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Stability of Ba,K/CeO_2 catalyst during diesel soot combustion: Effect of temperature, water, and sulfur dioxide

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Abstract

In this work we study the stability of Ba,K/CeO_2 catalysts, which have been shown to be very active for soot combustion. The effects of high-temperature treatments and the presence of water or sulfur dioxide on the catalytic properties for soot oxidation are studied. Fresh and deactivated catalysts are characterized by XPS, FTIR, XRD, and high-frequency CO_2 pulses, and the activity is measured by TPO. Barium has only a minor effect on the activity for soot combustion, whereas potassium has a pronounced effect in decreasing the temperature needed to burn soot. In the case of Ba,K/CeO_2, optimum activity as a function of potassium content of around 7 wt% is found. The optimum, which is very smooth, is due to the synergistic effect between K and CeO_2. This catalyst is thermally stable up to 830 °C and does not deactivate even after 30 h at 800 °C. At higher temperatures, a decrease in the K/Ce surface ratio and formation of the $BaCeO_3$ perovskite, indicated by the XPS analyses, are the causes of activity loss. In these cases, there is a decrease in the level of interaction with CO_2. The presence of water at 400 °C does not lead to any significant modification of catalytic activity. However, the presence of water at 800 °C leads to both a drastic decrease in activity and a change in surface composition as indicated by XPS, with a high degree of hydroxylation and probably a spreading of BaO on the ceria surface. The presence of SO_2 (1000 ppm in air) at 400 °C deactivates the catalyst for soot oxidation even after rather short times (32 h). Under these conditions, FTIR and XPS analyses show that barium, potassium, and cerium sulfates are formed. Consequently, the activity for soot oxidation is lost, and there is no interaction between the catalyst and the CO_2. This type of catalyst has good thermal stability and very good tolerance to water at low temperatures (e.g., 400 °C). However, high concentrations of SO_2 lead to rapid deactivation. This should not be a major drawback, because in the near future a much lower level of sulfur in diesel fuel is expected.

Keywords: Diesel soot combustion; Potassium; Barium; Ceria; Stability

1. Introduction

Emissions from diesel engines contain soot and nitrogen oxides as main pollutants. Emission standards in many countries impose very stringent limits on the levels of these contaminants in engine exhaust gases. Current technologies need further improvement to reach the limits expected to be set in the near future; therefore, an intensive research effort is currently under way. The catalytic filter seems to be one of the most important methods to decrease the amount of soot in exhaust gases [1]. The catalyst deposited on a ceramic filter or foam must be sufficiently active to oxidize the soot at the temperature of the exhaust gases, which can be 400 °C for heavy-load engines and 300 °C or even lower for light-duty engines. Studies with a large number of catalytic formulations have been reported, including oxide materials and their mixtures [2–5], perovskite-type oxides [6–8], spinel-type Cu-chromite [9], Cu/K/Mo/Cl [10,11], Cu-V-K-Cl/TiO_2 [12], promoted vanadium oxides [13,14], and molten salts [11,15–17].

There are several requirements other than being active that a catalytic filter for diesel exhaust treatment should fulfill [18]: good thermal shock resistance, low-pressure drop, high soot filtration efficiency, and high soot–catalyst contact efficiency. In addition to these requirements, the catalyst must be stable in the presence of high concentrations of CO_2, water, and certain lev-

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els of SO_2. Even though this is a key issue, only a handful of papers are related to the stability of soot combustion catalysts [1,19,20] or, specifically, to the effect of water and SO_2 tolerance for these catalysts [21,22], but none of them [1,19–22] has carried out a systematic study of the effect of sulfur, water, and temperature on soot combustion activity. Badini et al. [23] analyzed the effect of water, temperature, and SO_2 on the catalytic behavior of Cu-K-V-Cl catalysts. They found good sulfur tolerance in their experiments using 200 ppm SO_2 for 96 h at 380 °C or 24 h at 600 °C. van Setten et al. [24] studied molten-salt catalysts supported on ceramic foams (based on Cs_2O, MoO_3, and Cs_2SO_4) to determine their mechanical strength, hydrothermal stability, and loss of catalyst due to solubility in water. On the other hand, a number of recent studies have examined the effect of SO_2 on the catalytic performance of three-way catalysts. It has been observed that the poisoning of automotive three-way catalysts by SO_2 occurs mainly through the formation of sulfate species, affecting the oxygen storage capacity. Even though the sulfate species can undergo oxidation and reduction in the same temperature range as that of ceria, the rate of oxygen transfer for the sulfate is lower [25]. Sulfate formation occurs mainly when the ceria is exposed to SO_2 at temperatures above 473 K in the presence of O_2 [26]. Nevertheless, Waqif et al. [27] found that heating ceria under SO_2 without oxygen results in the formation of surface and bulk-like sulfate species. Recently, Flouty et al. [21] found that for molybdenum-cerium catalysts, adding small quantities of molybdenum to the ceria improved the resistance of the catalysts to sulfur poisoning during the soot combustion reaction. In this study [21], the sulfated catalysts were prepared by treating the calcined solids under a flow of pure SO_2 gas at room temperature.

