Catalysis Communications 86 (2016) 67–71

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Regeneration of sulfur-poisoned CeO_2 catalyst for NH_3-SCR of NO_x

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ARTICLE INFO

Article history:
Received 30 April 2016
Received in revised form 25 July 2016
Accepted 1 August 2016
Available online 2 August 2016

Keywords:
CeO_2
NH_3-SCR catalyst
Sulfation
Regeneration
NO_x
SO_2

ABSTRACT

The effects of regeneration on the activities and structure of CeO_2 catalysts for NH_3-SCR of NO_x have been studied in this article. CeO_2 catalyst is deactivated by SO_2 for NH_3-SCR of NO_x in a 200 h long-term operation at 350 °C due to the formation of sulfates, and its NO_x conversion decreases from 100% to 83% gradually. However, sulfates can be removed from sulfur-poisoned CeO_2 catalysts under high temperature thermal treatment in air. After regeneration, NO_x conversion of sulfur-poisoned CeO_2 catalyst is recovered to about 100% at 350 °C. Moreover, the regeneration temperature is related to the nature of the sulfates formed on the sulfur-poisoned CeO_2 catalysts.

1. Introduction

Cerium oxide is a common and inexpensive rare earth oxide. It has an ability to store and release oxygen. Addition of ceria in the catalyst helps form oxygen vacancies [1–5]. The Ce^{3+}/Ce^{4+} redox cycle plays an important role in catalytic reactions [6]. In view of these features, ceria-containing materials have attracted widely attention as SCR catalysts for NO_x reduction both in stationary sources and in mobile sources [7,8]. Although CeO_2 is a weakly basic oxide with poor NH_3-SCR activity [9–11], sulfated CeO_2 presents excellent NH_3-SCR activity [11–13]. The sulfur tolerance of SCR catalysts, such as Sb-V_2O_5-TiO_2, NiO-ZrO_2, Cu/ZSM-5, and Fe/β-zeolite, is also enhanced by the incorporation of CeO_2 [2,3,14,15]. From previous research, the improvement in SCR activity of CeO_2 by sulfation is mainly originated from the increase of NH_3 adsorption and the suppression of the catalytic oxidization of NH_3 to NO [11,12].

Although CeO_2 show excellent sulfur tolerance at the beginning of NH_3-SCR reaction in presence of SO_2, this work presents that the NH_3-SCR activity of CeO_2 decreases gradually in continuous operation. The formation of inactive sulfates is responsible for the deactivation because $Ce(SO_4)_2$ and $Ce_2(SO_4)_3$ are poisoning species for NH_3-SCR reaction [16]. There are two common ways to regenerate deactivated catalyst, namely washing and thermal treatment. It has been reported that sulfur-poisoned CeO_2 catalyst can be regenerated by H_2O washing [17]. However, the effects of thermal treatment on the characterization and activity of sulfur-poisoned CeO_2 catalysts have not been reported before. A comparison of the two methods to regenerate sulfur-poisoned CeO_2 catalyst is presented. This work shows that sulfur-poisoned CeO_2 catalyst could be regenerated under high temperature thermal treatment in air, but the low-temperature NH_3-SCR activity could only be partially recovered. To investigate the effects of regeneration, the physicochemical characterizations of the prepared catalysts are analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscope (HRTEM) and Brunauer-Emmett-Teller (BET) method. These results will help us to further understand the effects of SO_2 on CeO_2-containing catalysts and the regeneration of sulfur-poisoned CeO_2-containing catalysts.

2. Experimental

2.1. Catalyst preparation

Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$), provided by Sinopharm Chemical Reagent Co. Ltd., was calcined at 550 °C for 4 h in air to obtain CeO_2 catalyst. Afterwards, the catalyst was sieved to 40–60 mesh. The CeO_2 catalyst was sulfated at high temperature for 12 h in a mixture of 500 ppm SO_2, 10% O_2 and N_2 as balance gas. The obtained sulfated-CeO_2 catalysts are named as S-CeO_2-*x*, where *x* represents the sulfation temperature. The catalyst that was regenerated by calcining

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http://dx.doi.org/10.1016/j.catcom.2016.08.004
1566-7367/

at 850 °C in air was marked as Re-S-CeO_2-*x*. The $Ce_2(SO_4)_3$ was obtained by calcining $Ce_2(SO_4)_3 \cdot 8H_2O$ at 550 °C for 4 h in air.

