Catalysis Today 258 (2015) 205–213

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

NO oxidation to NO_2 over manganese-cerium mixed oxides

Gongshin Qi*, Wei Li

General Motors Global Research and Development, 30500 Mound Road, Warren, MI 48090, United States

ARTICLE INFO

Article history:
Received 29 November 2014
Received in revised form 15 January 2015
Accepted 5 March 2015
Available online 8 April 2015

Keywords:
Diesel aftertreatment
MnO_x-CeO_2
NO oxidation
MnO_x-CeO_2-ZrO_2 mixed oxides
Sulfur poisoning
Hydrothermal durability
HR-XRD

ABSTRACT

There is a recognized need for lowering greenhouse gas emissions from mobile sources in order to address concerns regarding global climate change. Diesel engines offer superior fuel efficiency and greenhouse gas reduction potential; however, the highly loaded Pt for converting NO to NO_2 in diesel aftertreatment catalysts is one of the major hurdles in the broad implementation of highly fuel efficient diesel engine vehicles. Here, we reported that manganese-cerium mixed oxides coated on monolith substrates demonstrated a superior NO oxidation to NO_2 activity, showing a promise for PGM thriftting for diesel or lean burn engines emission control catalysts. The mixed oxide (MnO_x-CeO_2) shows a much higher NO oxidation to NO_2 rate and is nearly 3 and 10 times active of that MnO_x and CeO_2 at 200 °C, respectively. Significantly lower reduction temperature of the mixed oxide (MnO_x-CeO_2) compared with MnO_x and higher Mn^{4+} to Mn^{3+} reduction peak intensity suggest that ceria helps stabilize higher oxidation state of Mn. The MnO_x-CeO_2 mixed oxide shows higher activity for NO oxidation due to the enhanced rate of nitrites decomposition to NO_2. The structure of the MnO_x-CeO_2 mixed oxide maintained during a cyclic treatment of oxidative/reductive gas conditions at 650 °C. Furthermore, the incorporation of ZrO_2 into MnO_x-CeO_2 mixed oxide not only increased NO oxidation activity but also the sulfur tolerance. About 70% of the activity of the MnO_x-CeO_2-ZrO_2 was recovered via regeneration in a H_2 rich stream.

1. Introduction

NO oxidation to NO_2 is a critical reaction step for various devices in a diesel or lean burn gasoline engine after-treatment system [1–3]. For urea selective catalytic reduction (SCR), an NO_2:NO ratio of 1:1 is the most effective. NO oxidation to NO_2 is also required for lean NO_x Trap (LNT) operations; during the lean period, NO needs to be oxidized to NO_2 before being absorbed on storage components, such as barium oxides. NO_2 has been reported to promote the passive regeneration of soot on Diesel Particulate Filters (DPF), reducing the required active regeneration frequency and then fuel consumption. However, diesel engine exhaust typically contains less than 10% NO_2 and hence a catalyst is required to convert NO to NO_2 in order to improve the aftertreatment efficiency. Several reports have found Pt to be the most active catalyst [4–6] for NO oxidation to NO_2. The need for high NO conversion to NO_2 has driven the commercial diesel oxidation catalyst (DOC) and LNT catalyst formulations to contain high concentration of platinum, contributing to the high cost of the after-treatment system. Consequently, there is substantial interest in developing better performing, lower cost and durable NO oxidation catalysts.

