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Structural Characteristics and Catalytic Performance of CeAl Nanoparticles in Soot Oxidation

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Abstract: ***CeO_2-Al_2O_3 mixed oxide was prepared by co-precipitation from nitrate precursors using 25% ammonia solution (NH_4OH) as the precipitating agent. The catalysts were calcined in air at 500 ºC and 800ºC for 4h to evaluate the thermal stability and compare catalytic activity. The catalysts were characterized by XRD and DLS techniques. Catalytic activity was determined using a Thermo gravimetric/Differential Thermal Analyzer (TG/DTA). CeAl nanosized catalysts calcined at 500ºC exhibited superior redox properties of the catalyst relative to the one calcined at 800ºC. The Ce-Al composite samples exhibited good soot catalytic combustion performance by decreasing soot oxidation temperature.***

Keywords: CeO_2- Al_2O_3, co-precipitation, diesel soot oxidation, catalytic efficiency.

1. Introduction

The use of diesel particulate filters (DPFs) among several techniques is one of the alternatives to effectively trap diesel soot and lower tailpipe emissions. However a major constrain associated with the use of these filters is the difficulty in self-sustained and passive regeneration of DPFs during soot combustion. Therefore one of the best approaches to address this issue is to coat the DPFs with efficient catalysts which are active enough to passively regenerate the filter at lower temperatures.In filter regeneration, the trapped soot at the filter surface is converted primarily to ash, CO_2, N_2, and H_2O [1-3].

CeO_2 has the potential to lower the onset temperature of the soot oxidation by involving the participation of active oxygen and heightening soot oxidation rate due to the Ce^{4+}/Ce^{3+} redox ability to adsorb oxygen gas, thus forming active oxygen at the ceria particle surface. This active oxygen can be brought about to the soot/catalyst interface by superficial diffusion [4,5]. The activity of ceria in complete oxidation reactions can be enhanced by doping mixed oxides. Doping in such a manner changes the redox capacity, structural features and physicochemical characteristics of CeO_2 [6-10].

Al_2O_3 has been widely used as a carrier for catalysts because of its high surface area, excellent thermal stability and good adherence to ceramic supports. It has been reported that the addition of alumina improves oxygen storage capacity and thermal stability of CeO_2-ZrO_2 [11-13]. Xiadong Wu et al. [14] proposed that the addition of Al_2O_3 was found to increase the thermal stability of Mn_xO-CeO_2 catalysts effectively by providing a high surface area and preventing the sintering of manganese oxide and ceria. Alumina's low price and innocuous chemical properties makes it an interesting option for the preparation of such catalytic systems. Marikawa et al. [15] reported that alumina acts as a diffusion barrier to suppress the sintering of CeO_2–ZrO_2 and hence improves catalyst durability at high temperatures. The co-precipitation method facilitates reasonably high surface area, homogeneous distribution of metal oxides in bulk and good thermal stability [16], and hence it is the synthesis technique used in this study.

In this paper Al_2O_3 was introduced to CeO_2 to gain further insight into the influence of calcination temperature and the distribution of active oxygen in CeO_2-Al_2O_3 catalysts on soot oxidation performance. We report the catalytic efficiency, reaction temperature, activity and selectivity of these mixed oxides in soot combustion.

2. Experimental

2.1 Catalyst preparation

CeO_2- Al_2O_3 mixed oxides (CeAl) were synthesized by co-precipitation method using 25% ammonia solution as precipitating agent. The metal ion precursors used were $Ce(NO_3)_3.6H_2O$ (Lobacheme, AR grade) and $Al(NO_3)_3.9H_2O$ (Lobacheme, AR grade). CeAl was prepared by dissolving $Ce(NO_3)_3.6H_2O$ and $Al(NO_3)_3.9H_2O$ in 200ml Millipore deionized water (18.2 MΩ.cm@25°C) in a 2:1 mole ratio respectively. A magnetic stirrer was used to ensure homogeneous mixing at 1000rpm speed for 1 hour. The mixture was precipitated by NH_4OH addition with magnetic stirring over a period until the solution pH was ~9. After room temperature aging of the mixed solutions for 20 hours, the resulting yellow coloured CeAl sample was decanted, filtered and rinsed several times with Millipore ultrapure water until free from anion impurities. The obtained precipitate was oven dried at 100°C for 5 h and ground in an agate mortar. Calcination was done under static air at 500°C and 800°C for 4h in a muffle furnace.