2.2. TPD experiment

Temperature-programed procedure was carried out to investigate the decomposition temperature of sulfate species on sulfur-poisoned catalysts using the SCR activity test reactor system. 0.04 g sample was purged with air at a flow rate of 400 mL min^{-1}. The temperature was then increased from 100 °C to 950 °C at a ramp rate of 10 °C min^{-1}.

2.3. Regeneration method

The regeneration procedure was carried out using the SCR activity test reactor system. 0.4 g sample was purged with air at a flow rate of 400 mL min^{-1}. The temperature was then increased from 100 °C to *X* °C at a ramp rate of 10 °C min^{-1}, and the dwell time at *X* °C is 20 min. *X* represents the regeneration temperature (730 °C for S-CeO_2-350 and 850 °C for S-CeO_2-500, respectively).

3. Results

3.1. Regeneration of sulfur-poisoned CeO_2 catalyst

A continuous experiment was done to evaluate the effects of SO_2 on NH_3-SCR activity of CeO_2 catalyst, as shown in Fig. 1. NO_x conversion of CeO_2 catalyst increases sharply in the initial period, and reaches nearly 100%. The promotional effects of SO_2 on NH_3-SCR activity of CeO_2 catalyst are originated from the enhancement of NH_3 chemisorption [11]. However, NO_x conversion gradually decreases from 100% to 83% during 200 h operation. This is due to the formation of sulfate species over CeO_2 catalyst [16]. Interestingly, the NO_x conversion is recovered to about 100% after regeneration.

To further investigate the effects of sulfur poisoning on NH_3-SCR activity of CeO_2 catalyst, CeO_2 catalyst is pretreated by sulfation at 500 °C. As shown in Fig. 1 inset, the NO_x conversion of S-CeO_2-500 is obviously lower than that of CeO_2. After regeneration, the NO_x conversion of S-CeO_2-500 is only partially recovered at low temperature, while it is fully recovered in the temperature range of 350 ~ 450 °C. The NH_3-SCR activity of $Ce_2(SO_4)_3$ is the poorest among all the prepared catalysts. This indicates that sulfates are a kind of inactive species for NH_3-SCR of NO_x.

As shown in Fig. 2, sulfur can be removed from the bulk of sulfur-poisoned CeO_2 catalysts according to TPD experiment. The regeneration temperature of S-CeO_2-350 is lower than that of S-CeO_2-500, and lower amount of SO_2 is released from S-CeO_2–350. This indicates that fewer sulfates are formed on S-CeO_2-350 confirmed by lower catalytic activity of S-CeO_2-500 (Fig. S1). The decomposition temperature of $Ce_2(SO_4)_3$ is higher than that of S-CeO_2-500. It is reported that the nature of sulfate species over sulfated CeO_2 is changed from surface sulfates to bulk sulfates with increase of the sulfation temperature [17]. This indicates that surface sulfates are easier to be removed from sulfur-poisoned CeO_2 catalysts. Thus, we chose the S-CeO_2-500 catalyst as the typical sulfur-poisoned CeO_2 catalyst to study the effects of regeneration.

