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SOOT COMBUSTION. CO AND K CATALYSTS SUPPORTED ON DIFFERENT SUPPORTS

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Abstract

The catalytic combustion of particulate material was studied on cobalt catalysts promoted with potassium using different supports for its preparation. Silica, aluminium oxides and hydroxides, zirconium oxide and hydroxide were used as supports. The catalytic activity for combustion depends on the type of support used, the higher activity corresponding to the supported catalyst on zirconium oxide. TPR studies indicate that the interaction metal/support allows to explain the higher activity of the CoK/SiO₂ catalyst with respect to the CoK/Al₂O₃ but the high activity found in CoK/ZrO₂ is not explained by this interaction. In all cases the Co and K improved the performance of the catalysts.

Keywords: Diesel particulate, soot, catalytic combustion, oxidation

INTRODUCTION

One of the principal problems in the large urban centers is the presence of particulate material in the atmosphere due to the emission of diesel engines [1]. One of the options to eliminate the particulate material is to impregnate the walls of a filter with an oxidation catalyst. For this, oxides of supported metals are used. Supports can be active or inactive in the burning reaction of particulate material (soot). Supports are divided in three groups: 1) very active: La₂O₂CO₃ and CeO₂; moderately active: TiO₂ and ZrO₂; 3) almost inactive: SiO₂ and

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Al₂O₃ [2]. The alumina is the support most commonly used. Metals of the group VIII are frequently used to control emissions. The cobalt oxide has been used as promoter in catalysts for soot combustion [3]. Lowe and Mendoza-Frohn [4] have worked with cobalt catalysts supported on alumina and they attribute the activity of these catalysts to the formation of an aluminate during calcination at high temperatures. Potassium is added as promoter but the action mechanism is not yet understood [5].

The aim of this work is to study the influence of the support on cobalt and potassium catalysts in the combustion reaction of particulate material.

EXPERIMENTAL

The following supports were used to prepare catalysts: γ -chi-alumina (Al1), Al(OH)₃ (Al2), silica (Si), Zr(OH)₄ (Zr). Alumina supports were provided by the Atomic Center of Bariloche (Argentina), silica is a commercial sample (Deggusa) and the zirconium oxide was prepared in the laboratory. Aluminium and zirconium hydroxides were previously calcined at 823 K and 873 K, respectively, for two hours (Al2C and ZrC) to obtain the corresponding oxides. Catalysts were prepared with aluminium and zirconium hydroxides as well as with their corresponding oxides. Catalysts were prepared by impregnation of the support with Co and K nitrates using the incipient humidity method. The material was dried at 353 K for 24 h and calcined at 873 K for 2 h. Catalysts were prepared with a nominal content of Co and K of 5% and 2%, respectively. They will be indicated from now on with the impregnant denomination followed by the support.

The crystalline structure was analyzed by X ray diffraction using a Rigaku D-Max III equipment, with CuK α radiation ($\lambda=1.5378$ nm, 40 K, 30 mA). The 2θ range was studied from 10 to 70° using a scanning rate of 5°/min.

Experiments of temperature-programmed reduction (TPR) were carried out in a conventional flow reactor using a mixture of 5% hydrogen in nitrogen, with a heating rate of 10 K/min, from 323 K to 1073 K. The sample was dried previously in nitrogen flow at 523 K for 90 min and then cooled at 323 K. The hydrogen concentration changes were analyzed by a thermal conductivity detector (TCD).

The catalytic activity test was carried out in a temperature-programmed oxidation (TPO) equipment. Before the reaction, the soot was carefully incorporated to the catalyst, at a ratio of 1:50, by mechanical mixing in an agate mortar. The oxidation of the mixture (10 mg) was studied in a Shimadzu TGA-50 thermobalance, applying a heating rate of 10 K/min in air/He (2:1) flow, and the weight loss was recorded as a function of the temperature. Weight loss data allowed a differential thermogravimetry curve to be obtained (DTGA). Another

similar experiment was conducted by using the same soot/catalyst ratio and the same air/He flow, but employing the Differential Thermal Analysis technique (DTA) in a DTA 50 model Shimadzu equipment.

