

Catalytic Activity of CeO₂-NiO for Low Temperature Soot Combustion

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Abstract— CeO₂ (Ce) and CeO₂-NiO (CeNi) nanocatalysts were synthesized by co-precipitation from nitrate precursors using 25% ammonia solution (NH₄OH) as the precipitating agent. The catalysts were calcined in air at 500 °C and 800°C for 4h to evaluate the thermal stability. XRD and DLS techniques were used for catalyst characterization. A Thermo gravimetric/Differential Thermal Analyzer (TG/DTA) was used to determine the catalytic activity and soot oxidation reactions. Compared with Ce, Ce-Ni nanocomposite showed lower soot oxidation temperature.

Keywords— CeO₂, CeO₂-NiO, co-precipitation, soot oxidation, catalytic activity..

I. INTRODUCTION

Ceria based catalysts are widely employed in three-way catalysts (TWC) for air pollution abatement and their redox properties are a key factor in the development of soot removal catalytic materials [1-5]. Ceria presents its capacity to store and release oxygen due to the ability of cerium to switch between the Ce⁴⁺ and Ce³⁺ oxidation states and to incorporate more or less oxygen into its crystal structure [3]. The doping of ceria favors creation of structural defects, accelerates oxygen diffusion and induces more surface active oxygen species which further promotes soot oxidation [2,4,6]. Previous reports have shown that the activity of ceria in complete oxidation reactions can be increased to a larger extent by doping transition metals [6]. Fe₂O₃-CeO₂ presents maximum soot oxidation rate at 366°C under tight contact conditions after a 12h calcination at 750°C [7]. Oxides of Mn have also shown superior catalytic activity in soot oxidation due to the synergetic effect between ceria and manganese oxide [6,8]. On the other hand CuO-CeO₂ mixed oxides have exhibited heightened catalytic performance for selective CO oxidation, which is attributed to the well dispersed copper oxide species strongly interacting with ceria [9]. Co-based oxide catalysts such as mixed oxides, perovskites and hydrotalcite-derived oxides have attracted much attention because of their excellent catalytic oxidation ability Luo et al. reported that mesoporous Co₃O₄/CeO₂ mixed oxides with encapsulated structures possess novel catalytic activity for CO oxidation, mainly attributed to the formation of interface oxygen vacancies [10].

In this paper a nickel oxide doped ceria (CeO₂-NiO) catalyst is synthesized and reported to lower soot oxidation

temperatures. This promotes passive regeneration of filter when coated in Diesel Particulate Filters (DPFs) in exhaust systems of diesel engines. In the present study, CeO₂-NiO powder catalysts are perfectly blended with printex U or model soot and subsequently these mixtures' activity are examined using a TG/TGA. Therefore, the objective of the present work has been to evaluate the catalytic oxidative properties of CeO₂-NiO upon reaction with soot.

II. EXPERIMENTAL

A. Catalyst preparation

CeO₂-NiO (CeNi, 2:1 mole ratio) was synthesized by co-precipitation method using 25% ammonia solution (NH₄OH) as precipitating agent. Nitrate precursors used were Ce(NO₃)₃.6H₂O, and Ni(NO₃)₂.6H₂O from Lobacheme and SDFCL respectively. CeNi was prepared by dissolving Ce(NO₃)₃.6H₂O and Ni(NO₃)₂.6H₂O on a 2:1 mole ratio in 200ml Millipore deionized water (18.2 MΩ.cm@25°C). Mixing was done on a magnetic stirrer at 1000rpm speed for 1 hour. The mixed solution was precipitated by drop-wise addition of aqueous ammonia solution over a period until the solution pH reached ~9. After room temperature aging of the mixed solutions for 20 hours, the resulting pale brown coloured CeNi was decanted, filtered and washed several times with Millipore ultrapure water (18.2 MΩ.cm@25°C) until free from anion impurities. The obtained precipitate was oven dried at 100°C for 5 h and ground in an agate mortar. Pure ceria was also prepared from Ce(NO₃)₃.6H₂O under the same conditions for comparison purposes. Calcination was done at 500°C and 800°C for 4h in a muffle furnace.

