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Activity of highly dispersed Co/SBA-15 catalysts (low content) in carbon black oxidation

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Abstract

Cobalt supported on mesoporous silica SBA-15 (0.75, 1.5 and 3 wt% Co) were used as catalysts for the oxidation of carbon black. Catalysts were characterized by N_2 sorption, XRD, TEM and TPR. The catalytic activity in CB oxidation was measured. It has been shown that only small cobalt domains (less than 5 nm) are present on all samples. A homogeneous dispersion was obtained for all catalysts. With increasing cobalt loading, crystalline species start to appear. Using an intermediate contact between the CB and the catalyst, the best activity is that of 0.75Co/SBA-15 catalyst where the oxidation reaches the maximum (Tmax) 68 K before the non-catalyzed reaction. On the same catalyst used in tight contact mode with CB, even if Tmax didn't decrease for more than additional 12 K but the Ti decreases by 38K and thus starts 83 K before.

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Keywords: SBA-15, cobalt, carbon black, oxidation

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1. Introduction

Particulate matter emissions are principally emitted from diesel engine exhausts and some industrial chimneys where heavy oils are used as fuels. These emissions (formed by carbon black and soluble organic compounds) are very harmful for the environment and for the health. One of the ways that can be used for their elimination is their catalytic oxidation. Precious metals (Ag, Pt, Pd) supported on CeO_2, TiO_2 and Al_2O_3 show good activity in soot combustion [1-5]. Ruthenium based catalysts are also promising in this reaction when supported on CeO_2 [6]. However these metals are expensive and their replacement by a cheap metal should be investigated. Cobalt based catalysts show promising properties in oxidation reactions, SBA-15 can be successfully used for the templating of cobalt oxide nanoparticles inside the porosity of the support [7, 8]. In this work SBA-15 was used as a support for the dispersion of cobalt oxides with three cobalt loadings: 0.75, 1.5 and 3 wt%. Characterizations by N_2 sorption, XRD, TPR, TEM were done in order to determine the texture of the catalysts and the nature of active species formed. Their reactivity in oxidation of carbon black was studied.

2. Experimental

SBA-15 was prepared by using sol-gel method reported by Zhao et al. [9] with the following modification: ten minutes after the addition of tetraethyl orthosilicate (TEOS) under stirring, the mixture was kept without stirring at 35°C for 24 hours. The solution was then filtered and dried at room temperature for 24 hours before calcination under air at 500°C for 9 hours with a heating rate of 2°C.min^{-1}. A metal loading ranging between 0.75 and 3% was obtained by using two-solvent technique [10] in the presence of a solution of cobalt nitrate (Cobalt nitrate hexahydrate, 98%, Sigma Aldrich). Impregnated catalysts were dried at room temperature for 24 hours then calcined under air at 450°C for 5 hours with a heating rate of 0.5°C.min^{-1}. Catalysts are labeled as xCo/SBA-15 with x the cobalt weight percentage. N_2 sorptions were performed on AutoChem 2920, Micromeritics, to estimate the BET surface area (single point). X-Ray diffractions were performed on a Brüker D8 (λ = 1.5406 nm). A JEOL JEM-100 electron microscope operating at 100 keV was used equipped with energy dispersive X-ray spectroscopy (EDX) and nanodiffraction. TPR profiles were recorded on an Autochem 2920, Micromeritics. TPO (used as a pretreatment for TPR experiments) was conducted from room temperature to 550°C under a flow (20 mL.min^{-1}) of 5 vol.% O_2/He. TPO was followed by a TPR under a flow of 5 vol.% H_2/Ar (20 mL.min^{-1}) from room temperature up to 1000°C. Water was trapped, by using a bath of ice and salt, during TPR experiments. Carbon black, Degussa N330, was used as a representative of soot. Catalysts were mixed with carbon black by using a mortar and a pestle for 3 minutes in order to achieve an intermediate contact and for 20 minutes in order to achieve a tight contact (90% catalyst, 10% carbon black). Each mixture was then heated (5°C.min^{-1}) from room temperature to 900°C in a Setaram differential scanning calorimetry/thermogravimetry (DSC/TG) apparatus under an industrial air flow of 50 mL.min^{-1}.

