Materials Chemistry and Physics 123 (2010) 557–562

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Cobalt and KNO_3 supported on alumina catalysts for diesel soot combustion

Claudia B. Grzona [a], Ileana D. Lick [b], Enrique Rodriguez Castellón [c], Marta I. Ponzi [a], Esther N. Ponzi [b,*]

[a] 25 de mayo 284, INTEQUI-CONICET-UNSL, Facultad de Ingeniería y Ciencias Económico-Sociales, Villa Mercedes, 5730, Argentina
[b] Calle 47 N° 257, CINDECA (CCT-LaPlata-CONICET-UNLP), Departamento de Química, Facultad de Ciencias Exactas, La Plata, 1900, Argentina
[c] Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, Málaga, 29071, Spain

ARTICLE INFO

Article history:
Received 21 April 2009
Received in revised form 1 October 2009
Accepted 7 May 2010

Keywords:
Diesel soot
Combustion
KNO_3
Cobalt

ABSTRACT

The catalytic combustion of diesel soot was studied in the presence of fresh and aged catalysts: Co/Al_2O_3, KNO_3/Al_2O_3 and $Co/KNO_3/Al_2O_3$. The catalysts were prepared by impregnation using nitrate solutions. The catalysts were characterized by X-ray diffraction, thermal programmed reduction, vibrational spectroscopy and X-ray photoelectron spectroscopy.

Fresh and aged catalysts present high activity in presence of O_2 and O_2/NO. The values of the combustion temperature decrease more than 200 °C with respect to that observed in the process without catalysis. The activity is associated with the presence of KNO_3 and the role of this salt can be attributed to the contribution of NO_3^-/NO_2^- redox cycle.

1. Introduction

Emissions of diesel engines contain among other contaminants, carbon oxides, nitrogen oxides, hydrocarbons and particulate matter in their composition. In order to preserve the environment, it is necessary to regulate emissions and to stimulate the search of new technologies able to decrease concentration of contaminants.

In the particular case of particulate matter, mainly composed by soot, it is possible to place a filter in the automobile exhaust pipe where the material is retained and removed by oxidation, thus avoiding the material accumulation with the consequent increase of pressure fall and decrease of engine efficiency.

The non-catalytic combustion of particulate matter occurs at higher temperatures than the temperature of effluent gases. To decrease the oxidation temperature of particulate matter, oxidation catalysts are used since they are able to burn the soot without need of an additional heat source. Among oxidation catalysts reported as active there are those ones that contain alkali metals in their composition [1–16].

Studies previously performed show that potassium nitrate supported on simple oxides presents a good catalytic activity and that the incorporation of copper in the catalyst formula improves the selectivity of carbon combustion to carbon dioxide [17,18]. The role of KNO_3 can be associated to: (i) increase of contact between soot and surface of the catalyst with the increase of possible effective collisions between soot and catalyst, generated by the melting of potassium nitrate on the catalytic surface, (ii) a redox reaction in which the nitrate is reduced to nitrite by reaction with carbon and again reoxidized to nitrate [18–21]. Water vapor can also affect to the performance of the catalysts since deactivation can occur due to chemical modifications that are more pronounced at high temperatures.

The aim of this work is the study of fresh and aged catalysis for the diesel soot oxidation reaction in the presence of O_2/inert and NO/O_2/inert. Furthermore, several characterization techniques have been performed to study the nature of cobalt and potassium and potassium nitrate.

2. Experimental

2.1. Preparation of catalysts

Precursors of catalysts containing cobalt and/or potassium nitrate were prepared by impregnation of gamma-alumina with an aqueous solution of $Co(NO_3)_2$ and/or KNO_3 in a rotavapor equipment. The equipment operates at 160 rpm, bath temperature 50 °C and vacuum pressure 50 mm Hg. The precursors were dried at 80 °C for 24 h and were named PCo/Al_2O_3, $PKNO_3/Al_2O_3$ and $PCo/KNO_3/Al_2O_3$.

