SYNTHESIS AND CATALYTIC PROPERTIES OF CeO$_2$ AND Co/CeO$_2$ NANOFIBERS FOR DIESEL SOOT COMBUSTION

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Introduction

It has been reported that CeO$_2$, in combination with other catalysts/metals, has the potential of increasing the oxidation rate of soot, because of the creation of active oxygen [1]. The promotional activity of CeO$_2$ has also been attributed to its oxygen storage capacity. In this way, The incorporation of CeO$_2$ is likely to improve the redox capacity of catalyst and in addition, it may also act as a stabilizer of O^{2-} ions on the catalyst surface [2]. It has been reported that transition metals, such as cobalt, copper and iron supported/doped ceria mixed oxide catalysts show strong soot oxidation activity through a redox-type mechanism on the basis of an oxygen spillover on CeO$_2$ or a synergistic effect between the transition metal oxides and ceria [3]. The activity and selectivity of such catalysts are related to the strong redox properties of CoO$_x$ [4]. In the present study we have designed fibrous structured cerium dioxide catalysts with the aim of enhancing the trapping and combustion of soot properties.

Experimental

The CeO$_2$ nanofibers were synthesized by the means of coprecipitation/ripening method [5]. A solution of Ce(NO$_3$)$_3$.6H$_2$O of 0.1 molar was prepared by dissolving it in distilled water. Different mole ratios of NaOH/citric acid (0.3, 0.6, 0.8 and 1.0) solution were prepared in another beaker. These solutions were mixed together in a separate beaker and then aged at 90°C for 24h until complete precipitates were obtained. The formed precipitates were then filtered, washed with distilled water, dried and calcined at different temperatures i.e., 300 and 600°C for 5h in air. The prepared CeO$_2$ (0.8) nanofibers obtained with the above method were used as a support for the impregnation of cobalt (Co(NO$_3$)$_2$.6H$_2$O) with different weight percentages of Co (1, 5 and 10 wt%) . They were then dried and calcined at 600°C for 3h in air.

All the prepared catalysts were fully characterized by means of atomic absorption analysis , X-ray diffraction, field emission scanning electron microscope, the BET-specific surface area. Temperature-programmed analyses were performed in a Thermoquest TPD/R/O 1100 analyzer, equipped with a thermal conductibility (TCD) detector with the methodology described in [6]. The activity of the catalysts was tested in a temperature programmed combustion (TPC) apparatus [6].

The possible thermal stability and poisoning effects of sulfur (present in diesel fuel) on Co/CeO_2 (0.8) catalytic activity was investigated by ageing the catalysts under air and 1030 ppm of SO_2 at 800°C for 12h in a tubular furnace.

Results and discussion

Three kinds of CeO_2 precipitates were obtained with different NaOH/citric acid ratios. The morphological structures of all the formed precipitates, analyzed by means of FE SEM, are shown in Fig.1. The formation of the different structures of the CeO_2 precipitates was influenced by the NaOH/citric acid ratio. At lower NaOH/citric acid ratio of 0.3 and 0.6, with aging time of 24 and 12h respectively, the formation of stick in bundle structure was observed and shown in the FESEM images in Figs. 1. A & B (a and b respectively). Fibrous structured precipitate formation was observed while increasing the ratio to 0.8 and the ageing time was decreased to 6h, as shown in the FE SEM images in figs. 1. A & B (c). When the ratio was increased from 0.8 to 1.0, the formation of flake structures was shown in the FE SEM images in figs. 1. A & B (d). It was observed that the fiber and flake structured precipitates were formed within 6h of ageing time. This is the minimum ageing time required to complete the precipitation. The ageing time and morphology were two key factors for the control of the NaOH/citric acid ratio of the precipitates. The special morphology of the CeO_2 (0.8) fiber structure retained even after thermal treatment at high temperatures of about 600°C (Fig. 1. B (c)) This morphology was strongly influenced by NaOH/citric acid ratio of 0.8 which induced the formation of appropriate fibrous structure. Thus, the CeO_2 (0.8) fibers were selected for further studies. Table 1 shows the specific surface area of different CeO_2 precipitates calcined at 300°C. All the types of CeO_2 precipitates show a high specific surface area with no significant differences among the values of the different samples. We selected CeO_2 (0.8) fibers as their special morphology leads to an increase in the contact points of the soot particles and catalyst, in the trapping capability as well as a decrease in pressure drop. Table 1 also reports the results of soot combustion tests carried out under a 10% O_2/N_2 atmosphere over both loose and close contact conditions. All the catalysts lower the peak soot combustion temperature significantly compared with that of the non-catalytic combustion of Printex U and The reported powder CeO_2 catalyst [7]. Similar peak combustion temperatures were obtained for the four different fibrous CeO_2 (0.3, 0.6, 0.8 and 1.0) catalysts prepared and calcined at 300°C; T_p ranged from 397 to 401°C under close contact conditions, but the shift in peak combustion temperature remained limited to less than 50°C under loose contact conditions (438-447°C).