3. Results and discussion

BET surface areas of SBA-15 is 357m^2.g^{-1}. After addition of cobalt, the BET surface areas of 0.75Co/SBA-15, 1.5Co/SBA-15 and 3-Co/SBA-15 become 321, 327 and 263 m^2.g^{-1}. The surface area decreases compared to SBA-15, but still comparable for 0.75Co/SBA-15 and 1.5Co/SBA-15. After the addition of 3wt% of cobalt, the surface area decreases significantly.

XRD patterns of different catalysts are represented on figure 1. For 0.75Co/SBA-15, no diffraction peaks were detected. By complementary techniques of characterizations, authors have attributed these cobalt species to isolated cobalt sites [10] or CoOx and cobalt silicate [11]. For 1.5Co/SBA-15, peaks with very low intensity are detected but their attribution is very hard. On the

3Co/SBA-15 catalysts, wide peaks with the more intense one around 37° (2 theta) can be attributed to cobalt oxide CoO (JCPDS 01-089-2803) or Cobalt silicate Co_2SiO_4 (JCPDS 00-029-0506). For this low cobalt loading, a distinction between these two species cannot be done and the presence of a mixture of these two species cannot be eliminated.

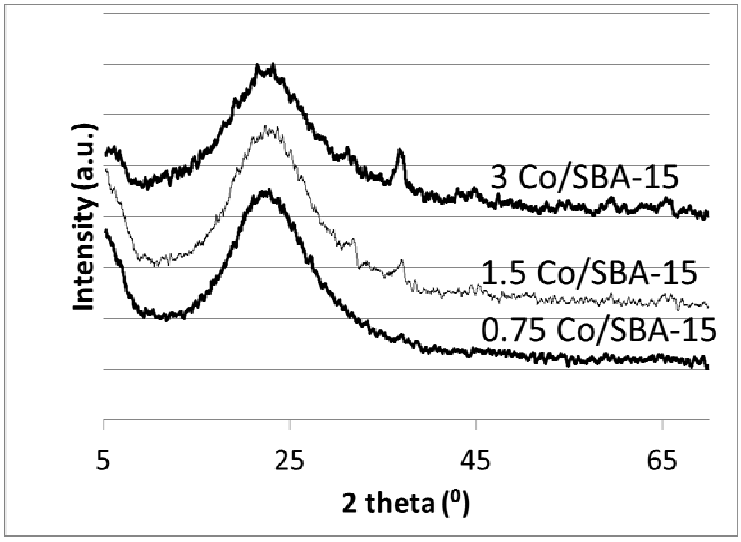

Figure 1: XRD patterns of 0.75Co/SBA-15, 1.5Co/SBA-15 and 3Co/SBA-15

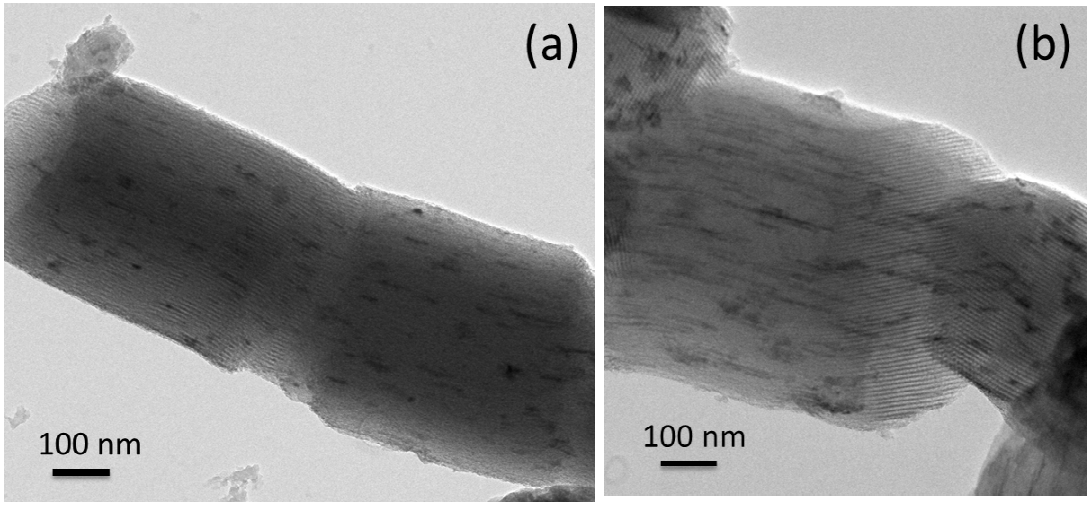

Figure 2: TEM micrographs of (a) 0.75Co/SBA-15 and (b) 1.5Co/SBA-15. Cobalt oxides appear darker than the support SBA-15

TEM micrographs show a very good dispersion of cobalt on the support SBA-15 for these three cobalt loadings. For the 0.75Co/SBA-15, cobalt species seem to be located inside the porosity of the support, they didn't have the shape of spherical particles but more like rods (figure 2.a). EDX analysis show a Co/Si molar ratio of 1.3.