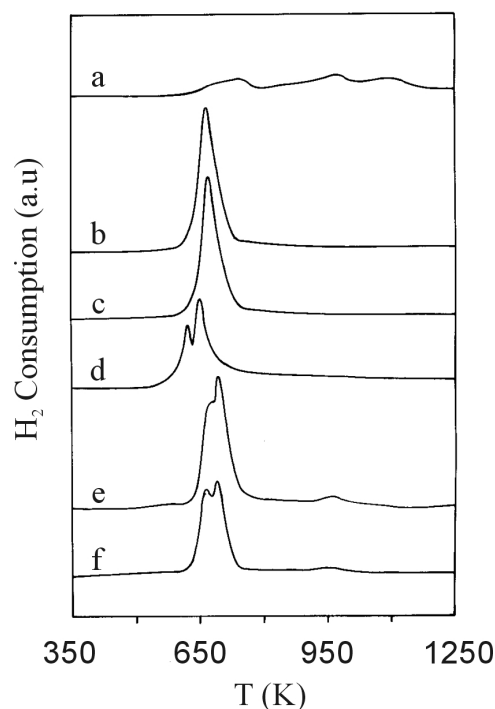


Fig. 1. Hydrogen TPR profiles of Co and K catalysts supported: a) CoKA11, b) CoKA12, c) CoKA12C, d) CoKSi, e) CoKZr, f) CoKZrC

RESULTS AND DISCUSSION

X ray studies show the signals corresponding to gamma and chi phases for the alumina provided by CAB (A11); A12 shows signals of an aluminium oxide called gibbsite that is very crystalline and Al2C presents signals corresponding to a γ -alumina with little crystallization. The CoKA11 catalyst does not present other additional signals than the ones corresponding to the support, while in CoKA12 and CoKA12C signals attributed to Co_3O_4 and/or Al_2CoO_4 species are observed as it was found by Lowe and Mendoza-Frohn [4]. The absence of signals of cobalt compounds in the XRD diagrams in the CoKA11 catalyst would indicate that these compounds are highly dispersed in the catalyst. The

CoKSi catalyst presents low Co_3O_4 signals besides the corresponding ones to the silica support.

For catalysts containing zirconium, the crystallinity depends on the catalyst preparation method. The ZrC support obtained by calcination of zirconium hydroxide crystallized in the monoclinic system. The tetragonal phase is present together with the monoclinic phase in the catalyst obtained from the impregnation of zirconium hydroxide with Co and K salts, (CoKZr). When the support is previously calcined and then followed by impregnation (CoKZrC), the only phase observed is the monoclinic one, which is present in the support prior to its impregnation. In the two catalysts containing zirconium, signals assigned to Co_3O_4 species are observed.

Figure 1 shows the profiles of hydrogen consumption (TPR) of catalysts. In the diagram corresponding to the CoKAl1 catalyst three signals are observed. The peaks show reduction temperatures higher than the temperature corresponding to the cobalt oxides, indicating a strong interaction with the support. Diagrams presented for CoKAl2 and CoKAl2C are practically identical, presenting only a sharp and intense peak whose maximum is placed around 670 K. The CoKSi catalyst is characterized by the presence of two peaks whose maximums are between 620 and 650 K. The presence of these two peaks is assigned to the reduction of the Co_3O_4 oxide, the first signal corresponding to the CoO and the second one to the Co formation [6][7].

Diagrams for CoKZr and CoKZrC catalysts also show the presence of two reduction peaks but not so well differentiated as in the previous catalyst. These signals are at 700 K for the higher reduction temperature.

The similitude observed in the profiles of pairs of CoKAl2, CoKAl2C as well as of CoKZr, CoKZrC catalysts makes one think that almost the same interaction degree is obtained, and the impregnation is carried out on the hydroxide or on the corresponding oxide.

The temperature, at which the combustion occurs at the maximum rate, corresponding to the soot combustion using the different supports studied in this work, is shown in Table 1. These results indicate the following activity order for the soot combustion reaction:

$$\text{Zirconium oxide} = \text{Silica} > \text{Alumina}$$

obtaining a decrease of 100 K for the most active support.

