Catalysis Today 253 (2015) 199–206

Contents lists available at ScienceDirect

Catalysis Today

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

MnO_x-CeO_2 catalysts synthesized by solution combustion synthesis for the low-temperature NH_3-SCR

S. Andreoli, F.A. Deorsola*, R. Pirone

Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

ARTICLE INFO

Article history:
Received 2 December 2014
Received in revised form 27 February 2015
Accepted 4 March 2015
Available online 30 April 2015

Keywords:
Selective catalytic reduction
Cerium oxide
Manganese oxide
Low-temperature activity
Nitric oxide

ABSTRACT

MnO_x-CeO_2 catalysts with different compositions have been investigated as catalysts for low temperature SCR by preparing a series of samples by the solution combustion synthesis (SCS) method. Variable amounts of two different organic fuels (glycine and citric acid) with respect to the stoichiometry of synthesis were investigated. The samples were characterized by XRD, BET, H_2-TPR, XPS, FESEM and their catalytic activity tested for NO_x abatement in the range of temperature of interest (120–350 °C). By varying the synthesis parameters it was possible to obtain catalysts different in terms of structure, morphology, specific surface area, Mn average oxidation state as well as superficial content of Mn, Ce and O atoms. These features were correlated with the resulting catalytic performances in the SCR reaction and compared to pure MnO_x phases obtained through the same synthesis method. All the developed catalysts were considerably active in the temperature range investigated and could be considered suitable for the low-temperature SCR process. The sample with the higher content of manganese oxide obtained with glycine in below-stoichiometric amount showed the best performance in terms of NO_x conversion and N_2 yield, likely due to the high reducibility as well as the presence of the Mn_3O_4 phase.

1. Introduction

The emissions of nitrogen oxides (NO_x) from power plant and vehicles are known to cause damages to human health and environmental safety. The introduction of the EURO 6 regulations have imposed new limits on emissions of different types of pollutants present in the flue gases of diesel engines.

Selective catalytic reduction of NO_x by using ammonia (NH_3-SCR) as the reducing agent, is a consolidate, efficient and widely used method for the abatement of NO_x, especially in stationary applications. The extension to vehicle exhausts is very interesting too, provided that a proper catalytic system is developed in ordered to answer to the different requests of mobile NO_x sources. The most important difference in the operating conditions can be represented by the range temperature of interest for the process.

In particular, the development of “Low Temperature” NH_3-SCR catalysts that work in the range of temperature from 120 to 300 °C is considered an ideal way to control NO_x emissions also from stationary sources besides being an unavoidable necessity for vehicles.

As a matter of fact, the reduction of the nitrogen oxides by means of ammonia in an oxidising atmosphere has raised the need of the development of new catalysts, characterized by low cost and capability of ensuring high conversions, even at relatively low temperatures.

In recent years, several catalysts among those working at low temperatures have received a particular attention, as for instance: noble metals [1], zeolites [2] and manganese oxides [3]. In particular, the latter system seems to be the most interesting since it conjugates the property of good activity without the presence of macroscopic drawbacks, such as the high costs of noble metals and the poor hydrothermal resistance of zeolites. We have recently shown that the maximisation of Mn_3O_4 phase in the mixed oxide is a significant factor in improving the performances of the catalyst [4], while other groups also showed that the mixing of MnO_x systems with cerium oxide is an interesting strategy to enhance the catalyst properties with the aim to conjugate in one catalyst the most suitable properties of both oxides.

Cerium dioxide is probably one of the most investigated compounds and attracted the interest in catalysis for its promoter and OSC functions. In fact, CeO_2 is not toxic, cheap and, most important, has a unique redox property and high storage capacity making it widely investigated also in the SCR [5]. The variable Ce valence state and the Ce^{4+} vs Ce^{3+} redox couple (1.3–1.8 V) are important factor

---

* Corresponding author. Tel.: +39 11 0904662; fax: +39 11 0904624.
E-mail address: fabio.deorsola@polito.it (F.A. Deorsola).

http://dx.doi.org/10.1016/j.cattod.2015.03.036
0920-5861/

that perform, under oxidizing and reducing conditions, the shift between CeO_2 and Ce_2O_3.

On the other hand, manganese oxides (MnO_x) have been studied as low-temperature SCR catalysts since they contain various kinds of labile oxygen, which is an important factor to complete the catalytic cycle. The additional advantage of coupling MnO_x with ceria lies in the multiple oxidation states of manganese joined with the redox couple of cerium.

A key role is played by the synthesis method of such a mixed Ce-Mn catalyst, so it is possible to find in the recent works new routes for the preparation of MnO_x-CeO_2 catalysts, such as co-precipitation [6], solution combustion synthesis (SCS) [7] and plasma method [8].

The SCS method is characterized by an exothermic redox reaction between nitrates of the metals of the desired oxides and an organic fuel. The first step is the dissolution of all the components in water and subsequently the formed solution is put in a pre-heated oven in order to evaporate the water and to ignite the reaction, which is able to self-sustain due to its high exothermicity. The very fast evaporation of the water and the decomposition of the reactants produce a considerable amount of gases developed, giving as product softly-agglomerated nanoparticles of the desired oxides [9]. By means of this kind of synthesis it is possible to achieve different phases, oxidation states and specific surface areas by easily modifying some synthesis parameters. As we studied in our previous work, MnO_x is a quite complex system where the single phases are difficult to be isolated and the SCS method allowed us to range among very different phase compositions and superficial properties by employing always the same technique in order to uniformly compare the catalysts. The results for the pure MnO_x catalysts were very interesting and so the same approach was adopted for the MnO_x-CeO_2 system.

