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WASH COATING OF CERAMIC HONEYCOMB WITH CE–AL–MN MIXED OXIDES FOR NO CATALYTIC REDUCTION IN DIESEL ENGINES

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ABSTRACT

Diesel engines produce high thermal efficiency and low CO_2but release more particulate matters (PM) and NOx which are harmful to atmosphere as well as human beings. In India, these emissions are controlled by after exhaust gas treatment and are regulated by Bharat Stage Emission Standards. The effective technology for NOx reduction is Selective Catalytic Reduction (SCR). In this study selective catalysis is carried out over $Mn/Ce/Al_2O_3$ catalysts which were prepared by sol-gel and combustion synthesis methods. These catalysts were coated on honeycomb ceramic samples and characterized by SEM. The coated samples were tested in Single cylinder Diesel Engine. The results showed nearly 60%NO conversion.

Key words: selective catalytic reduction, mn–ce-al composite catalyst, no reduction.

INTRODUCTION

The major source of air pollution from fossil fuel combustion is CO_2, CO and NOx. Among these NOx becomes a primary concern among the air pollutants. These oxides have caused environmental problems such as ozone depletion, greenhouse effects and acid rain. At present NOx releases can be attributed to vehicles (49%) and power plants (46%) [1-2]. Generally two methods have been used for the elimination of NOx, such as selective catalytic reduction (SCR) [3–5] and Lean NOx trap[6]. Different synthesis techniques have been used for the preparation of catalysts such as co-precipitation method[7], sol-gel synthesis[8],incipient wetness method(9), citric acid method (CA)[10-11], impregnation method (IM) [10-11],low temperature solid phase reaction method (SP),rheological phase reaction method (RP) [12], combustion synthesis[13]and polymerized complex process [15] technique for elimination of NOx in selective catalytic reduction (SCR). Several types of supported transition metal oxide catalysts such as amorphous chromia [16], carbon-supported vanadium [17-18], manganese [19], alumina supported manganese oxide [20], TiO_2 supported manganese [21] and ceria supported manganese [22] have been examined and generally, these show high activity for NO reduction with NH_3at lower temperature range of 80–250 ^oC for SCR reactions. SCR of NOx with NH_3 is an effective technique and has been commercialized in the post-treatment of flue gases of power plants and automobile vehicles. The Mn/CeO_2samples were prepared by the citric acid gel combustion method and show high activity for NO reduction [23]. This work reports the preparation of an active catalyst for the low temperature SCR for NO with Urea. The result shows that Mn/CeO_2 solid with alumina prepared by sol-gel gives higher reduction of NO at low temperature.

MATERIALS AND METHODS

Preparation of honeycomb sample catalysts

$Mn/Ce/Al_2O_3$ catalysts were prepared by two methods, namely, one-step sol–gel and combustion synthesis. The samples were cleaned by immersing in concentrated nitric acid for 1 day at 28 ^oC for removing the soluble impurities and roughening up the surface. Before coating the samples were washed completely with de-ionized water and then dried at 120 ^oCin air for 12hours. In sol-gel method nitrate precursors of cerium (III) ($Ce(NO_3)_3.6H_2O$), aluminium($Al(NO_3)_3.9H_2O$), and manganese ($Mn(NO_3)_2$, 45-50% solution in dilute nitric acid) were separately dissolved in ethanol and added together in order to get the different molar ratio of Al:Ce:Mn. The solution was heated at 80^oC and then added drop wise to de-ionized water under constant stirring. After few minutes sols were gradually formed. The deposition was carried out by immersing the samples in the prepared solution as shown in Figure-1. The unclogging of the channels was performed under air flow by blower. Then CeAlMn(x) (Material named M1) samples were calcined for 2 hours in air at 450 ^oC.

Figure-1. CeAlMn(x) powder using Sol gel synthesis.