Catalysts with a nominal cobalt content of 5% and/or a potassium nitrate content of 25% (%w/w K = 9.6 and %w/w NO_3^- = 15.4) were prepared by calcination of precursors at 600 °C for 2 h. Catalysts were generically denoted as Co/Al_2O_3, KNO_3/Al_2O_3 and $Co/KNO_3/Al_2O_3$.

2.2. Aging experiments with feed containing water vapor

Aging experiments were carried out on samples of fresh catalyst loaded in a quartz reactor fed with a gaseous current (QTotal = 30 ml min^{-1}) containing 10% O_2 and 90% N_2 saturated with water vapor (7 vol%). Aging treatments were performed at 800 °C for 2 h.

---

* Corresponding author. Tel.: +54 221 4211353.
E-mail address: eponzi@quimica.unlp.edu.ar (E.N. Ponzi).

0254-0584/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2010.05.014

Table 1
Chemical analysis according to AAS and size of Co_3O_4 crystals in fresh and aged catalysts.

Catalyst	Co[a] (wt%)	K[a] (wt%)	NO_3^- exp.[b] (wt%)	NO_3 estimated[c] (wt%)
KNO_3/Al_2O_3 fresh	–	9.50	7.91	15.10
KNO_3/Al_2O_3 aged	–	7.50	0.11	11.9
$Co/KNO_3/Al_2O_3$ fresh	4.85	9.00	10.45	14.3
$Co/KNO_3/Al_2O_3$ aged	4.85	8.00	0.42	12.7
Co/Al_2O_3 fresh	4.95	–		
Co/Al_2O_3 aged	4.95	–		

[a] By AAS.
[b] By UV–vis spectroscopic method.
[c] Calculated from %w/w K content.

2.3. Characterization of catalysts

Cobalt and potassium contents were determined by atomic absorption spectrophotometry with a spectrophotometer PerkinElmer AA 800.

The content of soluble nitrate ions in the catalyst was determined by UV–vis spectroscopic measurements at ~224 nm where the absorption spectrum for nitrate (NO_3^-) has a peak that is proportional to the nitrate concentration.

Crystalline phases within the catalysts were identified by powder X-ray diffraction (XRD) analysis using a Rigaku D-Max III diffractometer equipped with Ni-filtered Cu Kα radiation at $1^\circ\ min^{-1}$. The crystal size was calculated using the Scherrer equation and was determined with a scanning rate of $1/8^\circ\ min^{-1}$.

TPR (temperature programmed reduction) experiments were carried out with the conventional equipment. The TPR was performed using 10% hydrogen in nitrogen (flow rate = $20\ cm^3\ min^{-1}$) with a heating rate of $10\ ^\circ C\ min^{-1}$ up to 950 °C. The sample loaded was 20 mg.

The presence of nitrate anions on precursors and catalysts was studied by means of FTIR spectroscopy using a Bruker EXINOX 55 equipment. Spectra were recorded at ambient temperature in the $4000–400\ cm^{-1}$ range and the samples were prepared in form of pills with KBr.

The X-ray photoelectron spectroscopy (XPS) was performed with a spectrometer Physical Electronics PHI-5700, equipped with a dual X-ray source of Mg Kα (1253.6 eV) and Al Kα (1486.6 eV) and a multi-channel detector. Spectra of powdered samples were recorded in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian–Lorentzian curves in order to determine the binding energy of the different element core levels more accurately.

2.4. Catalytic measurements

The soot sample used in this work is synthetic flame soot named Printex-U manufactured by Degussa. This carbon is commonly used to substitute diesel soot in academic studies. Thermal programmed oxidation techniques were used to carry out the catalytic tests. In these techniques the contact between the catalyst and the soot is an important factor. When this contact is poor (loose contact) the catalysts can be less active than when the contact is tight. The first type of contact is more representative for practical applications.

