Chinese Journal of Catalysis 35 (2014) 1504–1510

available at www.sciencedirect.com

ScienceDirect

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

Article

Effect of sulfur poisoning on Co_3O_4/CeO_2 composite oxide catalyst for soot combustion

Xiaoyan Shi [a], Yunbo Yu [a], Li Xue [b], Hong He [a,*]

[a] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] School of Chemical Engineering, Shandong University of Technology, Zibo 255049, Shandong, China

ARTICLE INFO

Article history:
Received 23 February 2014
Accepted 21 March 2014
Published 20 September 2014

Keywords:
Soot oxidation
Cobalt oxide
Ceria
Composite oxide
Sulfur poisoning

ABSTRACT

CeO_2, Co_3O_4, and a series of Co_3O_4/CeO_2 composite oxides prepared by co-precipitation were exposed to SO_2 under an oxidizing environment at 400 °C. These fresh and SO_2-poisoned samples were characterized by in situ diffuse reflectance infrared Fourier transform spectroscopy, X-ray diffraction, temperature-programmed desorption, and X-ray photoelectron spectroscopy. Sulfates were formed on the oxides, with more sulfates on CeO_2 than on Co_3O_4. On the Co_3O_4/CeO_2 composite oxides, both cobalt sulphate and ceria sulfate were formed. Fresh and sulfated samples were tested for soot combustion in a NO/O_2 gas flow. The Co_3O_4/CeO_2 composite oxides showed better SO_2 tolerance and higher activity than CeO_2 but were more easily poisoned by SO_2 than Co_3O_4.

1. Introduction

A diesel particulate filter is applied for the removal of soot from diesel engine exhaust. The use of an oxidation catalyst coated on the filter is the preferred way to accelerate the combustion of accumulated soot and has been widely studied. Various soot oxidation catalysts have been developed, and many metal oxides can lower the soot oxidation temperature [1–5]. Ceria-supported cobalt oxides prepared by different routes exhibited good performance for soot combustion [6–12]. Harrison et al. [6] deduced that the high catalytic activity of Co/CeO_2 in soot combustion was due to the presence of cobalt in the catalyst as Co_3O_4 and the redox properties of CeO_2. A spillover mechanism at the cobalt oxide-ceria interface was postulated to drive the soot oxidation. Methane oxidation experiments are sometimes performed as a test of soot oxidation [13]. Co_3O_4/CeO_2 composite oxides prepared by a co-precipitation method showed a superior activity for methane oxidation and CO oxidation and have good resistance to water vapor poisoning [13,14].

From a practical point of view, studying the effect of SO_2 on Co_3O_4/CeO_2 composite oxides is of importance because SO_2 is present in the exhaust gases. In the present study, a series of Co_3O_4/CeO_2 composite oxide catalysts were prepared by the co-precipitation method. The sulfation of the Co_3O_4/CeO_2 catalysts was investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The soot oxidation activity of the fresh and SO_2-poisoned Co_3O_4/CeO_2 composite oxides was investigated and compared using temperature-programmed oxidation (TPO).

---

* Corresponding author. Tel/Fax: +86-10-62849123; E-mail: honghe@rcees.ac.cn

This work was supported by the National Basic Research Program of China (973 Program, 2010CB732304) and the State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex (SCAPC201302).

DOI: 10.1016/S1872-2067(14)60088-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 9, September 2014

2. Experimental

2.1. Catalyst preparation

Co_3O_4/CeO_2 composite oxides with increasing Co_3O_4 loading corresponding to Co/Ce atomic ratios of 0.05–5 (denoted by Co0.05Ce, Co0.2Ce, Co1.0Ce, Co2.0Ce, and Co5.0Ce), CeO_2, and Co_3O_4 were prepared by a co-precipitation method with a K_2CO_3 solution (15 wt%). In a typical preparation, K_2CO_3 solution was added dropwise to an aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ and $Ce(NO_3)_3\cdot 6H_2O$ in appropriate amounts until the pH was 9.10. The mixture solution was stirred for 1 h and was aged at room temperature for 3 h. Then the resulting precipitate was filtered and washed with distilled water until the filtrate pH was neutral. The precipitate was dried overnight at 110 °C and calcined for 2 h at 400 °C in air.

To sulfate the catalysts, 40–60 mesh catalysts were treated with 300 ppm SO_2 and 10% O_2 in N_2 at a flow rate of 400 ml/min at 400 °C for different times. The SO_2-poisoned catalysts were denoted according to the treatment time, for instance, Co1.0Ce-S-10h was the Co1.0Ce catalyst sulfated at 400 °C for 10 h.