2.2 Catalyst preparation

Powder x-ray diffraction (XRD) experiments were performed on a Bruker's D8 advanced X-ray Diffractometer employing Cu Kα (λ=1.5406 ̊A). The scanning range of 2θ is from 20° to 80° with a step size of 0.02°.The mean crystallite sizes were calculated from the full width at half maximum (FWHM) of the diffraction peak using the Scherrer's equation [16,17] and are shown in Table 3.1. 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.

2.3 Catalyst preparation

Printex-U (Degussa) with a particle size 25nm and specific surface 100 m^2g^{-1} was used as model soot. Real soot is heterogeneous, and therefore not convenient for catalysts screening. Depending on the type and age of the engine, running conditions, type of oil and fuel used, etc. important differences in the amount and type of ashes (sometimes metals with potential catalytic activity), amount of adsorbed hydrocarbons and degree of graphitization of the soot formed can be found [18,19]. The catalytic activity was evaluated by a Thermogravimetry and Differential Thermal Analysis (TG/DTA 6300) apparatus. Before reaction the soot-catalyst samples in a 1/9 weight ratio, were mixed 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 [17]. The temperature was ramped from room temperature to 900°C at 10 °C/min in 100 mL/min flow of air.

3. Results and Discussion

3.1 Structural and textural properties

The XRD patterns of the catalysts are shown in Fig. 3.1. In comparison to the peaks of a fluorite-like cubic phase analogous to that of pure CeO_2 (JCPDS 34-0394, space group Fm-3m) [9,16], all CeAl patterns displayed weak diffraction peaks, indicating a low crystallinity of CeAl mixed oxides. It is caused by the doping of Al^{3+} precursor which hindered the crystallization of CeO_2 within the calcination. This also explains the rough perturbations of the XRD patterns in fig. 3.1. The alumina serves as the thermal diffusion barrier and effectively inhibits the growth of ceria crystallites, resulting in the smallest crystallite size of 11.5nm for CeAl 500 (shown in table 3.1). The crystallite size of CeAl 800 obtained from Scherrer's equation was 27.2nm. Since this mixture of CeAl catalysts resembles an amorphous structure to some extent, the peaks of their particles became broader and shorter at a higher calcination temperature.

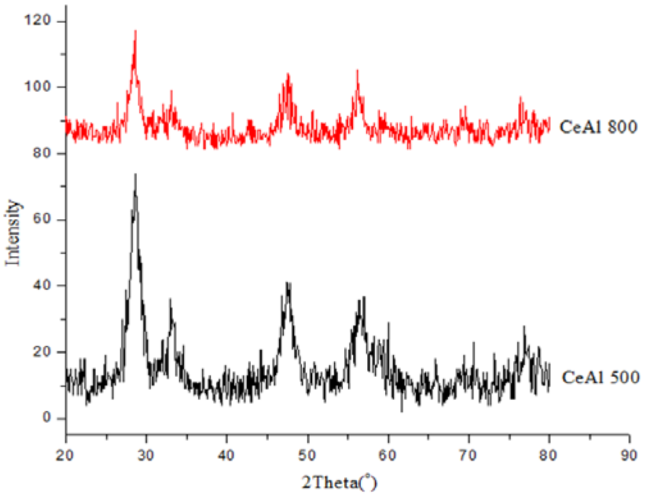

Figure 3.1: XRD patterns of CeAl 500 and CeAl 800.

Table 3.1: XRD crystallite and DLS size range

Catalyst	*Calcination temp. (°C)*	*XRD cryst. size(nm)*	*DLS size (nm)*
CeO_2-Al_2O_3	800	27.2	25.2
CeO_2-Al_2O_3	500	11.5	31.1

Fig. 3.2 below showed the particle size distribution of CeAl 500 and CeAl 800 as 31.1nm and 25.2nm respectively. These hydrodynamic sizes of the CeAl particles also confirmed the formation of nanocomposites, except that the size of the CeAl 500 sample was bigger than that of the CeAl 800 catalyst which was opposite of the XRD Scherrer's equation results.

