

Development of Low Cost Catalytic Caterials for Particulate Matter (PM) oxidation or Soot Emitted from Biomass Burning and Vehicles

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Abstract. The K₂O/Mn₂O₃ nanofibers were prepared by hydrothermal method. Morphology of the Mn₂O₃ nanofibers influenced by aging time. The potassium was impregnated on the prepared Mn₂O₃ nanofibers and investigated physico-chemical properties, diesel soot oxidation activities and deactivation. The K/Mn₂O₃ nanofibers were evaluated for the soot combustion in O₂ and NO/O₂. Morphology of the fibrous structure of Mn₂O₃ nanofibers and K₂O/ Mn₂O₃ nanofibers was observed by FE SEM images. The K/ Mn₂O₃ nanofibers catalysts showed improvement in the soot oxidation at low temperatures around 390 °C with 10%O₂ and decrease in the peak soot oxidation temperature about 110 °C was observed with the addition of 500 ppm NO_x. Thermal stability and poisoning effect of 5%K/ Mn₂O₃ nanofibers catalyst examined by ageing under air and 1030ppm SO₂ at 800 °C for 12 h.

Keywords: Nanofibers, Soot, Diesel Particulate Filter (DPF)

1. Introduction

One of the current environmental problems to be solved by vehicle manufactures is the elimination of nano/micro particles of carbon (soot) emitted by diesel engines and biomass burning. These soot particles can be trapped by diesel particulate filters (DPF) to avoid its release in the atmosphere during vehicle engine operation [1]. In order to periodically regenerate the filter, the loaded soot is oxidized by increasing the flue gases temperature (250-400 °C) to the reach soot ignition, which shows appreciable oxidation rates at around 550-650 °C. Since this temperature increase is obtained at the expenses of some post-injected fuel, a catalyst can be applied to promote soot combustion at lower temperatures [1]. Many catalysts have been reported to be effective for the soot combustion [2, 3]. It has been reported that Manganese oxides has the potential to increase the oxidation rate of soot, because of the strong oxidative properties [4].

Thus, it is very important to develop suitable catalytic materials which are active enough to ignite the particulate matter at low temperatures. The typical exhaust gases also consist of significant amounts of NO_x (100-600 ppm as NO). The combustion of soot proceeds more efficiently as NO is oxidised to NO₂ and acts as a oxidant for the soot oxidation at low temperatures [5, 6]. Most of studies were performed on readily available commercial model soot samples. The use of model soot, such as a carbon black (Printex-U), as a substitute of real soot can be considered suitable for catalysts screening, since real diesel soot features are heterogeneous [1].

Many perovskite and spinel type oxides have been reported to be effective for the soot combustion, especially under tight contact conditions [7-9]. Platinum based catalysts are exhibited high activity for NO assisted soot oxidation inspite of their expensive costs [10-11]. Recently, transition metals such as cobalt, manganese and copper based catalysts reveal strong soot oxidation activity because of their strong oxidative property [7-12]. The strong oxidative property of transition metals in combination with the oxygen storage property of ceria makes transition metal and cerium oxide catalysts as one group of cheap and efficient candidate catalysts for soot oxidation.

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In the present study we have designed fibrous structured Manganese oxide impregnated with potassium catalysts to have functions of trapping and oxidation of soot. This kind of fiber structured catalysts increase the contact point of the soot, trapping capability and decrease the pressure drop due to their special morphology. Mn_2O_3 nanofibers and potassium doped Mn_2O_3 nanofibers were prepared, characterized and evaluated for their soot oxidation activity.

2. Materials and Methods

Manganese oxide nanofibers were prepared by hydrothermal synthesis [5]. Typically, 30mmol nitrilotriacetate acid (NTA) and 30mmol $\text{Mn}(\text{Ac})_2$ (Aldrich, 99%) were dissolved in 100mL water. Then, the total solution mixture was transferred into a 200mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 6h. After that the autoclave was cooled down to room temperature, the white precipitate were filtered, and subsequently washed with ethanol and distilled water for several times and then dried and calcined in air at 600 °C for 2h. 5wt% of potassium (KNO_3 as precursor) was impregnated on Manganese oxide nanofibers and then dried and calcined at 600 °C.