B. Catalyst characterisation

Powder x-ray diffraction (XRD) patterns of the calcined catalysts were performed using a Bruker's D8 advanced X-ray Diffractometer using Cu Kα (λ=15.406 nm). The scanning range of 2θ was from 20° to 80° with a step size of 0.02°. The mean crystallite sizes were determined from the full width at half maximum (FWHM) of the diffraction peak using the Scherrer's equation [3,8] and are shown below in Table 1. Dynamic Light Scattering (DLS) model

no: HORIBA Nanoparticle analyzer SZ-100 was used to measure the size of the particles by analyzing the solution of catalysts in distilled water.

C. Activity measurement

Printex-U (Degussa) with a particle size 25nm and specific surface $100 \text{ m}^2\text{g}^{-1}$ was used as surrogate soot. The catalytic activity was evaluated by a Thermogravimetry and Differential Thermal Analysis (TG/DTA 6300) apparatus. Before reaction, the soot-catalyst mixtures were blended in a 1/9 weight ratio, in a small polyethylene container for "loose contact" and milled in an agate mortar for "tight contact". Tight contact forces the soot particle and catalyst to be in intimate contact and allows the activity of catalysts under optimum conditions to be investigated [3,8,10]. Furthermore the tight contact mode makes it possible to study intrinsic kinetics while loose contact is more similar to real engine conditions, as mass transfer limitations become important [11]. The temperature was raised at 10 oC/min from room temperature to $900 \text{ }^\circ\text{C}$ in 100 mL/min flow of air.

III. RESULTS AND DISCUSSION

A. Characterisation of the catalysts

Powder XRD patterns of ceria doped catalysts are shown in Fig 1. For comparison purposes pure ceria is also included and all materials were calcined at 500°C and 800°C . All the XRD pattern diffraction peaks of the catalysts corresponds to fluorite-like structure analogous to that of pure CeO_2 (JCPDS 34-0394, space group Fm-3m) [11-13].

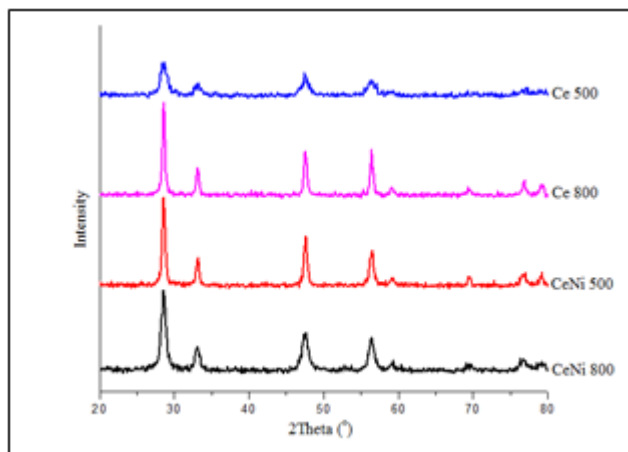


Fig.1 XRD patterns of Ce 500, Ce 800, CeNi 500 and CeNi 800

No XRD diffraction peaks of nickel oxide are found as shown by the similar peaks of the CeNi curves to that of ceria. However the less broad Ce 800 and CeNi 800 peaks recorded the highest crystallite as expected from Scherrer's equation [3,8,11], which shows that peak width is inversely proportional to crystallite size. The observation could be explained as; with the increase of calcination temperature, the growth rate of particles increases more rapidly than the

nucleation rate and the aggregation trend of particles becomes stronger.

The DLS analysis in Fig. 2a showed that the hydrodynamic sizes of Ce catalysts have a narrow size distribution as compared to the CeNi mixed oxides and the average particle sizes from the histograms was presented in table 1.

Table 1: XRD and DLS size range

Catalyst	XRD size(nm)	DLS size (nm)
CeO_2 500	18.9	25.5
CeO_2 800	24.9	29.3
CeO_2 -NiO 500	19.0	17.1
CeO_2 -NiO 800	38.0	26.5

This could be explained that by doping Ce with Ni the hydrodynamic size increases from that of undoped Ce. However nanoparticles calcined at 800°C (fig. 2b) showed larger particle size as compared to those calcined at 500°C .

