commun.,* **4,** 124 (2003).
5. J. Liu, Z. Zhao, C. Xu, H. Wang: *React. Kinet. Catal. Lett.,* **87,** 107 (2006).
6. H. An, P.J. Ginn: *Appl. Catal. B,* **62,** 46 (2006).
7. N.F. Galdeano, A. Carrascull, M.I. Ponzi, I.D. Lick, E.N. Ponzi: *Therm. Acta*, **421,** 117

(2004).
8. A. Carrascull, C. Grzona, I.D. Lick, M.I. Ponzi, E.N. Ponzi: *React. Kinet. Catal. Lett.,* **75,** 63 (2002).
9. A. Bueno Lopez, J.M. Soriano, A. García García: *Catal. Comm.,* **7,** 678 (2006).
10. J.A. Sullivan, O. Keane: *Catal. Today,* **114**, 340 (2006).
11. S. Wang, B.S. Haynes: *Catal. Comm.,* **4,** 591 (2003).
12. D. Fino, N. Russo, G. Saracco, V. Specchia: *J. Catal.,* **217,** 36 (2006).
13. J. Liu, Z. Zhao, C. Xu, A. Duan, L. Zhu, X. Wang: *Appl. Catal. B,* **61,** 36 (2005).
14. S.J. Jelles, B. Van Setten, M. Makkee, J.A. Moulijn: *Appl. Catal. B,* **21**, 35 (1999).
15. A. Setiabudi, N.K. Allart, M. Makkee, J.A. Moulijn: *Appl. Catal. B,* **60,** 241 (2005).
16. A. Carrascull, M.I. Ponzi, E.N. Ponzi: *Ind. Eng. Chem. Res.*, **42,** 692 (2003).
17. Y. Zhang, X. Zou: *Catal. Comm.,* **7,** 523 (2006).