Applied Catalysis A: General 399 (2011) 161–171

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

# Diesel soot and $NO_x$ abatement on $K/La_2O_3$ catalyst: Influence of K precursor on soot combustion

María A. Peralta, María S. Zanuttini, María A. Ulla, Carlos A. Querini*

*Instituto de Investigaciones en Catálisis y Petroquímica-INCAPE-(FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina*

ARTICLE INFO

*Article history:*
Received 26 January 2011
Received in revised form 19 March 2011
Accepted 28 March 2011
Available online 9 April 2011

*Keywords:*
Diesel soot
Potassium precursor
Lanthanum

ABSTRACT

Soot particles and $NO_x$ are the main pollutants emitted by diesel engines. The $K/La_2O_3$ catalyst is active for soot combustion and it is able to adsorb $NO_x$; therefore, it could work as $NO_x$ trap. In this work, the effect of the chemical state of K on the catalytic activity is addressed. Both, the influence of the precursor used in the preparation and the effect of NO in the gas phase, are studied. Potassium nitrate, carbonate, and hydroxide were used to prepare the $K/La_2O_3$ catalysts. The catalytic activity for soot combustion was studied by TPO. XRD and FTIR were used to characterize the different crystalline phases found in the catalyst. Pulses of $CO_2$ and $CO_2$-TPD were useful to understand the effect of each precursor on the catalytic activity. The analysis of $CO_2$ adsorption–desorption dynamics made it possible to determine that the strength of the interaction between this molecule and the catalyst depends on the K precursor, and follows the order: $KOH > KNO_3 > K_2CO_3$. The presence of $La(OH)_3$ leads to a strong and irreversible interaction between the catalyst and the $CO_2$, while the interaction is reversible with the dehydroxilated catalyst. The shape of the TPO profiles is related to the basicity of the surface, which according to the dynamics of the $CO_2$ adsorption–desorption is significantly affected by the potassium precursor used during the preparation, the thermal treatment, and the treatment with gases normally found in the diesel exhaust, such as the NO.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The main pollutants emitted by diesel engine exhausts are nitrogen oxides and soot particles. One of the possibilities to avoid diesel soot particles to be emitted to the environment is to employ catalytic filters in the exhaust pipe [1]. In this work, $K/La_2O_3$ catalysts were studied in order to be employed as a soot oxidation catalyst and as $NO_x$ trap. Potassium is a known active element in carbonaceous materials oxidation reactions [2–5]. $La_2O_3$ and $K/La_2O_3$ are able to adsorb $NO_x$, thus acting as a $NO_x$ trap material [6,7]. These catalysts, after being calcined at 400 °C presents $La(OH)_3$ and $La_2O_2CO_3$ crystalline phases, as determined by XRD and FTIR. The presence of these phases is due to a strong interaction with gas phase components, especially $H_2O$ and $CO_2$. As both gases are products of the soot combustion reaction, catalyst's phases transformations are expected to occur during reaction, i.e., during operation in a real exhaust system. Thus, this catalytic system is particularly complex and very interesting to study in detail.

As will be shown in this work, the $K/La_2O_3$ catalyst prepared using KOH as precursor presents two main maxima in the TPO profile. Many experiments were performed in order to discriminate the processes associated with each TPO maximum. This catalytic system was previously studied addressing the stability in the presence of $SO_2$ [8]. In addition, since this support dehydroxilates by an endothermic process at the same temperature range as the soot is burnt, it is able to dampen the runaway phenomenon [9].

Alkaline metals and particularly potassium have been investigated by many research groups as active components for soot combustion. The high mobility of some K compounds improves the effective contact with soot and, consequently, K-promoted catalysts have good activity. In addition, due to its basic character potassium can be used in the formulation of $NO_x$ traps. However, the high mobility causes K to present a technological problem associated with its interaction with the monolith support, and looses due to volatilization and/or stripping by condensed water. In spite of these shortcomings, basic research and application developments are being carried out. It is important to study this compound in order to better understand the fundamentals of this system. This is demonstrated by recent publications, addressing the role of alkaline metals in the soot oxidation reaction [10–17]. The patent literature also includes potassium in several devices developed for

---

* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068.
*E-mail address:* querini@fiq.unl.edu.ar (C.A. Querini).

0926-860X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2011.03.046

soot combustion [18,19] and also for simultaneous abatement of soot and $NO_x$ [20–22]. In many cases, other alkaline metals such as Li, Cs and Na are included in basic studies or technological applications [23].

The soot–catalyst contact is an important problem [24]. It has been proposed that for laboratory studies, the most realistic method for bringing soot into physical contact with an oxidation catalyst is soot filtration from a diesel-exhaust gas [25]. However, other methods were also recommended by these authors, such as simply mixing with a spatula, shaking in a sample bottle, dipping in soot dispersion, or filtering from an artificial soot aerosol. These procedures lead to the loose contact mode. The tight contact mode, consists of mixing the catalyst and the soot in a mortar or in a ball mill, and makes it possible to determine intrinsic kinetics. This latter type of mixing procedure has been extensively used to study this catalytic system [16,17,26–34].