Base metal oxide catalysts have been investigated for NO oxidation, such as, Co_3O_4 [7], $La_{1-x}Ce_xCoO_3$ [8], $La_{1-x}Sr_xCoO_3$ and $La_{1-x}Sr_xMnO_3$ [9]. Among these catalysts, Co based oxides showed a higher NO oxidation activity; however, $La_{1-x}Sr_xCo_xO_3$ is not stable in 5%H_2/Ar at temperatures above 500 °C [9]. In addition, cobalt is a major cause of contact dermatitis and is considered carcinogenic [10], so the use of cobalt as a catalyst is restrained in some regions. MnO_x based oxides have been reported to be highly active for the oxidation of light oxygenates [11–13], CO [14] and soot [15,19], wet ammonia oxidation [16,29], low temperature ammonia-SCR [17,18] reactions and NO_x absorption [20]. For example, MnO_x-CeO_2 mixed oxides showed total oxidation of ethanol to CO_2 at only 200 °C [14], which compares favorably with a Pt/Al_2O_3 catalyst that achieves complete ethanol oxidation at 280 °C [21]. Encouraged by the results of NO oxidation over $La_{1-x}Sr_xMnO_3$, manganese based oxides were investigated for NO oxidation to NO_2. The MnO_x-CeO_2 mixed oxides usually have much higher catalytic activities than those of the individual MnO_x and CeO_2 because of the strong interaction due to the formation of solid solution [13,22–24]. The incorporation of manganese ions into cerium dioxide lattice greatly improved the oxygen storage capacity and the oxygen mobility on the surface of the mixed oxides. Although the manganese based oxides have been extensively studied as oxidation catalysts, reports of their use for NO oxidation are few [53]. Li and co-workers reported that manganese-

---

* Corresponding author. Tel.: +1 586 986 1058; fax: +1 586 986 8697.
E-mail address: gongshin.qi@gm.com (G. Qi).

http://dx.doi.org/10.1016/j.cattod.2015.03.020
0920-5861/

cerium oxides were active for NO oxidation to NO_2 reaction [53]. However in their work the catalyst activities were measured using a space velocity that was 5–6 times lower than realistic vehicle exhaust conditions on fresh samples; the hydrothermal durability, sulfur poisoning and mechanistic aspects have not been investigated. Therefore their results, while interesting, did not provide sufficient information to evaluate the potential for practical applications.

GM R&D has discovered that MnO_x-ZrO_2 and MnO_x-CeO_2 catalysts coated on monolith substrates showed excellent activities for NO oxidation to NO_2, a critically important step for a range of the devices in a diesel after-treatment system. Based on our previous study, under realistic conditions, MnO_x-CeO_2 catalysts achieved higher NO oxidation to NO_2 activity than a Pt-based commercial catalyst. 50% NO conversion can be achieved over the MnO_x-CeO_2 mixed oxide, while, only 35% NO conversion observed on the Pt catalyst at 250 °C. In order to fully understand the mechanism of NO oxidation to NO_2 reaction, this report is to explore the synergistic effects between manganese and cerium using multiple characterization techniques; the hydrothermal durability and sulfur poisoning and sulfur regeneration are investigated in this report too.

2. Experimental

2.1. Catalyst preparation

MnO_x, CeO_2 and MnO_x-CeO_2 catalysts were prepared by a co-precipitation method [13]. Briefly, appropriate amounts of metal nitrates were dissolved in de-ionized water at room temperature and an aqueous solution of ammonia was added as a precipitate agent with stirring until the pH value reached 10. The precipitate was further aged at the same temperature for 2 h in the mother liquid. After filtration and washing with deionized water, the obtained solid was dried at 120 °C for 12 h and then calcined at 550 °C in air for 5 h. For the MnO_x-CeO_2 mixed oxides, the weight percent of Mn metal is 4% from ICP analysis, corresponding a mole ratio of Mn/(Ce + Mn) = 0.12. 4 g of each oxides catalyst and 15 g of water were ball milling for 18 h, the slurry was washcoated onto monolith core samples (¾ in. diameter × 1 in. length, 400 cells per square inch (cpsi) with 4 milli-inch wall thickness cordierite). The total washcoat loading for all catalysts are 100 g/L. After washcoating, the monolithic catalyst was dried at 120 °C and calcined at 550 °C for 2 h. All the catalysts were pretreated at 750 °C for 1 h under 10%H_2O/air in oven before performance evaluation. The fresh and hydrothermally treated catalysts are labeled with a suffix of F (fresh) and HT (hydrothermally treated), respectively.