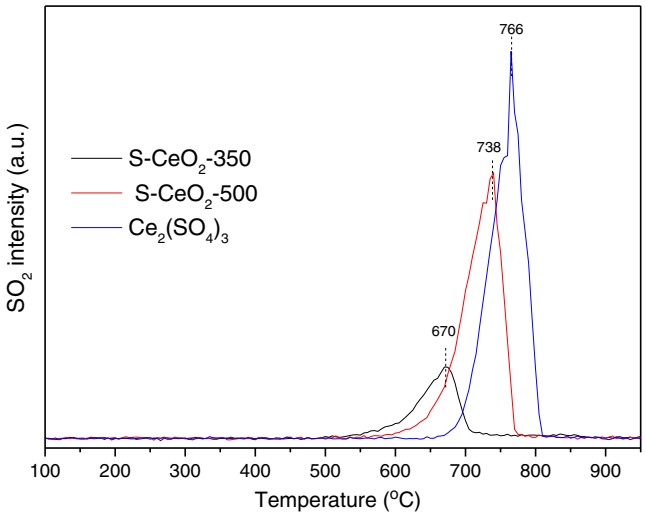

Fig. 2. The decomposition temperature of sulfate species on sulfur-poisoned catalysts.

3.2. XRD and XPS analysis

As shown in Fig. 3, XRD peaks of CeO_2 match well with the JCPDS (card no. 43-1002) data. Sulfation process has only little effect on the intensity of the CeO_2 reflections of S-CeO_2-350. However, new phase reflections are detected in the XRD pattern of S-CeO_2-500. These new reflections are attributed to $CeOSO_4$ (JCPDS 39-0515), $Ce_2(SO_4)_3$ (JCPDS 01-0208) and $Ce(SO_4)_2$ [17], respectively. The reflections of sulfate species disappear after regeneration, and the reflections of CeO_2 recover in the XRD pattern of Re-S-CeO_2–500.

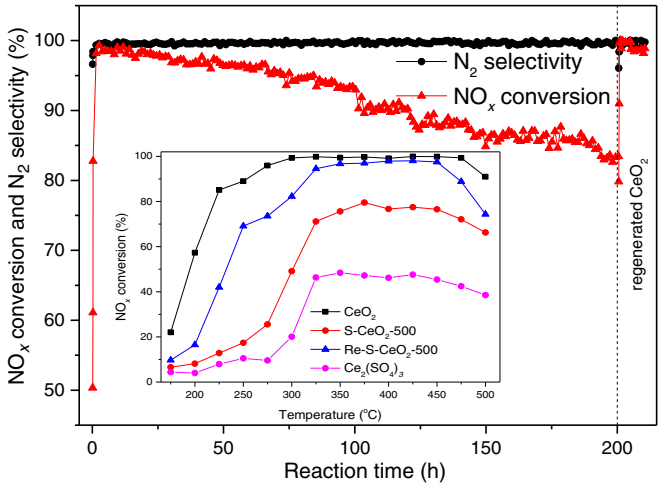

Fig. 1. Regeneration of sulfur-poisoned CeO_2 catalyst. Reaction conditions: 500 ppm NO + 500 ppm NH_3 + 5% O_2 + 25 ppm SO_2 + N_2 balance. GHSV = 175,000 h^{-1}, 350 °C.

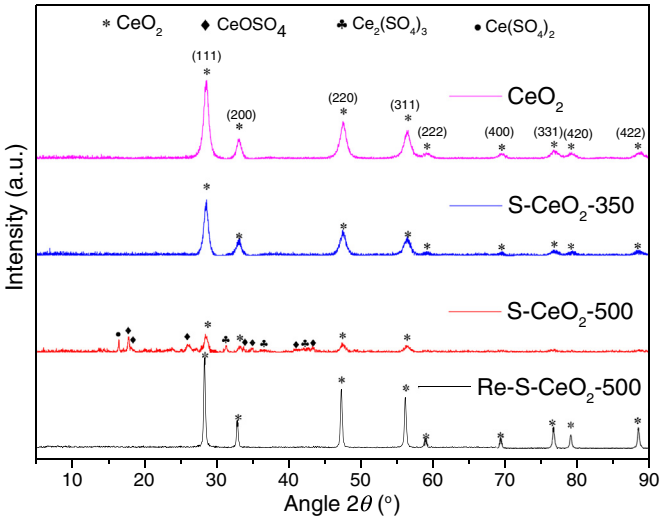

Fig. 3. The XRD patterns of ceria-based catalysts.