2.1. Catalyst characterization

The catalysts were then characterized by using X-ray diffraction (PW1710 Philips diffractometer equipped with a monochromator, (Cu $K\alpha$ radiation), A field emission scanning electron microscope (FE SEM Leo 50/50 VP with a GEMINI column), BET-specific surface area (Brunauer Emmet Teller) and Temperature-programmed analyses were performed in a Thermoquest TPD/R/O 1100 analyzer. Catalytic activity of the catalysts was tested in a temperature programmed combustion (TPC) apparatus. This equipment consists of a fixed bed inserted into a quartz microreactor. The fixed bed was prepared by mixing 50 mg of a 1:9 by weight mixture of Printex U and a powdered catalyst treated in mortar by gentle mixing with spatula (loose contact), with 250 mg of silica pellets (0.3–0.7 mm in size). TPC run was carried from 200 to 700 °C at 5 °C/min rate; total flow of 100 Nml/min (O_2 and NO); and the outlet gases were analyzed by a $\text{CO}_2/\text{CO}/\text{NO}$ NDIR analyzer. The possible thermal stability and poisoning effects of Manganese oxide nanofibers 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.

2.2. Catalytic activity tests

The catalytic activity of the catalysts was tested in a temperature programmed combustion (TPC) apparatus. This equipment consists of a fixed bed inserted into a quartz microreactor (i.d.: 4 mm). The fixed bed was prepared by mixing 50 mg of a 1:9 by weight mixture of Printex U and a powdered catalyst treated in a colloidal mill for 15 min, with 150 mg of silica pellets (0.3–0.7 mm in size); these inert pellets were added in order to reduce the specific pressure drop across the reactor and to prevent thermal runaways. The close (tight) contact conditions between the catalyst and the carbon obtained in the ball mill allow good reproducibility which is a condition equal to draw reliable comparisons between the intrinsic activities of different catalysts. Loose contact conditions obtained gentle mixing of the soot and catalyst powders in a vessel, provided a better approximation of the contact conditions of the soot accumulated in a catalyst lined trap [7]. The TPC reactor temperature was controlled through a PID regulated oven and it was increased during a TPC run from 200 to 700 °C at a 5 °C/min rate. The inlet gas mixture was 10% O_2 or 500 ppm NO/10% O_2 in N_2 with a flow rate of 100 Nml/min. The analysis of the reactor outlet gas was performed by means of a $\text{CO}/\text{NO}/\text{CO}_2$ NDIR analyzer (ABB). A computer was used to record both the fixed-bed temperature (measured by a thermocouple placed close to the sample) and the concentration of CO_2 in the outlet gas as a function of time. The temperature corresponding to the CO_2 concentration peak (T_p) was taken as an index of the catalytic activity of each tested catalyst: the lower the T_p value, the higher the catalytic activity. A TPC run was also performed in the absence of the catalyst in order to set a reference for comparison purposes. On the grounds of the area of the TPC plots, estimates of the overall CO_2 amount produced per run were calculated and the selectivity of carbon combustion towards CO_2 was also estimated.

3. Results and Discussion

Fig.2 shows that the TPR profile of the Mn₂O₃ nanofibers. Two peaks of H₂ consumption are observed at 224°C and 412°C. Because the initial species is Mn₂O₃ (see the XRD patterns fig.1), we believe that the low temperature peak should be attributed to the reduction of Mn₂O₃ to Mn₃O₄, where as the high temperature peak should be attributed to the reduction of Mn₃O₄ to MnO [13].