The mixed solution was heated in a self timer muffle furnace maintained at 500ºC. Initially the solution boils and combustion reaction was completed by dehydration followed by decomposition with development of gases N_2 and CO_2. Thus, The CeAlMn(x) powder was obtained as shown Figure-2. Slurry of wash coat component was prepared by using kaolin. Samples were immersed in the slurry by using dipping machine as shown in Figure-3.The unclogging of the channels was performed under air flow by blower. Then, these CeAlMn(x) powders (named M2) were calcined for 2 hours in air at 450 ºC.

Figure-2. CeAlMn(x) powder using combustion synthesis.

Figure-3. Dip coating machine.

Catalyst activity measurements

Experiments were carried out inconstant speed, four stroke, vertical single cylinder and water cooled Compression Ignition (CI) engine. Specification of test rig is shown in the Table-1 and the experimental setup is shown in Figure-4.and Figure-5. The engine is coupled with an SWINGFILED electrical dynamometer to apply 0%, 25%, 50%, 75% and full loads. Combustion parameters were measured by AVL pressure transducer fixed on the cylinder head and an AVL 365C angle encoder fixed on the output shaft of the engine. Chromel-alumel (k-type) thermo-couples were fixed for measuring the gas temperature at inlet, exit ducts and cylinder wall. The 50cc graduated burette and stop watch was used to measure the fuel consumption of the engine. The engine speed was determined by in-house designed magnetic pick-up sensor connected to a frequency meter. The smoke intensity was measured by an AVL 415 smoke meter. AVL DI GAS 444 exhaust gas analyzer is used to measure the nitrous oxides (NOx), hydrocarbon (HC), carbon monoxide (CO) and carbon dioxide (CO_2). The fuel injection pressure was maintained at 1 bar throughout the experiment.

Table-1. Engine specification.

1	Type	four stroke, Vertical single cylinder, constant speed, water cooled, direct injection CI engine
2	Number of cylinders	One
3	Cylinder Bore, d	87.5 mm
4	Stroke length, L	110 mm
5	Compression ratio, r	17.5:1
6	Capacity, cc	661.5 cm^3
7	Max. power	4.4kW
8	Rated speed	1500 rpm
9	Fuel injection	Direct injection
10	Dynamometer type	Electrical dynamometer
11	Orifice diameter	13.6 mm
12	Co-efficient of Discharge	0.6
13	Injection pressure	220 bar

Figure-4. Experiment test rig set up.

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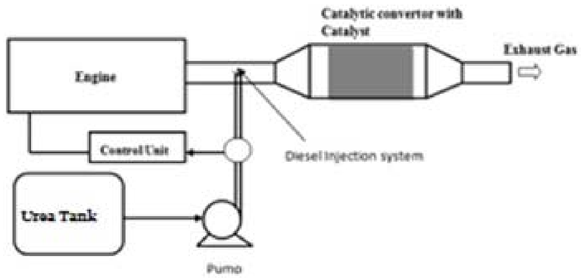

Figure-5. Block diagram for experimental set-up for the catalyst tests.

SEM

Scanning Electron Microscopy (SEM) of the prepared catalyst powders was done using GEMINI Carl Zeiss Supra 55 high resolution electron microscope. The powders were fixed to conductive carbon tape attached to the stub and this was viewed under microscope.

RESULTS AND DISCUSSION

Reduction of nitrogen oxides

Figure-6 shows the NO emission for different load conditions of diesel engine with injection of urea at exhaust tail pipe. The lower NOx emission was observed for titanium dioxide and M1 as catalyst in exhaust pipe. Urea solution was injected in exhaust tail pipe at a constant flow rate of 0.75lit/hr. The lower Nitrogen Oxides was obtained due to uniform dispersion of Manganese and Cerium in alumina catalyst by solgel method (M1). These tests were conducted under normal diesel engine working conditions.