Due to its special morphology, the fibrous structured CeO_2 (0.8) sample catalyst was selected for thermal a ageing test at 800°C for 12h in air; the results of the ageing treatment were evaluated by repeating the soot combustion tests under both loose and close contact conditions, the results of which showed that the thermal stability of the material could be considered as satisfactorily since only a very small shift in the T_p (no more than 10°C) was measured compared to the fresh

catalysts in spite of the severe loss in specific surface area. In fact, as a general trend, it is possible to state that the specific surface area of ceria fiber catalysts does not affect the soot combustion activity. Finally, we selected the sample CeO_2 (0.8) which is characterized by a NaOH/citric acid of 0.8 in the preparation procedure, and submitted it to further studies as a support for cobalt impregnation due to its special morphology and high thermal stability.
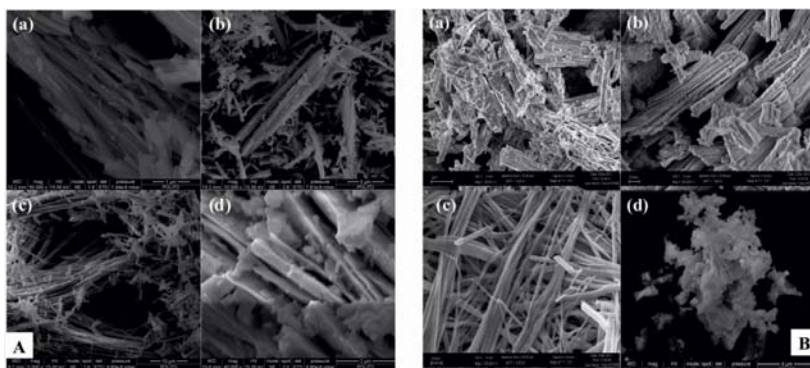
Figure 1. FE SEM images of calcined CeO_2 at different temperatures (A) 300°C and (B) 600°C. CeO_2 (0.3) (b) CeO_2 (0.6) (c) CeO_2 (0.8) (d) CeO_2 (1.0).

Table 1. Soot combustion activity results and BET-SA of CeO_2 calcined at 300°C under loose and tight contact conditions.

Samples	BET-SA (m^2/g)	T_p (°C) Tight	T_p (°C) Loose
Printex-U	-	-	600
CeO_2 (0.3)	112	400	440
CeO_2 (0.6)	107	399	445
CeO_2 (0.8)	115	401	447
CeO_2 (1.0)	120	397	438
CeO_2 (0.8) calcined @ 600°C for 3h	21.5	400	445
CeO_2 (0.8) aged @ 800°C in air or 12h	8.3	409	457

T_p – peak combustion temperature.

Thermally stable and fibrous structured CeO_2 (0.8) was selected for the impregnation of cobalt for further studies. The composition of the cobalt content in all the prepared catalysts, was determined by atomic absorption spectroscopy (AAS) and is shown in Table 2. The results of all the cobalt impregnated CeO_2 (0.8) specific area measurements fiber catalyst are shown in Table 2. Cobalt impregnation on the CeO_2 (0.8) fibers shows a decrease in the specific surface area of the CeO_2 (0.8) support. It can be observed that the loss of surface area increases with an increase in the cobalt content, which is due to the dispersion of the cobalt on the surface of the CeO_2 (0.8). However, a further loss in the specific surface area of the 10%Co/CeO_2 (0.8) catalysts was observed after ageing at 800°C; this is

due to the formation of larger agglomerated particles of cobalt on the CeO_2 (0.8) fibers.

