Available online at www.sciencedirect.com
ScienceDirect
Catalysis Communications 8 (2007) 1659–1664
CATALYSIS COMMUNICATIONS
www.elsevier.com/locate/catcom

Simultaneous catalytic removal of NO_x and soot particulate over Co–Al mixed oxide catalysts derived from hydrotalcites

Zhongpeng Wang, Zhi Jiang, Wenfeng Shangguan *

Research Center for Combustion and Environmental Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

Received 2 November 2006; received in revised form 25 December 2006; accepted 23 January 2007
Available online 30 January 2007

Abstract

Co–Al mixed oxides (CAO) was prepared by co-precipitation method from hydrotalcites (HT) as precursors, and their catalytic activity was investigated for the simultaneously catalytic removal of NO_x and diesel soot particulates by the temperature-programmed reaction (TPR) technique. All HT samples present well crystallized, layered structures, no excess phases were detected. A nonstoichiometric spinel phase was formed by calcining the CAO at 500 °C and 800 °C, irrespective of the Co/Al ratio. Both the activity of soot oxidation and the selectivity to N_2 formation of CAO catalysts calcined at 800 °C were higher than that at 500 °C. The observed difference in the catalytic performance was related to the redox properties of the catalysts and the crystallite size of HT precursors. The active species might come from Co_3O_4, which acted for redox-type mechanism for soot oxidation in the NO_x-soot reaction.

Keywords: Hydrotalcites; Mixed oxides; NO_x; Soot; Simultaneous removal

1. Introduction

Nitrogen oxides (NO_x) and soot particulates are the main pollutants in diesel engine emissions and they can cause serious problems to global environment and human health. There are many countries, such as US, Japan and Europe which have introduced specific and severe limits to the exhaust-gas emissions [1]. As the legislation limitation goes more stringent, there is a growing interest in developing the process which enables the reduction of such emissions.

As a promising alternative, the simultaneous catalytic removal of NO_x and soot particulates in a single trap was proposed by Yoshida et al. [2]. Mixed metal oxides with the perovskite-related [3–6] and spinel [7–9] structures are promising catalysts for this reaction. Potassium modified iron oxide [10–12], Co, K supported catalysts [13,14] and zeolites [15] also display activities for the simultaneous removal of nitric oxide and soot. Cu containing catalysts have been found active for reduction of nitric oxide by solid carbonaceous materials under lean conditions [16]. However, most of pervious studies were carried out under tight contact conditions between soot and catalysts. Further efforts should focus on the activity of the catalysts under loose conditions, i.e., higher selectivity to CO_2 formation, and higher selectivity to N_2 from NO reduction [17].

Recently, calcined hydrotalcite-like compounds (HTLCs) have received increasing attention, which are excellent catalysts or catalyst supports owing to their large surface areas, basic properties, high metal dispersions and thermal stability [18,19]. Such mixed oxides containing transition metals also show redox properties, which have been applied in the catalytic removal of NO_x and SO_x [20,21], as well as in oxidation reactions [22,23]. Their redox performances are strongly related to the metal spe-

---

* Corresponding author. Tel.: +86 21 64076226; fax: +86 21 64075359.
E-mail address: shangguan@sjtu.edu.cn (W. Shangguan).

1566-7367/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2007.01.025

cies, contents and calcined temperatures. In this work, we have examined the catalytic property of Co–Al mixed oxides derived from hydrotalcites as a new active catalyst for the simultaneous NO_x-soot removal reaction.

2. Experimental

2.1. Catalyst preparation

The synthesis of Co–Al HT (Co/Al molar ratio equals to 2, 3, 4, 5, and 7, respectively as shown in Table 1) followed the reference [22] by co-precipitation of an aqueous solution of suitable metal nitrates with an aqueous solution of 2 M NaOH and 1 M Na_2CO_3. The two solutions were mixed under vigorous stirring at 25 °C with the pH maintained constant at 10.0 ± 0.5. The resulting slurry was aged in the mother liquor at 80 °C for 18 h. It was then filtered and washed with distilled water until the pH of the filtrate was around 7. The precipitate was then dried at 100 °C for 12 h to obtain Co–Al HT (designated as *i*CA-HT). The two series of Co–Al mixed oxides were obtained by calcining HT either at 500 °C for 5 h or at 800 °C for 5 h. The oxides catalysts are denoted as *i*CAO-*m*, where *i* represents Co/Al molar ratio and *m* represents calcinations temperature. For example, CAO-800 refers to all the catalysts calcinded at 800 °C, while 5CAO-800 refers to the catalyst with the Co/Al ratio of 5 and calcinations temperature of 800 °C.