More recently, MnO_x-CeO_2 catalysts have been reported not only to achieve high activity in the selective catalytic reduction of NO_x with NH_3 but also proved to exhibit promising resistance to SO_2 poisoning [10,11], that is a several obstacle to the development of any NH_3-SCR technology due to the catalyst deactivation for the presence of SO_2 [12].

In the present work, the solution combustion route was chosen for synthesizing MnO_x-CeO_2 catalysts. The Mn/Ce molar ratio as well as quality and quantity of organic fuel in the reaction were investigated as key parameters and their influence on the structural, microstructural and superficial properties was studied. Moreover, the redox property of MnO_x-CeO_2 samples and the synergistic effect of Ce^{4+} and Mn^{n+} ions were analysed. All these properties were correlated to the catalytic activity in order to optimize the parameters for the best catalytic performance. In particular, we have already tried to correlate some chemical properties of the surface with the performances in the NH_3-SCR of pure MnO_x samples prepared by the SCS technique and in this paper a direct comparison among those results and the evidences obtained for the Mn-Ce catalysts will be performed.

2. Material and methods

2.1. Catalyst preparation

The SCS method employed for the synthesis of the catalysts involved the use of manganese(II) nitrate $Mn(NO_3)_2$ tetrahydrate and cerium(III) nitrate $Ce(NO_3)_3$ hexahydrate as metal precursors and two different organic fuels, such as glycine ($C_2H_5NO_2$) and citric acid ($C_6H_8O_7$), with different Mn/Ce ratios, in order to investigate the influence of different compositions of the CeO_2-MnO_x system as well as of different synthesis procedures on the catalytic activity. In our previous work, it was concluded that the Mn_3O_4 phase seemed to be a key factor for the achievement of remarkable catalytic performance [4]. Consequently, the following stoichiometric redox reactions were considered in order to get Mn_3O_4 as main MnO_x phase:

$$\begin{aligned}&18Ce(NO_3)_3 + 27Mn(NO_3)_2 + 56C_2H_5NO_2\\&\quad \rightarrow 18CeO_2 + 9Mn_3O_4 + 82N_2 + 112CO_2 + 140H_2O\end{aligned}$$

$$\begin{aligned}&18Ce(NO_3)_3 + 27Mn(NO_3)_2 + 28C_6H_5NO_7\\&\quad \rightarrow 18CeO_2 + 9Mn_3O_4 + 54N_2 + 168CO_2 + 112H_2O\end{aligned}$$

The catalysts can be identified into three groups, depending on the ratio Mn/Ce present and the type of oxidizer. The samples were labeled as MnXCeY_OF±, where X and Y indicated respectively the Mn and Ce quantities in the Mn/Ce molar ratio, OF the abbreviation of the fuel employed and the symbol + or − if the fuel was introduced in a quantity below or above the stoichiometric one, with respect to the nitrate groups present in the reaction. If the symbol was not present, the sample was synthesized under stoichiometric conditions.

The first series of samples was obtained with a Mn/Ce molar ratio equal to one and the use of glycine in both below and above stoichiometric conditions.

The second involved the use of citric acid, again below and above the stoichiometry, and an equal amount of Mn and Ce atoms (Mn/Ce = 1). The third group of catalysts showed a molar ratio Mn/Ce equal to 9 and the use of glycine under stoichiometric or below-stoichiometric conditions.

In all cases, the reactants were weighted in suitable amounts in order to obtain 2 g of catalysts and they were subsequently mixed in 100 ml of distilled water for 30 min, obtaining a homogeneous mixture. This was poured inside an alumina capsule and placed in a preheated oven at 600 °C, where it remained for 20 min.

The synthesis temperature of 600 °C was the only considered, since the effect that the temperature has on the activity of the catalysts has previously been examined by Yang et al. [13],

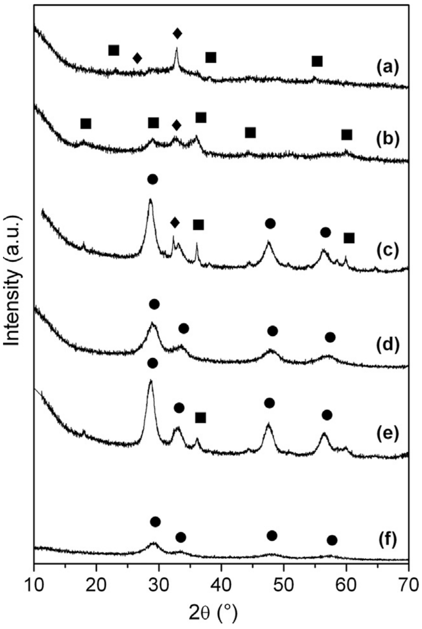

Fig. 1. XRD patterns of the MnO_x-CeO_2 catalysts developed: (a) Mn9Ce1_Gly, (b) Mn9Ce1_Gly−, (c) Mn1Ce1_Gly+, (d) Mn1Ce1_Gly−, (e) Mn1Ce1_CA+, (f) Mn1Ce1_CA− (■ Mn_3O_4, ♦Mn_2O_3, ● CeO_2).