Table 2. BET, AAS and activity results of Co impregnated CeO_2 fibers @ 600°C.

Samples	AAS-Co (wt%)	BET-SA (m^2/g)	T_p (°C) with O_2	T_p (°C) with NO
CeO_2 (0.8)	-	21.5	445	412
1% Co/CeO_2 (0.8)	0.94	11.4	390	381
5% Co/CeO_2 (0.8)	4.79	9.2	400	369
10% Co/CeO_2 (0.8)	9.81	7.5	410	357
10% Co/CeO_2 (0.8) aged @800°C in air for 12 h	-	3.5	416	375
10% Co/CeO_2 (0.8) aged@800°C under 1030 ppm of SO_2 for 12 h	-	3.1	506	485

T_p – peak combustion temperature.

The morphology of the cobalt impregnated CeO_2 (0.8) fiber catalysts was observed by means of FESEM image (not reported) shows the fibrous structure of the 1%Co/CeO_2 (0.8), 5%Co/CeO_2 and 10%Co/CeO_2 (0.8) catalysts respectively. The CeO_2 (0.8) nanofibers had diameters that varied from 30 to 90 nm; segregation of cobalt on the CeO_2 (0.8) nanofibers was observed on the FE SEM images. The segregated cobalt particles are clearly observed in the FE SEM images of 10%Co/CeO_2 (0.8) sample and were also confirmed by the XRD spectra (not reported).

The fiber structure did not collapse after the impregnation of cobalt and calcination at 600°C, which is further confirmation of the stability of the fibers.

The soot combustion activity of the CeO_2 (0.8) and cobalt impregnated CeO_2 (0.8) catalysts was investigated under both an O_2/N_2 and an $NO/O_2/N_2$ atmosphere. The results of these tests are given in Table 3. As expected, the catalytic activity of the Co impregnated CeO_2 (0.8) catalysts significantly lowers the peak soot combustion temperature compared with that of the non catalytic combustion of Printex U and CeO_2 (0.8), even though no significant effect of cobalt content can be observed. The CeO_2 (0.8) nanofibers clearly display the peak soot combustion at 445°C in the presence of 10%O_2, while soot combustion was promoted by the cobalt loading on the CeO_2 (0.8) nanofibers at even lower temperatures. The 1% Co/CeO_2 catalyst is in fact able to lower the T_p value of 45°C with respect to pure ceria, while to Co-richer samples exhibit even slightly higher peak combustion temperatures (410-416°C). The low temperature soot combustion promoting effect of the cobalt impregnated CeO_2 (0.8) fibers is due to the presence of Co_3O_4, which shows a very high oxidation activity [26]. The maximum low temperature activity may be due to the better dispersion of Co_3O_4 on the fibers since the contact between the soot particles and redox active sites could be enhanced.

The soot combustion activity of all the catalysts was shifted to significantly lower temperatures with the introduction of NO/O_2. In this case, the effect of cobalt loading is much more relevant and positive, as the Co-richer sample is the catalyst that exhibits the best performances. A drop in T_p of 55°C was observed on the 10% Co/CeO_2 (0.8) catalyst compared to the CeO_2 (0.8) fibers in the presence of

NO/O_2. The presence of more Co_3O_4 species in the catalysts promoted the Ce^{4+}/Ce^{3+} redox pair and this is probably at the basis of the soot oxidation performances through the formation of NO_2. This suggested that the formed in-situ NO_2 significantly promotes the soot combustion at low temperatures for the higher loadings of the Co/CeO_2 (0.8) catalysts. Uner et. al., [8] reported that the pronounced activity of cobalt oxide catalysts seems to be due to the presence of reducible oxides such as CeO_2. The oxygen needed for the oxidation reaction would therefore be provided by the second oxide (cobalt oxide). A spillover mechanism can be postulated for the soot oxidation at the cobalt oxide-ceria interface [3]. The generation of active oxygen induced by cobalt cations could be the reason for the low temperature soot combustion activity of the cobalt impregnated CeO_2 (0.8) catalysts compared to CeO_2 (0.8) fibers. High selectivity towards CO_2 was obtained for the CeO_2 (0.8) and Co/CeO_2 (0.8) nanofiber catalysts in the soot combustion temperature range. The non-catalytic combustion of Printex U, in fact occurred at rather high temperatures and with low CO_2 selectivity.