For the 1.5Co/SBA-15 catalyst, cobalt species are also well dispersed and they always look like rods. EDX analysis gives Co/Si ratios of 2.1 and 1.4 at two different locations in the sample. For the 3-Co/SBA-15, silica grains become more charged with cobalt species, and one can distinguish two different shapes; rods and spherical particles. Rods are located inside grains and spherical particles seem to be external to the grains. Nanodiffractions (Figure 3) were done on these two different aspects (rods and crystals), and the first one lead to a bad diffraction while the other one show a diffraction of well crystallized cobalt species. EDS analysis show a Co/Si ratio of 4.8.
For the 3-Co/SBA-15, diffraction peaks are detected by XRD and by TEM crystals and poor-crystallized cobalt species coexist in this catalyst. For the diffraction on the crystal, measured inter-reticular distances are: 2.58, 1.54, 1.31 1.19 and 0.99 Angstroms. The inter-reticular distance of 2.58 corresponds probably to CoO FCC (JCPDS 089-1300) or CoO Hexagonal (JCPDS 01-089-2803). The other distances may be attributed to Co_3O_4, Co_2SiO_4 and CoO. A mixture of cobalt species can be present and a strict attribution cannot be done with these conventional techniques of characterization. TEM results show a good correlation with XRD; for 0.75Co/SBA-15 and 1.5/SBA-15, no clear diffraction was detected by XRD and in TEM no crystals were found on these catalysts. Li et al. [12] have attributed the amorphous species of cobalt on SBA-15 to CoO_x clusters and cobalt silicate.

Tempearture programmed reduction profiles of 0.75Co/SBA-15 and 3C-SBA-15 catalysts show a reduction starting above 400°C. This reduction continues up to 1000°C (hydrogen consumption appear as a negative signal on the graph). The TPR profiles of these two catalysts are quite similar with more intense contribution of the 3Co/SBA-15 which is containing a higher concentration of cobalt. These reduction behaviors are similar to those obtained by Wang et al. [11] on highly dispersed cobalt on SBA-15, where cobalt was bonded to silica surface.

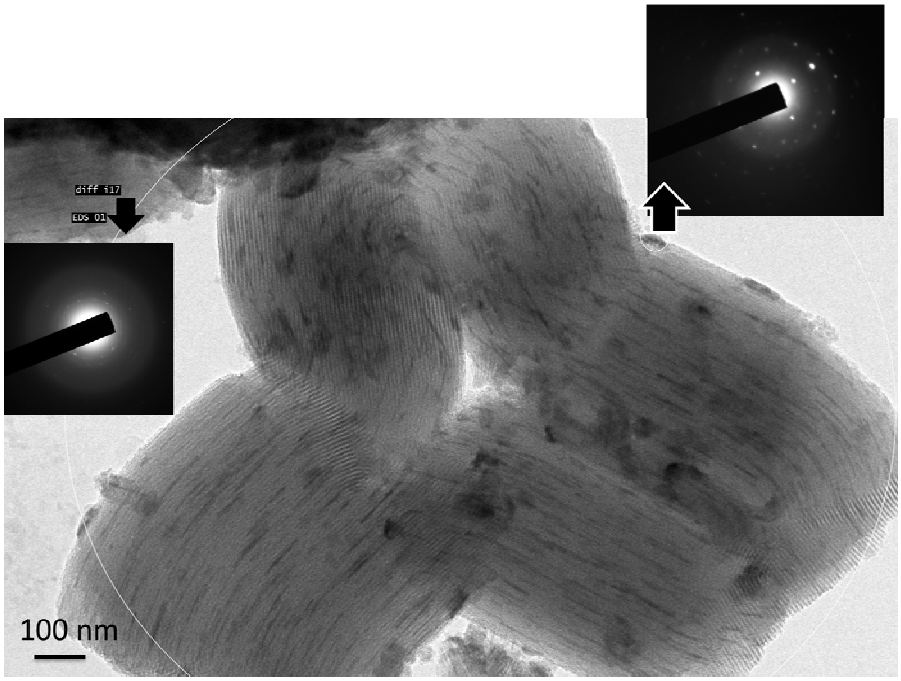

Figure 3: TEM micrograph of 3Co/SBA-15 with corresponding nano-diffrcations done on indicated areas