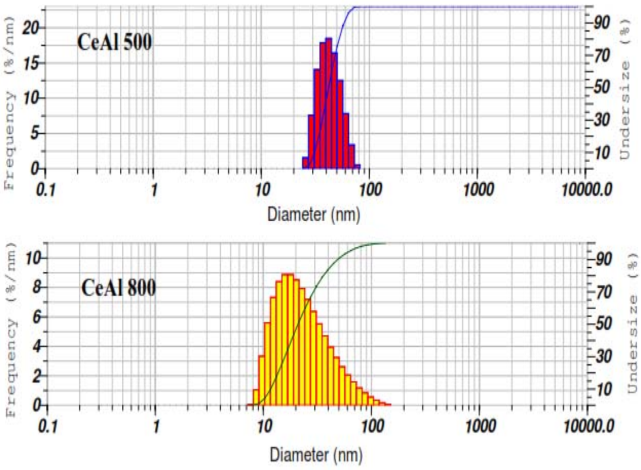

Figure 3.2: Particle size distribution histograms of CeAl calcined at 500°C and 800°C

3.2 Soot oxidation activity

Fig. 3.3 below shows the thermograph and DTA curves of the model soot (printex U) without catalyst. The DTA peaks at 11.8μV and 17.9 μV recorded temperatures of 252°C and 637°C respectively as shown in table 3.2.

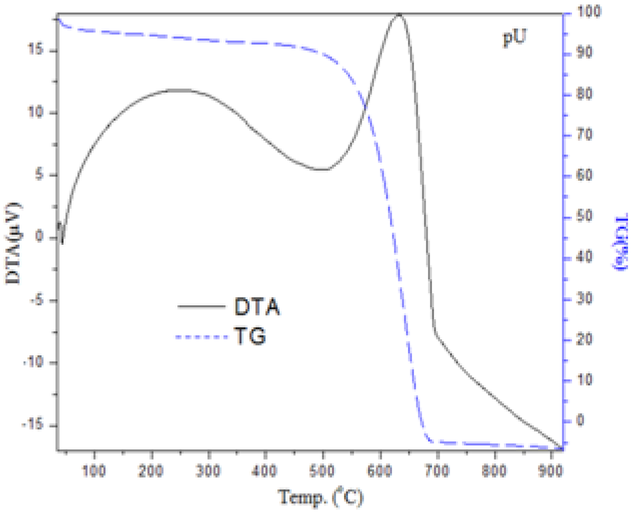

Figure 3.3: TG/DTA in air atmosphere of the soot (pU).

These values of uncatalysed soot are to be used for comparison purposes upon introducing the prepared CeAl catalysts. As a result all the catalyst/soot mixtures were analysed at the same conditions as the printex U. All the CeAl-pU samples showed a soot oxidation temperature reduction as compared to the uncatalysed sample. As depicted by fig. 4 below, CeAl-pU calcined at 500°C had good catalytic activity and registered a 113 °C temperature reduction from the 637°C oxidation temperature of the model soot.

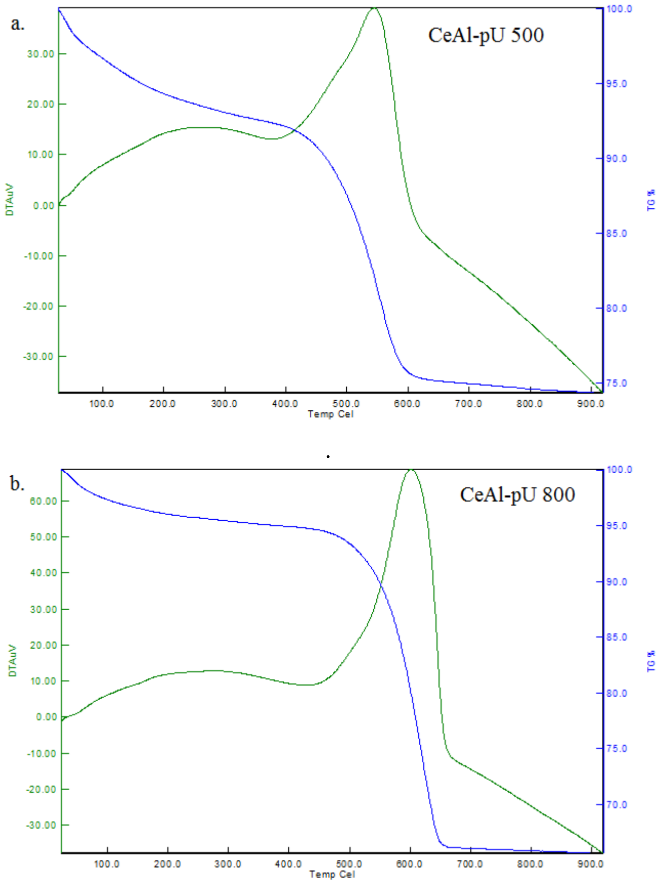

Figure 3.4: TG/DTA in air atmosphere of the CeAl samples

Low activity of CeAl sample calcined at 800°C negatively affect catalyst's redox properties due to sintering at higher temperatures. This sintering might have caused the loss of surface area, pores and the elimination of active sites. Since the catalytic reactions mainly take place on the surface of the catalyst, only surface active sites are considered functional here. Table 3.2 clearly shows the comparative TG/DTA soot oxidation temperatures of the uncatalysed and catalyzed soot activity.

