

## BaKCo/CeO<sub>2</sub> catalysts for diesel soot and NO<sub>x</sub> abatement

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### Introduction

Soot particles and NO<sub>x</sub> are the main pollutants from diesel engines. Good alternatives to abate these contaminants are the use of catalytic filters, which burn the soot particles, and NO<sub>x</sub> traps which adsorb the NO<sub>x</sub> during normal operation and released them during reduction cycles [1]. We recently studied BaK/CeO<sub>2</sub> catalysts for this application[2]. Barium plays the role of NO<sub>x</sub> adsorbent, and K and CeO<sub>2</sub> are a good combination to oxidate soot, due to the high K movility, improving the soot-catalyst contact, and the redox behavior of CeO<sub>2</sub>. The addition of Co improved the behavior of the catalyst as a NO<sub>x</sub> trap, since the nitro-compounds formed upon treatment with NO<sub>x</sub> resulted to be less stables as compared to barium nitrate formed on BaK/CeO<sub>2</sub> [3]. In this work, the stability of BaKCo catalysts was studied, including thermal stability and stability in presence of water, NO + O<sub>2</sub> and SO<sub>2</sub>, all these compounds being present in the diesel exhaust atmosphere. The influence of Co precursors on the catalyst soot combustion activity, stability and behavior as a NO<sub>x</sub> trap was also analyzed.

### Materials and Methods

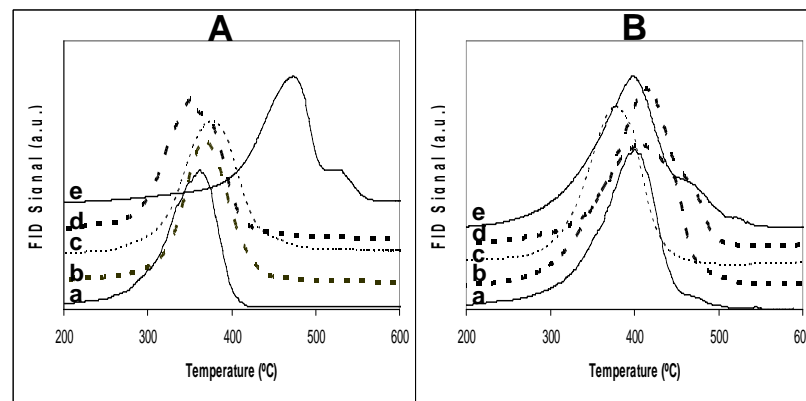
The catalysts were prepared by coimpregnation of solutions of Ba(AcO)<sub>2</sub> and KNO<sub>3</sub> on the CeO<sub>2</sub> support and calcined at 400 °C. The cobalt was added to the BaK/CeO<sub>2</sub> catalyst as a solution of either Co(NO<sub>3</sub>)<sub>2</sub> or Co(AcO)<sub>2</sub> and then calcined at 400°C. The catalytic activity was determined by TPO of a tight contact mixture of catalyst and soot. The catalysts were characterized by FTIR, XRD and A.A. The catalysts were treated sequentially at 700°C, 800°C and 850°C in dry air in order to evaluate thermal stability, and at 400°C in wet air for evaluating the stability in a humid atmosphere. For the stability in presence of SO<sub>2</sub> the catalysts were treated with 100 ppm of SO<sub>2</sub> at 400 °C. The behavior as a NO<sub>x</sub> trap was studied flowing NO + O<sub>2</sub> in a microbalance and ramping up to 490°C.

### Results and Discussion

The soot oxidation activity is higher for the catalysts prepared using Co(NO<sub>3</sub>)<sub>2</sub> (Figure 1), most probably due to the presence of KNO<sub>3</sub> with high movility, which was not found in the catalysts prepared from Co(AcO)<sub>2</sub> although KNO<sub>3</sub> was also used as a K precursor. Additionally, after treatment of the catalysts with NO + O<sub>2</sub>, the activities of both catalysts became similar, due to the formation of KNO<sub>3</sub> in the catalyst prepared from Co(AcO)<sub>2</sub>, as detected by FTIR, these results being consistent with the higher activity when K is as KNO<sub>3</sub>.

The main advantage of the catalyst prepared from Co(NO<sub>3</sub>)<sub>2</sub> was the unstability of the nitro-compounds formed on the catalyst, which decompose around 350 °C, while the Ba(NO<sub>3</sub>)<sub>2</sub> formed on the catalysts prepared using Co(AcO)<sub>2</sub> was stable at least up to 490°C, as also occurred in the BaK/CeO<sub>2</sub> catalysts. It was suggested that the formation of a BaCoO<sub>2.93</sub> perovskite, only found in the catalysts prepared with Co(NO<sub>3</sub>)<sub>2</sub>, probably led to the formation of an unstable nitro-compound bound to barium, instead of the stable Ba(NO<sub>3</sub>)<sub>2</sub> [3]. FTIR spectra carried out on these catalysts also suggested the formation of this type of compound.

The thermal stability up to 850°C was excellent for the catalyst prepared with Co(AcO)<sub>2</sub>, as seen in Fig. 1, meanwhile for the catalyst prepared with Co(NO<sub>3</sub>)<sub>2</sub> it was stable only up to 700°C, with a higher loss of K for severe treatments as detected by A.A. The stability in presence of water is good in both catalysts. In presence of 100 ppm of SO<sub>2</sub> the catalysts prepared with Co(AcO)<sub>2</sub> is slightly deactivated due to formation of sulfates, as observed by FTIR. On the other hand, the catalyst prepared with Co(NO<sub>3</sub>)<sub>2</sub> is not deactivated in these conditions, probably due to the formation of an eutectic mixture of lower melting point, as those formed between K<sub>2</sub>SO<sub>4</sub> and transition metal oxides including Co oxides [4], thus the higher movility compensating the sulfur poisoning as regard catalytic activity. Results are discussed and explained based on characterization results.



**Figure 1.** TPO for mixtures of soot and BaKCo/CeO<sub>2</sub> prepared with Co(NO<sub>3</sub>)<sub>2</sub> (A) and Co(AcO)<sub>2</sub> (B) with different pretreatments: a) fresh, b) H<sub>2</sub>O, c) NO+O<sub>2</sub>, d) SO<sub>2</sub> and e) 850°C.

### Significance

The BaKCo/CeO<sub>2</sub> is a plausible alternative to be used as a catalytic filter and trap in a diesel exhaust, since it presents a good soot combustion activity and it can adsorb NO<sub>x</sub>. The catalyst prepared with Co(NO<sub>3</sub>)<sub>2</sub> can trap and decompose NO<sub>x</sub> in the temperature range of soot combustion. Although the thermal stability of this catalyst is lower than the corresponding to the catalyst prepared with Co(AcO)<sub>2</sub>, it is good enough up to 700°C. Both catalysts present good stability in a humid atmosphere and in presence of SO<sub>2</sub> during short expositions. Although eventually the SO<sub>2</sub> would poison the catalysts, the deactivation is slower for the catalyst prepared with Co(NO<sub>3</sub>)<sub>2</sub> probably due to a low melting point mixture formed on it.

### References

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