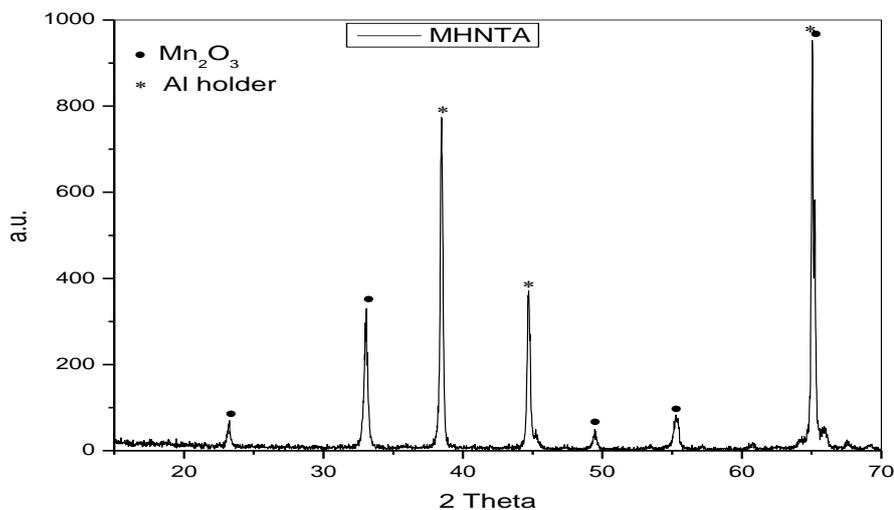


Fig.1: XRD of MHNTA calcined at 600 °C.

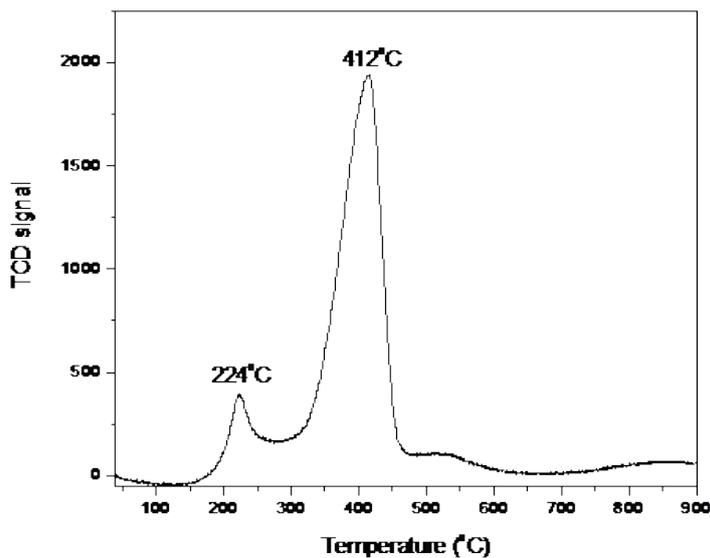


Fig.2: Temperature programme reduction (TPR) profile of MHNTA

The XRD and TPR profiles of Manganese oxide nanofiber catalysts confirm that the Mn is present as Mn₂O₃. Fig.3 FE-SEM confirms fibrous structure of Mn₂O₃.