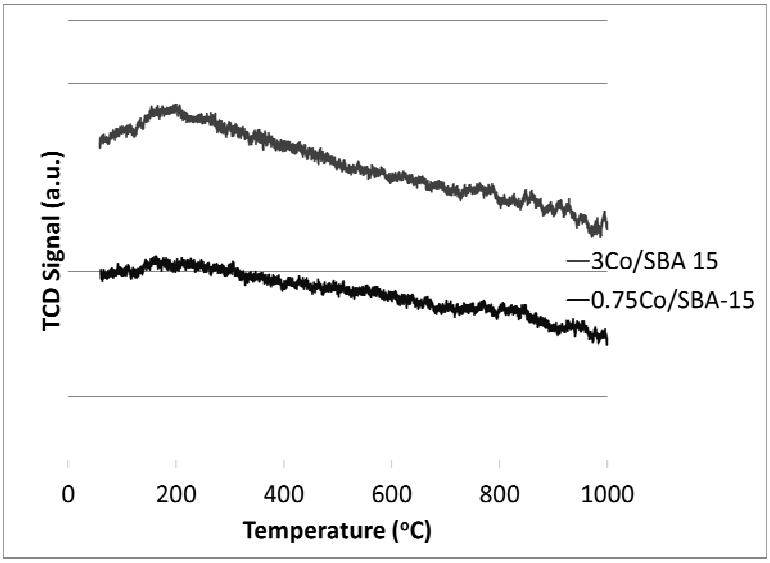

Figure 4: TPR profiles of 0.75Co/SBA-15 and 3Co/SBA-15 catalysts

Thermodynamic oxidation of carbon black, in absence of catalyst, starts at 508°C (Ti), reaches it maximum at 630°C (Tmax) and is achieved at 647°C (Tf, table 1). In presence of SBA-15 mixed with CB, Ti decreases to 499° and Tmax to 603°C while Tf remains approximately the same. For 1.5Co/SBA-15 and 3Co/SBA-15, Ti starts around 500°C, Tmax around 583-589 and Tf at 644 and 633 respectively. The better reactivity is that of 0.75Co/SBA-15, an important decrease in the Ti (463°C), Tmax at 562°C and Tf at 628°C. Tight contact leads to a better interaction between active species and soot. In tight contact, reactivity of this catalyst increases; Ti becomes 425°C, Tmax 545°C and Tf 591°C. This result is acceptable for this cheap catalyst keeping in mind that these nanoparticles are maintained inside the support and their sintering can then be lowered compared to other catalysts supported on non-porous ceria, titania or alumina.

In this solid state reaction, the accessibility of CB to cobalt active sites can be restricted by the pores of SBA-15, thus this type of catalyst can be more reactive in gas phase reactions. But since soot contains gaseous reactants in addition to carbon black, it is important to study this solid state reaction on these catalysts in addition to the study of the gas phase reaction.

Table 1: Reactivity of catalysts in oxidation of carbon black, Ti: iginition temperature, Tmax: Temperature of maximum conversion and Tf: temperature of 100% conversion

Sample	Ti	Tmax	Tf
Carbon black, CB	508	630	647
SBA-15 + CB	499	603	646
0.75Co/SBA-15+CB	463	562	628
1.5Co/SBA-15+CB	500	589	644
3Co/SBA-15 + CB	501	583	633
0.75Co/SBA-15 + CB tight contact	425	545	591

4. Conclusion

Well dispersed cobalt species were supported on SBA-15 with a cobalt loading between 0.75 and 3 wt%. Small cobalt domains (< 5nm) were formed on all catalysts. Cobalt species start by forming rods and with increasing cobalt loading, some cobalt crystals are formed outside silica grains. These external particles are probably corresponding to CoO. Catalytic oxidation of CB on these catalysts show that the best reactivity is obtained for the lower cobalt content where only poor reducible cobalt species are detected by TEM and XRD. In tight contact mode, the reactivity increases and Tmax decreases by 85°C. The result is acceptable for this type of inexpensive catalyst that has the advantage of avoiding sintering by the presence of cobalt species inside the porosity of SBA-15.

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