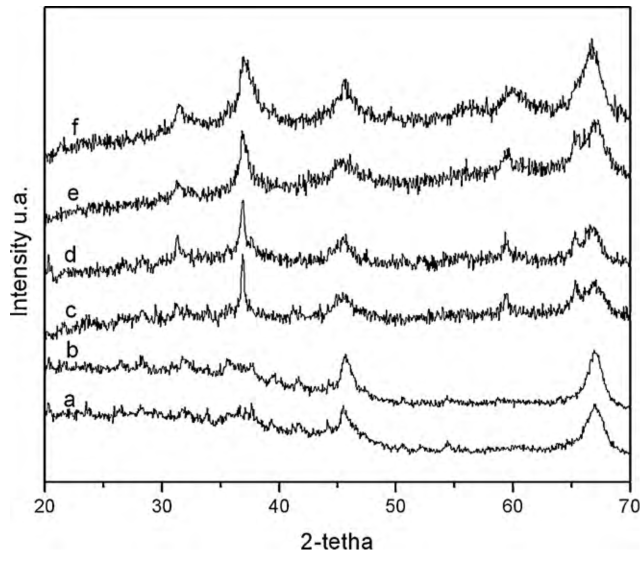

Fig. 1. XRD diagrams of fresh and aged catalysts: (a) fresh KNO_3/Al_2O_3, (b) aged KNO_3/Al_2O_3, (c) fresh $Co/KNO_3/Al_2O_3$, (d) aged $Co/KNO_3/Al_2O_3$, (e) fresh Co/Al_2O_3, and (f) aged Co/Al_2O_3.

In this work two equipments were used to carry out 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, the soot combustion was performed in a thermobalance (TGA-50 Shimadzu) with a heating rate of $10\ ^\circ C\ min^{-1}$ and an O_2/He feed (2:1). In order to carry out activity experiments, the soot and the catalyst, in a 1/10 ratio, were milled carefully in an agate mortar before introduction into the reactor (tight contact). The weight loss and the temperature were recorded as a function of time. The derivative curve (DTG) was obtained from the weight loss information as a function of time, and from this curve the temperature where the combustion rate is maximum (T_{max}). In the second case, a quartz reactor (i.d. = 0.8 cm) was used simulating conditions near to the ones found in an exhaust pipe (loose contact, NO presence, high space velocity and 8% of O_2). The mixture composition was 8 vol% of O_2 and 1500 ppm of NO (total flow = $50\ ml\ min^{-1}$). The mass of soot/catalyst (1/10, w/w) loaded in the reactor was 33 mg. The soot was mixed with the catalyst with spatula (loose contact). The temperature range studied between 200 °C and 700 °C and the heating rate $2\ ^\circ C\ min^{-1}$. Reaction products were analyzed with a gas chromatograph Shimadzu model GC-8A provided with a TCD detector. The separation of 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 of CO_2 and CO.

3. Results

3.1. Chemical analysis

Cobalt and potassium contents in fresh and aged catalysts were obtained by means of atomic absorption spectroscopy and it is shown in Table 1. In the same table, the content of soluble nitrate ions is shown obtained by the UV–vis spectroscopic method.

Results obtained indicate that the cobalt concentration of Co/Al_2O_3 and $Co/KNO_3/Al_2O_3$ catalysts is very near to the nominal one and that the aging treatment does not modify the concentration of this transition metal.

The potassium concentration in fresh catalysts is near to the nominal value (9.6%, w/w) and the aging treatment decreases such concentration. The aged $Co/KNO_3/Al_2O_3$ catalyst loses 11% potassium and the KNO_3/Al_2O_3 catalyst loses 21% with respect to the fresh catalyst concentration.

Table 1 also includes the soluble nitrate content determined by UV–vis spectroscopy in the washing water. Fresh catalysts contain soluble nitrate in their composition and the content is noticeably lower than the nominal value (15.4%, w/w). This would indicate that during precursor calcination, a nitrate part is decomposed. The $Co/KNO_3/Al_2O_3$ catalyst shows higher content of soluble nitrate ions than in the case of the KNO_3/Al_2O_3 catalyst. The aging treatment decreases substantially the content of soluble nitrate ions.

Since the aging at 800 °C for 2 h partially modifies the potassium content and even more noticeably the soluble nitrate content, it is possible to postulate that the nitrate interacts with the catalyst being transformed into a nitrate coordinate with the support (insoluble) or that the potassium nitrate decompose to K_2O. Also, part of the KNO_3 can be lost by volatilization due to the high temperature (800 °C) of the ageing treatment.