Reference spinel oxide Co_3O_4 was prepared by decomposition of cobalt (Π) nitrate at 800 °C for 5 h in air.

2.2. Catalyst characterization

XRD was conducted with a BRUKER-AXS D8Adance X-Ray Diffractometer using Cu Kα radiation. The bulk structures of the samples were observed by scanning electron microscopy (Hitachi S-3000H). N_2 Adsorption–desorption isotherms were measured on a Quantachrome NOVA1000 Sorptomatic apparatus. The specific surface area was calculated with the BET equation. H_2-Temperature-programmed reduction (H_2-TPR) analysis was carried out using a gas mixture of H_2–N_2 (5% vol.) and the gas flow (50 ml/min), sample weight (50 mg), and heating schedule (10 °C/min). H_2 consumption was measured with a thermal conductivity detector.

2.3. Catalytic activity testing

In this paper, a commercially available carbon black (Shanxi Luan Carbon Black Science & Technology Co. Ltd., China) was used as a model of diesel soot, with specific surface area of 120.6 m^2/g^{-1}, heating loss of less than 0.4% and ash content of less than 0.3% [24]. The catalytic activity tests were carried out by TPR technique [3–5,7–9]. The well mixed Catalyst and soot (20:1 w/w) were palletized, crushed and sieved to 20–40 mesh. The tight mixture (0.33 g) was placed in an 8 mm U-shaped quartz reactor, and pretreated in a helium flow at 300 °C for 2 h in order to eliminate possible contaminants. After cooling down to 100 °C and replacing the helium flow with the reaction gas flow, TPR was started at a heating rate of 1.4 °C/min. The reaction gas consisted of 0.25 vol.% NO, 5 vol.% O_2 with the balance being helium. The total flow rate was 80 cm^3/min. The outlet gas was analyzed with intervals of about 15 min using a TCD gas chromatograph (Shimazu GC-8A) with columns of Porapak Q for separating CO_2 and N_2O and molecular sieve 5A for N_2, O_2, NO and CO.

3. Results and discussion

3.1. Characterization of catalysts

The XRD patterns of CA-HT precursors and derived CAO samples are given in Fig. 1. All the HT precursors (Fig. 1a) showed the typical diffraction patterns of hydrotalcite-like materials having layered structure with intercalated carbonate anions [25,26]. Only hydrotalcite phases were detected in all the HT precursors. The intensity or sharpness of all the peaks corresponding to the hydrotalcite phase decreases with the increase in Co/Al ratio, suggesting a decrease in the crystallinity of the solids. The results from the calculation with Debye–Scherrer equation is shown in Table 1. From the sample 2CA-HT to 5CA-HT, the average crystallite size decreases with the increase of the Co content in the sample. The 5CA-HT sample with Co/Al ratio equal to 5:1 exhibits the smallest crystallite size at about 4.0 nm. The special case appears in 7CA-HT sample. The crystallite size for 7CA-HT sample is 7.9 nm. Obviously, it does not show regular pattern as the previous samples.

Table 1
Composition and textural properties of the samples

Sample	Co/Al molar ratio	Average crystallite size (nm)	Calcined 500 °C			Calcined 800 °C		
			S_{BET} ($m^2\ g^{-1}$)	V_P ($cm^3\ g^{-1}$)	D_P (nm)	S_{BET} ($m^2\ g^{-1}$)	V_P ($cm^3\ g^{-1}$)	D_P (nm)
2CA-HT	2:1	23.0	114	0.573	20.1	47.0	0.163	13.9
3CA-HT	3:1	12.6	83.0	0.413	19.9	30.9	0.160	20.7
4CA-HT	4:1	9.3	72.2	0.315	17.5	30.9	0.231	29.8
5CA-HT	5:1	4.0	79.9	0.351	17.6	35.2	0.305	34.7
7CA-HT	7:1	7.9	64.9	0.385	23.7	18.5	0.211	45.7

Average crystallite size of CoAl-HT calculated from *d*(003) and *d*(006) planes using Debye–Scherrer equation. S_{BET} – BET specific surface area, V_P – Total pore volume, D_P – Average pore diameter.