2.2. Catalyst evaluation

The catalysts (1.0 in. length with 0.75 in. diameter) were tested in a quartz tubular reactor (i.d. 0.75 in.) operated at atmospheric pressure. The gases were fed using a series of mass flow controllers. The total feed flow rate was 3.0 L/min, corresponding to a space velocity of 25,000 h^{-1}, with 8% O_2, 5% H_2O, 8% CO_2, 200 ppm NO and a balance N_2. The reactor was heated in a tube furnace that controlled the temperature just upstream of the catalyst and thermocouples were used to measure the temperatures upstream and downstream of the catalyst sample. The reactor outlet stream was analyzed with a Fourier Transform Infrared (FTIR) analyzer (ThermoNicolet NEXUS 670), calibrated at 940 Torr and 165 °C. A pressure controller at the outlet of the FTIR was used to maintain the calibration pressure, and the line downstream of the reactor was heated to 165 °C. The lines upstream of the reactor were also heated to 165 °C to assure complete vaporization of water.

Table 1
BET surface area, crystallite size and lattice parameters.

Catalysts	BET surface area (m^2/g)	Lattice parameters (Å)	Crystallite size (nm)
CeO_2-F	37.56	5.4116	12
MnO_x-F	13.15	n/a	49
MnO_x-CeO_2-F	88.56	5.3918	5
CeO_2-HT	17.55	5.4119	19
MnO_x-HT	9.50	n/a	70
MnO_x-CeO_2-HT	13.75	5.4091	14

NO uptake measurements were performed at 50 °C using the same setup mentioned above. Before the measurements, the samples were pre-oxidized at 500 °C for 30 min under the flow of 8% O_2/N_2. The sample was cooled to 50 °C and then 200 ppm NO was introduced for 30 min. After NO gas was shut off, the sample was purged by N_2 for 30 min to allow weakly adsorbed species to desorb at the same temperature. Finally, a temperature programmed desorption (TPD) run was performed from 50 °C to 500 °C under the flow of 8%O_2/N_2, with a heating rate of 10 °C/min. The adsorbed NO amount was calculated based on the NO_x desorption curve.

2.3. Catalysts characterization

Specific surface areas were measured by N_2 adsorption at liquid nitrogen temperature using a Micromeritics 2020 apparatus, with values listed in Table 1. X-ray Diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RB diffractometer with Cu Kα radiation (λ = 1.5418 Å) operated at 40 kV and 100 mA.

Temperature programmed reduction by H_2 (H_2-TPR) and oxygen temperature programmed desorption (O_2-TPD) were carried out on a commercial instrument (Micromeritics, Autochem2920) with MS. Before the TPR measurements, the samples were pre-oxidized at 500 °C followed by helium flow to purge the residual gaseous and weakly adsorbed oxygen. The temperature programmed reduction profile was measured in a flow of 10 vol.% H_2/Ar (30 ml/min) from room temperature to 800 °C at a rate of 10 °C/min. For the O_2-TPD experiment, 100 mg of the sample was preheated in pure O_2 at 500 °C for 30 min. After cooling to room temperature, the sample was heated from room temperature to 800 °C in pure helium at a heating rate of 10 °C/min.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurement was performed on a ThermoNicolet NEXUS 670 with a MCT detector and an in situ chamber allowing the sample heated up to 600 °C. Gases were mixed by mass flow controllers and introduced into the DRIFTS chamber at a rate of 100 ml/min. The sample was pretreated at 600 °C in 8%O_2/He for 30 min. After cooling to 200 °C, the background spectra were collected. Then, 200 ppm NO and 8% O_2 balanced by He were introduced into the chamber for adsorption. The spectra at different times were recorded, accumulating 32 scans at a resolution of 2 cm^{-1} and displayed in Kubelka–Munk unit.

In situ High Resolution X-ray Diffraction (HRXRD) measurement was conducted in Argonne National lab. The sample was first pretreated in air at 650 °C for 45 min, then at 3%H_2/N_2 for 90 min at the same temperature. Then further the sample was treated in air for 90 min and cooled down to room temperature in air. There is 3% water vapor in the feed gas during the whole treatment. X-ray Diffraction (XRD) patterns were recorded during the process with a beam light (λ = 0.413 Å) at 30 kV.