The long-term thermal stability and poisoning resistance of the 10% Co/CeO_2 (0.8) nanofiber catalyst was studied by ageing it under air and 1030 ppm SO_2 at 800°C for 12h. After having carried out the ageing treatment on the 10%Co/CeO_2 (0.8) nanofiber catalyst, the soot combustion activity was tested under both an O_2/N_2 and an $NO/O_2/N_2$ atmosphere. It was observed that a loss occurs in the soot combustion activity compared to the fresh catalysts (Table 2). However, the activity of the SO_2 aged catalysts occurred to a very high temperatures. This loss may be caused by the poisoning effect of the huge amount of SO_2 which is the worst condition that can be used to explore the stability of the 10%Co/CeO_2 (0.8) nanofiber catalysts. However, in real conditions, especially in Europe, diesel fuels contain few ppm of sulfur. FE SEM image of the SO_2 aged catalyst, no reported for the sake of briefness, confirms the presence of agglomerated cobalt particles on the CeO_2 fibers and the loss of the specific surface area. The loss in the activity is due to the formation of cobalt sulfates during the ageing process under SO_2 at 800°C. Further studies are planned to grow these Co/CeO_2 (0.8) nanofibers on a SiC (silicon carbide) disks in order to observe the effect of the direct contact of the soot particles with the fibers using a special setup which would be similar to those of the catalyst/filter housings that are actually placed after diesel engines.

It is well known that the high mobility of oxygen on the surface and in the bulk leads to an important contribution to soot combustion/oxidation activity. In the context, H_2-TPR and O_2-TPD experiments were carried out in order to study the redox properties of the Co/CeO_2 (0.8) nanofiber catalysts. The O_2-TPD profiles (not shown) for the fresh catalysts after a pretreatment at 750°C under an oxygen flow. None of the catalysts showed any kind of even weakly chemisorbed oxygen desorption during the O_2-TPD experiment below temperatures of 600°C. A noticeable release in the oxygen can be observed at high temperatures of around 750 to 950°C. This high temperature oxygen release, which is centered at 880°C, is probably due to the thermal reduction of Co_3O_4 to CoO [6].

The presence of ceria in synergism with cobalt oxides leads to catalyst with significant reducibility [6]. The TPR profiles of all the Co/CeO_2 catalysts (not shown) look very similar, since the three Co/CeO_2 (0.8) catalysts exhibit two reduction peaks in the 300-450°C temperature range. It has been demonstrated, from the literature [9], that the first step reduction is a one-electron process (Co^{3+} + $e^- \rightarrow Co^{2+}$), whereas the second step is a two-electron reduction process (Co^{2+} + $2e^- \rightarrow Co^0$) [6]. The H_2/Co ratio between the hydrogen uptake in the TPR and the amount of cobalt in each sample, in fact ranges from 1.24 to 1.27, which is a very close value to the expected one from the stoichiometry of a complete reduction of Co_3O_4 to Co° (1.33). A similar result is obtained with the Co_3O_4 bulk sample, which is reduced in the same temperature range, across two peaks, and with an overall H_2/Co ratio equal to 1.23.

In conclusion, the redox properties of the Co/CeO_2 (0.8) fiber samples have revealed that neither self-reduction to CoO (measured by O_2-TPD) nor complete reducibility to metallic cobalt (measured by H_2-TPR) do not significantly depend to any great extend on the amount of cobalt. The activity of catalysts in the absence of NO does not seem to be affected by the cobalt content, but seems to depend on the surface area. On the other hand, the activity in the presence of NO is an increasing function of the copper content, probably due to the increasing activity towards the catalytic oxidation of NO to NO_2. Such a reaction is boosted by the enhanced capacity of the Co_3O_4/CeO_2 system spontaneous release of oxygen (even in the absence of a reductant), as shown by the TPD results (the amount of desorbed O_2 increases with the cobalt content in a linear way).

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