It has been reported that SO_2 in low doses promotes activity, as in the case of KVO_3/SiC catalysts [28]. Water was also found to increase the activity of this catalyst, which was attributed to improved contact between the catalyst and the carbon.

In preliminary studies, we also found a promotion effect of SO_2 at low doses on Co,K/MgO catalysts [29], and a moderate deactivation on powder or monolith supported K/La_2O_3 catalysts [30]. In addition, we found that potassium-promoted CeO_2 catalysts have very good activity for soot combustion, and when Ba is included in the formulation, they are able to work as a NO_x trap [31–33].

This paper addresses the stability of Ba,K/CeO_2 catalysts during the oxidation of diesel soot. The effect of temperature, water, and SO_2 is studied measuring the activity by temperature-programmed oxidation (TPO) to determine whether this material could be stable under real conditions. Preliminary results regarding aging treatment in liquid water are also presented. Catalysts are characterized by FTIR, XPS, XRD, BET, and high-frequency CO_2 pulses.

2. Experimental

2.1. Soot and catalyst preparation

The soot used in this work was prepared by burning commercial diesel fuel (Repsol-YPF, Argentina) in a glass vessel. After being collected from the vessel walls, it was dried in a stove for 24 h at 120 °C. Its specific surface area was 55 m^2/g. Temperature-programmed experiments performed using helium as carrier gas provided information regarding the amount of partially oxidized groups of the soot surface and the amount of hydrocarbons that could remain adsorbed after the diesel combustion. In this way, the amount of carbon released as CO, CO_2, and hydrocarbons represents 9.3% of the soot [33]. The same batch of soot was used in all of the experiments presented in this study, to avoid possible differences in surface oxygen groups, which could affect activity results.

The Ba,K/CeO_2 catalysts were prepared by the wet-impregnation method, using CeO_2 (Sigma, p.a.) as a support, to which a solution containing barium acetate and/or KNO_3 was added to obtain loads of 10, 16, and 22 wt% of Ba and loads of 2, 4.5, 7, 10, and 15 wt% of K. These values are referred to the CeO_2 support (e.g., 22 g of Ba per 100 g CeO_2). The initial concentration of the starting solutions was 0.1 M of both barium acetate and KNO_3. The suspension was evaporated at 85 °C while being vigorously stirred until achieving a paste, which was dried in a stove for 24 h at 120 °C and calcined for 2 h at 400 °C (fresh catalyst), heating from room temperature to the final temperature in 2 h. The nomenclature adopted for the catalysts was Ba(x),K(y)/CeO_2, where "x" indicates the weight percentage of barium and "y" is the weight percentage of potassium.

2.2. Activity test

The catalytic activity of Ba(x),K(y)/CeO_2 for the combustion of soot was determined by TPO. The soot and the different catalysts were mechanically mixed in an agate mortar for a prescribed period (6 min), so as to obtain a soot/catalyst ratio of 1/20 (wt/wt). A gaseous flow (40 mL/min) with 6% oxygen in nitrogen was used, and the temperature was increased at a rate of 12 °C/min, using 10 mg of the catalyst–soot mixture. A modified TPO technique [34] was used that involved passing the gases coming from the reactor through a methanation reactor, where CO and CO_2 were converted into CH_4. Afterward, methane was measured continuously with a flame ionization detector (FID). The methanation reactor contained a nickel catalyst and operated at 400 °C.

The mixing procedure followed in this study was checked to determine its reproducibility. We found that it is possible to reproduce the TPO profile if the mixing time is controlled. The TPO maximum temperature falls in a window of ± 10 °C when two mixtures are prepared using the same batch of catalyst and soot, which is a very good result, mainly if the heterogeneity of the system is taken into account. The loose-contact mixtures were also prepared with the selected catalysts by shaking the catalysts and the soot in a vial for 2 or 6 min.

The selectivity to CO_2 and CO was measured only with the potassium-containing catalysts in the TPO experiments, by analyzing the gases coming out of the cell with a gas chromatography column and a thermal conductivity detector.