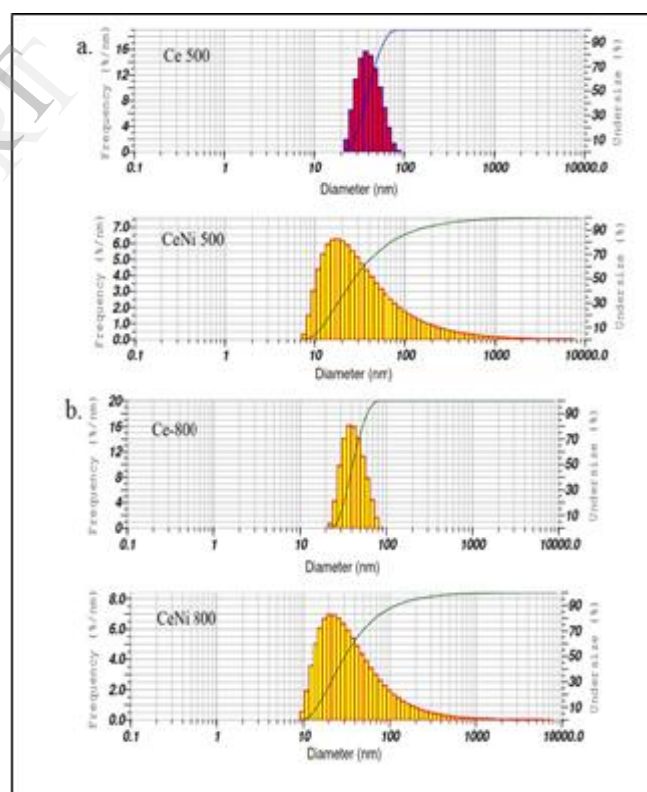


Fig. 2 Particle size distribution histograms of Ce and CeNi calcined at a. 500°C and b. 800°C

B. Soot oxidation tests

The catalytic activity of the catalysts for soot combustion in air are presented by the TG/DTA curves in Fig. 3 and Fig. 4. It is vividly observed that the onset temperature (T_i) of the soot in the absence of catalyst in

Fig. 3 (624°C) was reduced when the soot was mixed with catalyst as shown in Table 2.

Table 2. TG/DTA catalytic performance for soot combustion by CeNi catalysts.

Sample	DTA peak 1		DTA peak 2	
	T(°C)	DTA(μV)	T(°C)	DTA(μV)
pU	244	14.2	637	-9.9
CeNi-pU (L)500	262	14.5	590	29.39
CeNi-pU (T)500	273	14.88	497	59.51
CeNi-pU (L)800	228	14.42	655	10.98
CeNi-pU (T)800	280	14.88	612	35.99

The highest change in ignition temperature was observed when CeNi catalyst was mixed with soot ('loose contact' mechanism). The change was 228°C lower than that for uncatalysed soot. Overall all the tight contact mixed samples showed lower onset temperatures (DTA Peak 2) as compared to the loose contact composition which is in agreement with what is found in literature [10,11,13].

The DTA curves in Fig. 3 and Fig.4 shows the thermal behaviour of the catalyst-soot system and illustrates that combustion takes place in two stages: the first one, associated to a flat exothermal peak within 228-280 °C corresponds to the oxidation of light hydrocarbons.

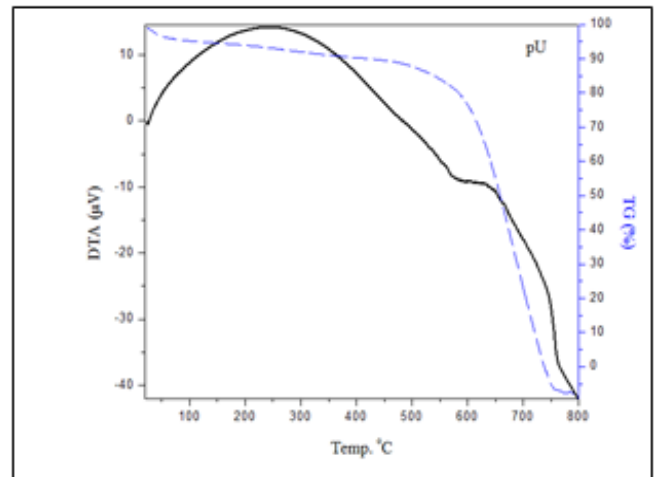


Fig 3. TG/DTA in air atmosphere of the noncatalytic combustion of soot (pU = printex U)

