

Soot combustion: reactivity of alkaline and earth-alkaline metal oxides in full contact with soot

L. Castoldi, R. Matarrese, L. Lietti, P. Forzatti
Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta"
Centro NEMAS - Nano Engineered Materials and Surfaces,
Politecnico di Milano - p.za Leonardo da Vinci, 32 - 20133 Milan (Italy)

Introduction

Particulate matter (soot) and NO_x are the main pollutants in diesel engine emissions. In view of increased concerns regarding the effects of soot and NO_x emissions on human health and the environmental, new legislations have been enforced for their reduction. In this respect, Toyota has developed the Diesel Particulate- NO_x Reduction (DPNR) technology for the simultaneous removal of NO_x and diesel particulate matter [1]. In a previous work from our group [2] the reactivity of a typical Pt-Ba/ Al_2O_3 catalyst according to the DPNR concept has been addressed. It has been found that this system shows good performances both in removal of particulate matter and NO_x . Recently the potentiality of K-based catalyst in the simultaneous removal of particulate matter and NO_x has also been investigated and compared with that of the corresponding Ba-containing systems. The data pointed out the higher activity of the K-containing catalyst in the soot combustion with respect to the Ba-based catalyst.

To better enlighten the different reactivity of the K vs. Ba systems, and to point out the key-parameters involved in the oxidation of particulate, in the present study the soot combustion has been investigated both in the presence of Ba, K and Pt supported catalysts (loose contact) and after direct impregnation with K, Ba and Pt precursors (full contact) as well. Thus, the role of the various catalyst components and of the type of contact could be evaluated.

Materials and Methods

Ba/ Al_2O_3 (16/100 w/w), K/ Al_2O_3 (4/100 w/w) and Pt/ Al_2O_3 (1/100 w/w) catalysts were prepared by impregnation of γ -alumina [2]. Subsequently, the samples have been gently mixed with the soot (catalyst/soot 9/1 w/w) for 24h, realizing a loose contact. Degussa Printex U has been used as model soot. At opposite, an intimate interaction of the catalytic elements with soot has been accomplished by direct impregnation of the soot with Ba, K and Pt aqueous solutions (full-contact). All reactivity tests were performed in flow-reactor equipment, consisting of a quartz tube connected to a mass spectrometer (Omnistar 200, Pfeiffer) and to a micro GC (Agilent 300A) for the continuous on-line analysis of the outlet gases. The behaviour of the catalysts in the soot combustion was addressed by means of Temperature Programmed Oxidation (TPO), with O_2 (3% v/v) or O_2 (3% v/v)+ NO (1000ppm) in the presence of CO_2 and water (total flow 100 Ncc/min) and heating up to 800°C at 15°C/min. 66 mg of the soot/catalyst (70-100 μm) mixture (loose contact) or 6 mg of impregnated soot (full contact) diluted 1/5 with quartz has been used in each run.

Results and Discussion

The results of TPO experiments obtained in the case of the loose contact mixtures and full contact samples are shown in terms of CO_2 production in Figure 1 (solid and dotted lines, respectively). The results obtained in the case of the soot/bare alumina mixture are also shown

for comparison purpose. In the case of the loose contact systems (solid lines) the onset for soot oxidation is near 450°C for Ba/ Al_2O_3 , Pt/ Al_2O_3 and bare support/soot mixtures. A lower onset temperature is observed for the K/ Al_2O_3 -soot system, i.e. at 300-350°C.

Notably, the presence of K significantly affects the temperature onset of soot combustion while the presence of Pt increases the rate of oxidation. In fact, after ignition, the soot combustion rapidly proceeds in the case of Pt/ Al_2O_3 sample, whereas in the other cases it shows a slower increase with temperature. The Ba/ Al_2O_3 system shows a reactivity similar to that of the bare Al_2O_3 support.

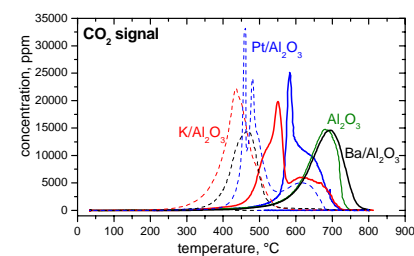


Figure 1 – TPO experiments over loose contact systems (solid lines) and full contact systems (dotted lines)

When an intimate contact is guaranteed between the active elements and soot, significant changes in the TPO spectra are observed (dotted lines). In fact, in all cases the onset temperature for soot oxidation significantly decreases. The shift towards lower temperatures of the onset for soot combustion is particularly evident in the case of the Ba/soot sample, which shows a reactivity similar to that of the K-containing sample.

Accordingly, when an intimate contact is guaranteed between the active elements and

soot, the soot combustion is enhanced. In line with other literature reports, these data pointed out the key-role played by the alkaline or earth-alkaline metal oxide in the soot combustion, suggesting that K and Ba itself have an oxidant capacity that play in the soot combustion. When the contact between active component and soot is poor (loose contact systems), the active element is blocked on the alumina surface; as consequence it can perform its oxidant capacity only if the active element has high mobility, which favours the catalyst/soot contact thus improving activity. This might suggest that the higher reactivity of the Pt-K/ Al_2O_3 catalyst in the combined NO_x and soot removal with respect to Pt-Ba/ Al_2O_3 is likely related to the higher mobility of K-containing species, which favours the catalyst/soot contact thus improving activity. The presence of sublimation phenomena, with K migrating from one carbon grain to another, might also be invoked. These aspects are presently under investigation in our labs.

Significance

A relationship between alkaline and alkaline-earth metal oxide and soot contact has been pointed out, which is helpful in understanding the catalytic behavior of DPNR systems and which is relevant for the selection of appropriate key-parameters.

References

1. N. Koichiro, S. Hirota, S. Takeshima, K. Itoh, T. Tanaka, K. Dohmae, SAE paper (2002) N. 01-0957
2. L.Castoldi, R.Matarrese, L.Lietti, P.Forzatti, Appl.Cat B:Environmental 64 (2006) 25-34