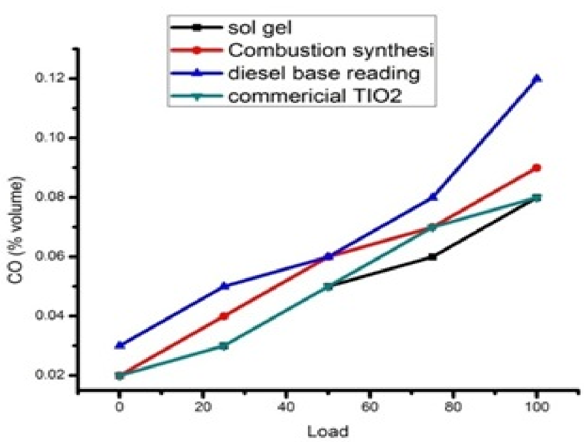

Figure-6. Variation of Oxides of Nitrogen with injection of urea solution.

Variation on unburned hydrocarbon

Figure-7 shows the unburnt Hydrocarbon (HC) emissions for different load conditions of diesel engine with injection of urea in exhaust tail pipe at constant flow rate of 0.75lit/hr. The figure shows that HC emissions gradually decrease upto 30 to 40% drastically due to presence of excess oxygen at higher load conditions.

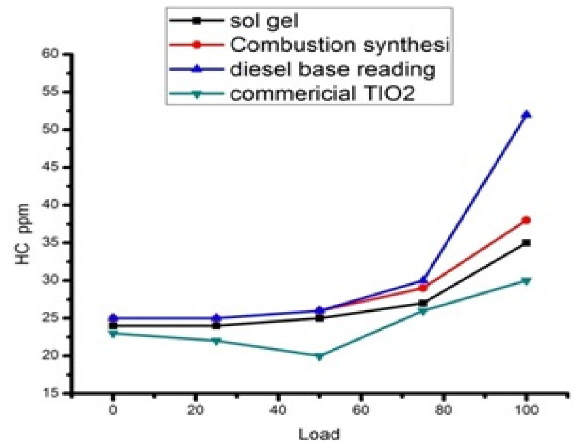

Figure-7. Variation on unburned hydrocarbon with injection of urea solution.

Variation of carbon monoxide

Figure-8 shows that Carbon Monoxide (CO) emissions for different load conditions of diesel engine with injection of urea solution in exhaust tail pipe at constant flow rate of 0.75lit/hr. From the graph it can be seen that the CO emissions decrease upto 50% due to oxidation of excess oxygen.

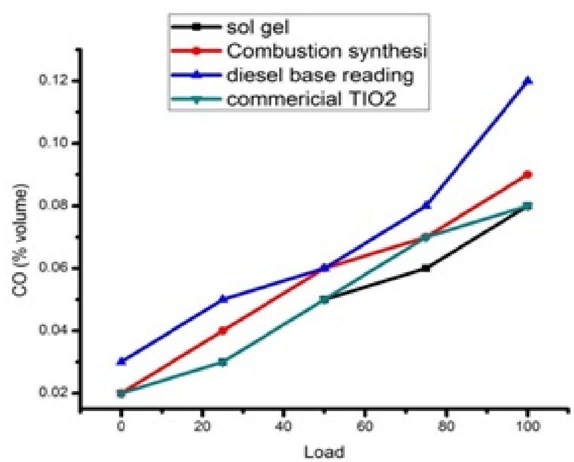

Figure-8. Variation of carbon monoxide with injection urea solution.

SEM analysis

Figure-9 and Figure-10 shows scanning electron micrographs (SEM) of CeAlMn powders obtained from Combustion synthesis and Sol-gel at 500 ^{o}C. In Fig 10.surface looks brighter and has more white spots than Figure-9 which indicates good manganese and cerium adhesion to the alumina surface. SEM images revealed clear morphological differences between sol-gel and combustion methods. The average particle sizes of powders prepared by sol gel are in the range of 40 - 60nm.

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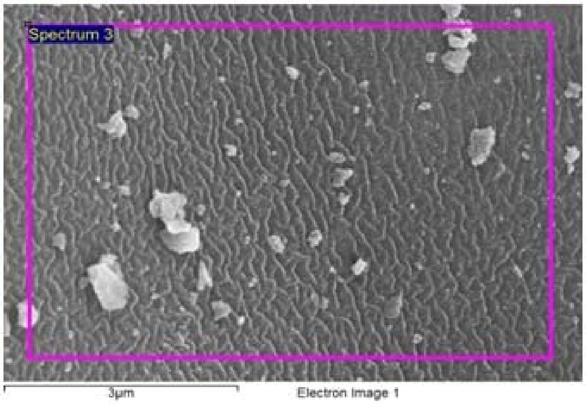

Figure-9. (a) SEM micrographs of CeAlMncatalysts prepared by Combustion synthesis techniques.