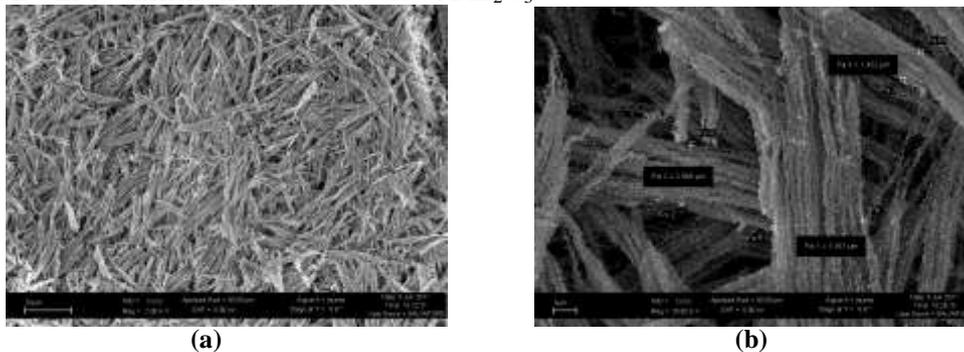


Fig. 3: FE-SEM images of (a) MHNTA and (b) K/MHNTA

BET surface area of the calcined (600 °C) Manganese oxide nanofibers is 59 m²/g. The soot conversion profiles obtained in the soot combustion tests are compiled in Figure 4. Peak combustion temperature (T_p) of un-catalyzed is observed at 610 °C temperature. However, Manganese oxide catalysts shows improved low temperature T_p at 435 °C in 10%O₂ and 396 °C in 10%O₂ + 500ppm NO. Impregnation of potassium on manganese oxide nanofibers favors the soot combustion at much lower temperatures. Potassium may be adding to the basicity of the catalyst and it appears unlikely that the promotional effect of potassium is due to its volatility [6], which can improve the soot-catalyst contact. The addition of potassium decreased the peak soot combustion temperature by 203 °C as compared to the un-catalyzed. Further decrease in peak soot combustion temperature is observed over potassium promoted manganese oxide nanofibers in the presence of 10%O₂ and 500ppm NO by 250 °C.

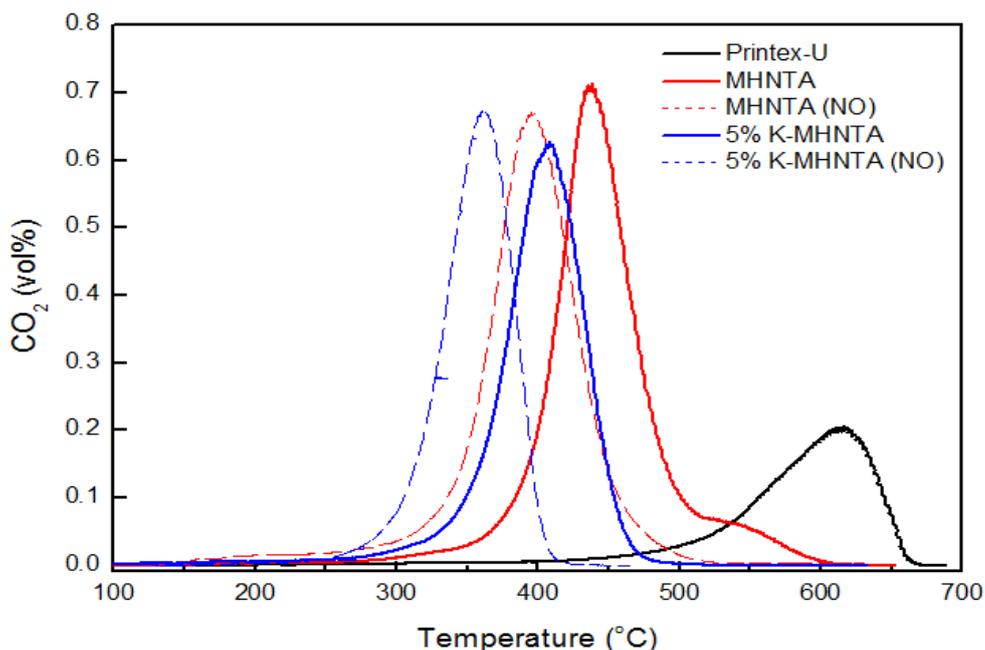


Fig. 4: Soot combustion activity results in the presence of 10% O₂ and 500 ppm NO

Thermal deactivation studies also performed in presence of SO₂. Finally, it can be concluded that the fibrous structure is very much feasible in trapping and combusting the soot at low temperatures. Further studies are under progress to grow the manganese oxide nanofibers on SiC DPFs and evaluate their soot trapping, filtering and combustion properties.

4. Conclusions

Hydrothermally synthesized manganese oxide nanofibers show the highest catalytic activity for soot combustion, lowering the soot combustion temperature by 173 °C regarding the un-catalyzed reaction. The addition of potassium is further decreased the soot combustion temperature by 203 °C. This is very significant because the good quality results obtained under loose contact conditions.

5. References

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