2.2. Catalytic activity measurements

The soot used in this work was Printex-U (Degussa), which is a model soot reported elsewhere. The catalyst-soot mixture (9:1 w/w) for the TPO reaction was obtained by careful grinding in an agate mortar for 10 min (tight contact). It is known that the contact between the soot and catalyst influences the oxidation reaction significantly [3,15]. Although the soot/catalyst contact obtained by the current mixing procedure did not reflect the actual contact conditions in a catalytic soot trap, nevertheless it permitted reproducible results under the present experimental conditions [16,17]. A catalyst-soot mixture diluted with 1.00 g quartz pellets was carefully mixed and put into the quartz tube reactor (internal diameter 6 mm). The TPO test was carried out by heating the soot/catalyst mixture from 200 to 600 °C (heating rate 2 °C/min) under a total flow rate of 100 ml/min (NO 1000 ppm, O_2 5%, Ar as balance). CO_2 analysis was performed by GC/TCD (Porapak Q, Agilent) at intervals of 5 min.

2.3. Catalyst characterization

The samples were characterized by XRD using a computerized Rigaku D/max-RB diffractometer (Japan, Cu K_α radiation). Data were recorded in the 2θ range of 10°–90° with an angle step size of 0.02° and a scanning speed of 4°/min.

XPS analysis was performed with an EASY ESCA instrument. The spectra were excited by an Al K_α source (1486.6 eV), and the analyzer was operated in the constant analyzer energy (CAE) mode. Survey spectra were measured at 50 eV pass energy. Charging of the samples was corrected for by referencing all the energy to the C 1*s* peak energy (set at 285.0 eV).

TPD was performed in a system equipped with a quadrupole mass spectrometer (Hiden HPR20). In the SO_2-TPD, the SO_2-poisoned sample was placed in a quartz tube reactor (internal diameter 4 mm). Pure He was used as the carrier, and the total flow of carrier was held at 30 ml/min with the temperature increase rate of 30 °C/min. All the samples used in the TPD experiments were the same weight of 300 mg and the same size of 40–60 mesh.

DRIFTS spectra were recorded in situ with a Nexus 670 FT-IR spectrometer (Thermo Nicolet) equipped with a diffuse reflection chamber and a high sensitivity MCT/A detector cooled by liquid nitrogen. The catalysts for the DRIFTS study was finely ground and placed in a ceramic crucible. All spectra were measured with a resolution of 4 cm^{-1} and with an accumulation of 100 scans. Sulfate accumulation on test catalysts was investigated by DRIFTS in a flow of SO_2 300 ppm, O_2 20%, and N_2 as balance for 60 min at 400 °C.

3. Results and discussion

3.1. Activity test

The TPO results of soot combustion in a NO/O_2 mixture over the various Co_3O_4/CeO_2 oxides, pure CeO_2, and Co_3O_4 are shown in Fig. 1(a). Clearly, the presence of cobalt greatly improved the soot oxidation activity of CeO_2 even at as low a content as Co/Ce = 0.05. The catalytic activity for soot combustion showed

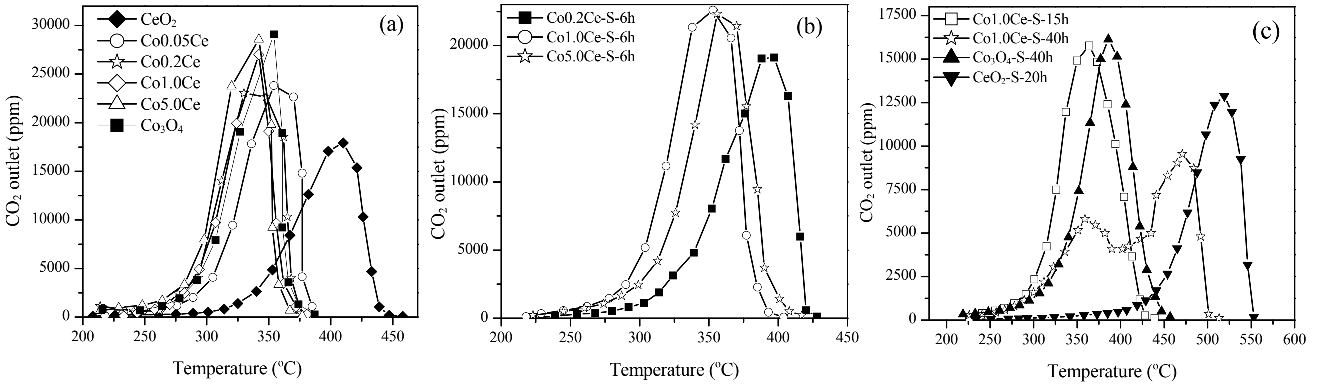

Fig. 1. TPO profiles of soot-catalyst mixtures (soot:catalyst = 1:9 by weight). (a) Fesh catalysts; (b) 6 h SO_2-poisoned catalysts; (c) Various SO_2-poisoned catalysts. Reactant gas: 1000 ppm NO + 5% O_2 in Ar. Heating rate: 2 °C/min. SO_2 poison conditions: 300 ppm SO_2 and 5% O_2 in N_2 at 400 °C.