Figure 2 shows results corresponding to all the prepared catalysts. The Co and K addition increased the activity for the combustion and it was beneficial for all supports tested. The temperature at which the combustion occurred at maximum rate was lower in all cases than when only the support was used. A temperature decrease of 100 K of maximum rate of soot combustion was observed for catalysts supported on alumina, of 150 K for the catalyst supported

on silica and of 210 K for the catalyst supported on zirconium oxide. In these three cases the temperature decrease is taken with reference to the soot combustion temperature (Printed U). The combustion temperature decrease between catalysts supported on silica and alumina CoKSi, CoKAl1, CoKAl2 and CoKAl2C can be explained by the higher reducibility of the silica catalyst. The CoKSi catalyst presents a reduction temperature lower than that of the catalysts supported on alumina (Fig. 1). However, the temperature decrease of maximum combustion rate of the supported catalyst on zirconium oxide, CoKZr, is not related with the reduction temperature of cobalt phases. Probably, the zirconium oxide acts not only as support of cobalt phases but also it can participate providing active sites. The zirconia is characterized by its acid-base sites as well as redox sites [8]

Table 1
TPO and TPR results on different catalysts

Material	TPO (K)	TPR (K)	Material	TPO (K)	TPR (K)
Printex U	923	----	Si	823	----
Al1	923	----	CoKSi	770	621-650
CoKAl1	838	744-974-1100	Zr	824	----
CoKAl2	821	668	CoKZr	708	684-702
CoKAl2C	824	671	CoKZrC	717	670-703

CONCLUSIONS

- Alumina, silica and zirconia present different soot combustion rates; zirconia is the most active support.
- The metal-support interaction, and consequently the reducibility of cobalt oxides, studied by means of TPR allows to explain the activity differences for the combustion reaction observed between catalysts supported on alumina and silica. The increase of soot combustion rate for the catalyst supported on zirconia cannot be explained with this mechanism.
- In all cases Co and K increase the activity of catalysts with respect to their supports.
- The lower combustion temperature was obtained for the cobalt and potassium catalyst supported on zirconia.

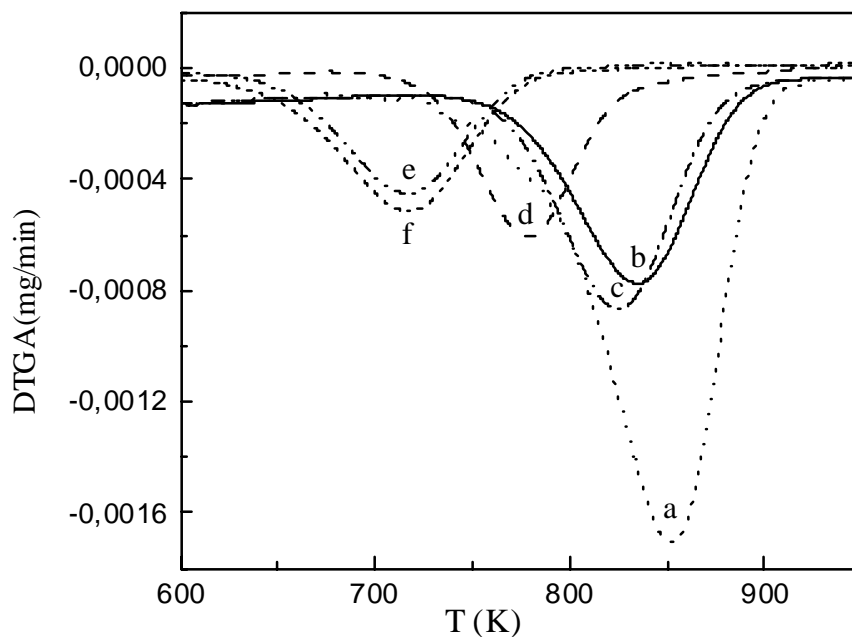


Fig. 2. DTGA curves in the catalytic combustion of soot on catalysts supported: a) CoKAl1, b) CoKAl2, c) CoKAl2C, d) CoKSi, e) CoKZr, f) CoKZrC

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