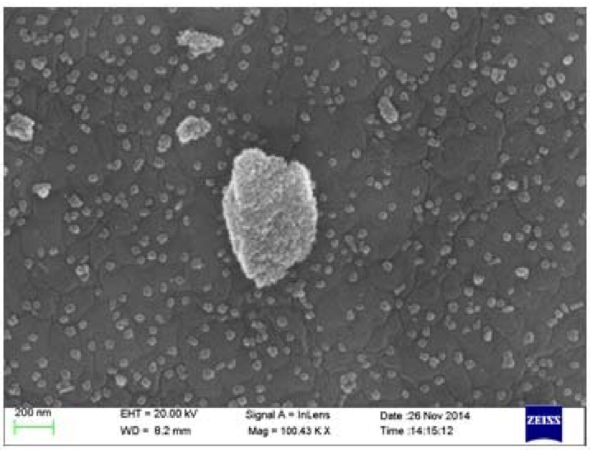

Figure-9. (b) SEM micrographs of CeAlMncatalysts prepared by Combustion synthesis techniques (Enlarged image).

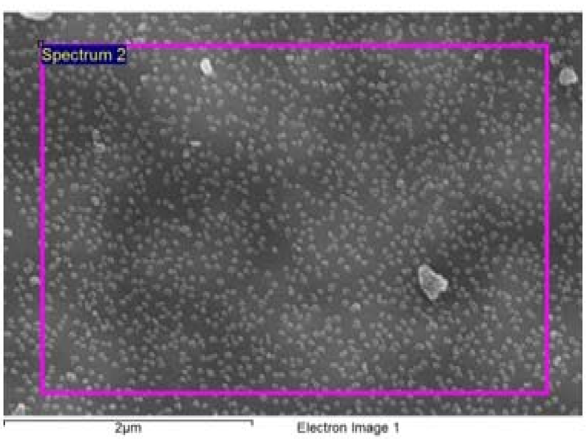

Figure-10. (a)SEM micrographs of CeAlMncatalysts prepared by solgel techniques.

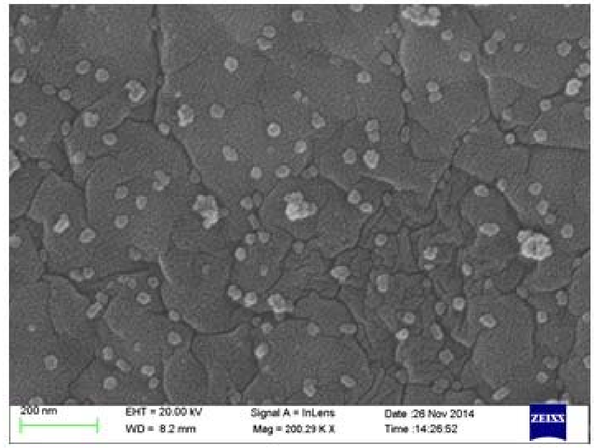

Figure-10. (b) SEM micrographs of CeAlMncatalysts prepared by solgel techniques (Enlarged image).

CONCLUSIONS

Based on the experimental investigation the NOx emission was reduced on a four stroke single cylinder diesel engine using SCR technique with urea injection in the engine exhaust with different catalysts. The result showed that the CeAlMn prepared by sol-gel and commercial titanium oxide content strongly influences the reduction of NOx by ammonia in Selective Catalytic Reduction system. Uniform dispersion of MnOx–CeO_2/Al_2O_3crystals led to the perfect performance in the low temperature. It was confirmed that the addition of Mn metal could improve the reduction of NOx.

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