The second sharp exothermal peak within 497-637 °C corresponds to oxidation processes of branched hydrocarbons and heavy compounds. Thence Ce-Ni calcined at 500°C (CeNi 500) recorded the lowest temperature reduction upon reacting with printex U. As listed in Table 2 CeNi (tight contact mechanism) which was calcined at 500 exhibited the lowest onset temperature at 497°C shown in fig. 4a.

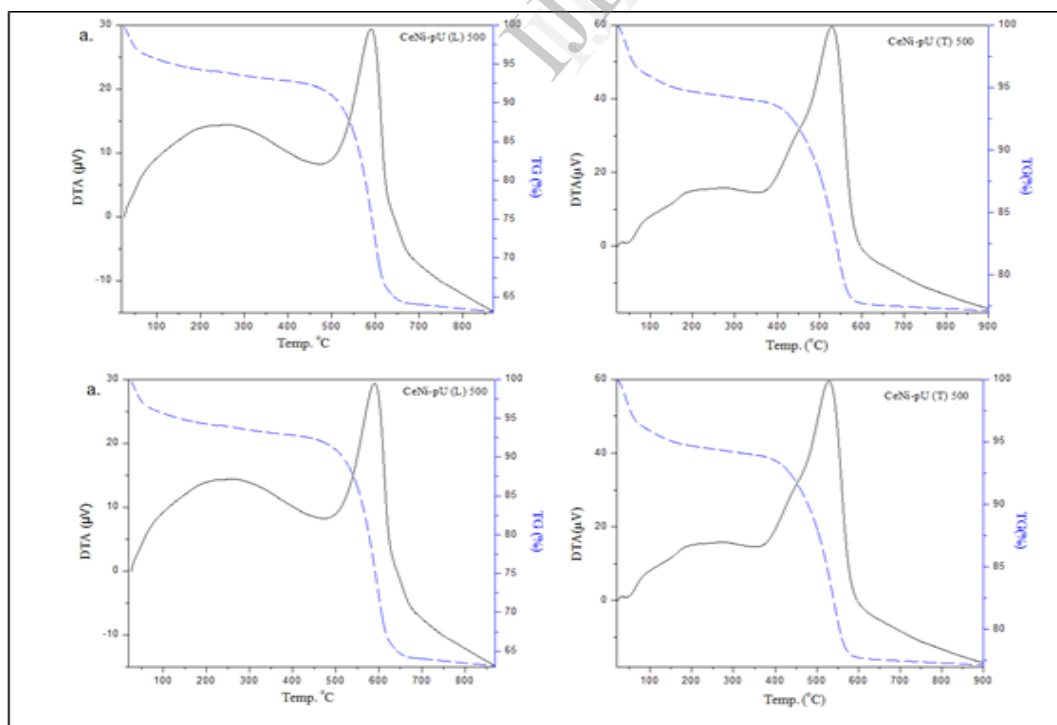


Fig 4. TG/DTA in air atmosphere of the soot/catalyst mixtures

IV. CONCLUSIONS

CeNi catalysts were successfully prepared by a co-precipitation method using nitrate precursors and characterised by XRD and DLS. A TG/DTA apparatus was used to determine catalytic activity. XRD and DLS confirmed the formation of nanosized crystallites for particles calcined at 500°C and 800°C.

CeNi are promising candidates for the selective soot oxidation with CeNi 500 showing remarkable catalytic activity and a significant reduction in soot reaction temperature. This temperature reduction implies that coating CeNi to particulate filters lowers the regeneration temperature which avoids thermal stress of the DPF. Nonetheless, optimization of the composition and preparation of these samples is still a key step in the development of the best CeNi catalysts for the oxidation of soot.

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