A large number of catalytic formulations have been tested for the catalytic combustion of diesel soot. Despite of this, the reaction mechanism for this system has been scarcely addressed and therefore a lot of work is still needed in order to advance towards a rational catalyst design. To get information regarding the reaction mechanism and the role that each of the catalyst components plays, intrinsic reaction rates must be evaluated. This means that phenomena like mass and heat transfer limitations must be minimised. Working under realistic soot–catalyst contact (loose contact), implies that mass transfer limitations become very important, thus decreasing the overall reaction rate. On the other hand, working under tight contact conditions does not represent the situation in a real application, but it is relevant in order to study the intrinsic catalytic chemistry. Thus, results obtained with both types of contacts are of interest.

It has to be emphasized that the behavior of the catalytic system based on $La_2O_3$ is extremely complex, due to the variety of superficial and bulk compounds that can be formed on this oxide, and its strong dependency on variables such as temperature and media composition ($H_2O$, $CO_2$, $NO_x$). These variables provoke superficial (and eventually bulk) changes during the storage, the calcination and the catalyst operation [44]. We have previously analyzed this problem [44], and found that when the gas phase composition is similar to that found in a real diesel exhaust containing $CO_2$, $H_2O$, NO, and $O_2$, the catalytic surface equilibrates by forming nitrates, and maintaining a very good activity.

This reaction involves three phases: the soot, the catalyst, and the gas phase. The contact between the two solid phases has an important effect on the reaction rate. If the contact is very good, such as when mixing both solids in a mortar for several minutes, it is called tight contact mode. This type of contact makes it possible to study the intrinsic kinetic of the catalytic combustion of soot. Therefore, in order to study the reaction mechanism and better understand this system, the tight contact mode has been extensively used. However, it is also important to have an insight of the kinetic behavior of this system when the contact mode is more similar to that found in a real exhaust, i.e., a loose-contact mode. In this case, the physical contact between the two solids is poor, and this limits the reaction rate.

In this work, the effect of the potassium precursor used during the preparation on the catalytic activity, is studied. Potassium nitrate, hydroxide, and carbonate are used. The effect of treating the catalyst with NO on the surface composition is also addressed. A comparison of the catalytic activity obtained under tight and loose contact modes is presented.

## 2. Experimental

### 2.1. Soot and catalysts 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 $55\,m^2\,g^{-1}$. Temperature-programmed experiments performed using helium as carrier gas provided information regarding the amount of partially oxidized groups on the soot surface and the amount of hydrocarbons that could remain adsorbed after the diesel combustion. In this way, it was determined that the amount of carbon released in an inert gas as CO, $CO_2$ and hydrocarbons was 9.3% of the soot [35].

The catalyst labeled as $K_{OH}/La_2O_3$ was prepared from a $La_2O_3$ (Alpha, p.a.) support to which a KOH-containing solution was added in order to obtain 4.5 wt% loading of K. The suspension was evaporated while being vigorously stirred until achieving a paste, which was dried in a stove for 24 h at 120 °C, and then calcined at 400 °C. In order to study the K precursor effect, $KNO_3$ and $K_2CO_3$ solutions were used to prepare the catalysts labeled as $K_{NO3}/La_2O_3$ and $K_{CO3}/La_2O_3$, respectively. In all cases, the catalysts were calcined at 400 °C.

Throughout the paper, those catalysts whose activities were determined immediately after being prepared are referred to as: "*recently prepared catalysts*". If the activities were determined few days after catalyst preparation, the samples are mentioned as "*fresh catalysts*". Finally, for the case in which the activities were determined some months after preparation, the samples are called "*aged catalysts*". The $La_2O_3$ as received will be referred to as *pure* $La_2O_3$.

### 2.2. Activity test: temperature programmed oxidation (TPO)

The catalytic activity of $K/La_2O_3$ for the soot combustion was determined by temperature-programmed-oxidation (TPO). The soot and the catalyst were mechanically mixed in an agate mortar during 6 min (tight contact) to obtain a soot/catalyst ratio = 1/20 (wt/wt). A gaseous mixture of 5% $O_2$ in $N_2$ with a flow rate of $40\,mL\,min^{-1}$ was used. The temperature was increased at a rate of $12\,°C\,min^{-1}$, using 10 mg of (catalyst + soot) mixture. A modified TPO technique [36] was employed, which consisted on passing the gases coming out from the analysis cell through a methanation reactor, where CO and $CO_2$ were converted into $CH_4$. Afterwards, methane was continuously measured with a FID detector. The methanation reactor contained a nickel catalyst and operated at 400 °C. The experimental conditions were carefully adopted in order to: (1) avoid mass and energy transfer limitations, (2) assure that all soot particles are in good contact with the catalyst, and (3) avoid the soot combustion reaction runaway [9,37]. We have recently shown that if a lower catalyst/soot ratio is used, reaction runaway may occur if the catalyst has a good activity [9,37]. Consequently, the real kinetics would be masked by this effect and, therefore, the experiments must be designed in order to avoid this phenomenon.

In the case of the loose contact mode, the catalyst and the soot particles were mixed in a vial just by shaking during 6 min. The soot/catalyst ratio was 1/20 (wt/wt).

In order to determine the selectivity of soot oxidation to $CO_2$, the reactor outlet was connected to a sampling valve. Every 2 min a sample was sent to a silica-gel column to separate CO and $CO_2$ using He as carrier gas. These gases were detected by FID after methanation.

Download English Version:

https://daneshyari.com/en/article/41441

Download Persian Version:

https://daneshyari.com/article/41441

Daneshyari.com