Table 3.2: TG/DTA catalytic performance for soot combustion by Ce based nanocomposites

Sample	DTA peak 1		DTA peak 2	
	T(°C)	DTA(µV)	T(°C)	DTA(µV)
pU	252	11.8	637	17.9
$CeAl_{500}$+pU	271	15.5	524	39.1
$CeAl_{800}$+pU	273	12.8	597	68.7

4. Conclusions

CeAl catalysts were successfully prepared by a co-precipitation method using nitrate precursors and were calcined at 500°C and 800°C. All the samples were characterised by XRD, DLS and TG/DTA was used to determine catalytic activity upon soot oxidation. XRD and DLS confirmed the formation of nanosized catalysts. The calcined catalysts were mixed with model soot and the resulting samples were heat ramped in a TG/DTA to evaluate soot oxidation activity.

CeAl catalysts calcined at 500°C exhibited a higher catalytic performance as compared to CeAl calcined at 800°C. This is because calcination at higher temperatures decreases the surface contents of active metal oxides and degrades the soot oxidation activity. In spite of being slightly inferior in catalytic activity than other elements used as dopants, aluminium is abundant and less expensive, compared to other dopants like lanthanides. The possibility to further increase its performance and stability by precise screening of the catalyst composition must also be considered when CeAl is regarded as potential automotive catalyst.

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References

[1] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Diesel particulate emission control, Fuel Processing Technology 47 (1996) 1–69.
[2] P.A. Kumar, M.D. Tanwar, S. Bensaid, N. Russo, D. Fino: Chemical Engineering Journal 207–208 (2012) 258–266.

[3] Balle P, Bockhorn H, Geiger B, Jan N, Kureti S, Reichert D, Schroder T: Chemical Engineering and Processing 45 (2006) 1065–1073.
[4] Trovarelli Alessandro, Boaro Marta, Vicario Michela, Leitenburg Carla de, Dolcetti Giuliano: Catalysis Today 77 (2003) 407–417.
[5] A. Trovarelli, Catal. Rev. Sci. Eng. 38 (1996) 439
[6] Benjaram M. Reddy, Lakshmi Katta, Putla Sudarsanam, Gode Thrimurthulu: Applied Catalysis B Environmental 101 (2010) 101–108.
[7] Atribak I, Bueno-López A, Garcıa-Garcıa A: Catalysis Communications 9 (2008) 250–255.
[8] Trovarelli Alessandro, Boaro Marta, Hwang Jin-Ha, Mason Thomas O: Solid State Ionics 147 (2002) 85–95.
[9] Liang Qing, Wu Xiaodong, Weng Duan, Lu Zhenxiang: Catalysis Communications 9 (2008) 202–206.
[10] LU Hanfeng, Zhou Ying, Sheng Yeqin, Zhang Zekai, Chen Yinfei: Chinese Journal of Catalysis 34 (2013) 567–577.
[11] J.Kaspar, P.Fornasiero, J. Solid State Chem. 171 (2003) 19-29.
[12] J. Wang, J. Wen, M.Q. Shen, J. Phys. Chem. C 112 (2008) 5113–5122.
[13] Fan Lin, Xiadong Wu, Shuang Liu, Duan Weng, Yuying Huang, Chemical Engineering Journal 226 (2013) 105-112.
[14] X.D. Wu, S. Liu, D.Weng, F. Lin, R. Ran, J. Hazard. Mater.187 (2011) 283-290.
[15] A. Morikawa, T. Suzuki, T. Kanazawa, K. Kikuta, A. Suda, H. Shinjo, Appl. Catal. B 78 (2007) 210–221.
[16] Benjaram M. Reddy, Lakshmi Katta, Gode Thrimurthulu, Chem. Mater. 2010, 22, 467-475
[17] Atribak I, Bueno-López A, Garcıa-Garcıa A: Catalysis Communications 9 (2008) 250–255.
[18] I. Atribak, A. Bueno-López, A. García-García, P. Navarro, D. Frías, M. Montes,Applied Catalysis B 93 (2010) 267.
[19] N. Nejar, M. Makkee, M.J. Illán-Gómez, Applied Catalysis B 75 (2007) 11.

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