Journal of Catalysis 271 (2010) 228–238

Contents lists available at ScienceDirect

Journal of Catalysis

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

Effects of CO_2 and steam on Ba/Ce-based NO_x storage reduction catalysts during lean aging

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ARTICLE INFO

Article history:
Received 10 September 2009
Revised 12 January 2010
Accepted 18 January 2010
Available online 13 February 2010

Keywords:
NO_x storage reduction
Aging
Barium cerate
Barium carbonate
Ceria
Support oxides

ABSTRACT

The effects of CO_2 and steam on the morphological and chemical properties of Ba/Ce-based NO_x storage reduction (NSR) catalysts during the aging were investigated. At 800 °C, $BaCeO_3$ formation was prevented by a CO_2 concentration as low as 5%, which shows little effect on suppressing $BaAl_2O_4$ and $BaZrO_3$ formation. CO_2 protects hexagonal $BaCO_3$, BaO_2, and CeO_2, to form $BaCeO_3$, by increasing one time higher activation energy for decarbonation, and maintaining orthorhombic $BaCO_3$ as the most stable storage component. Steam accelerates the particle aggregations, but it does not determine the above chemical equilibrium. In NSR reactions, although $BaCeO_3$ formation can be excluded in an atmosphere containing CO_2, the nitrite/nitrate bonding stabilization and the complete NO_x reduction are hindered by the highly crystallized materials (induced by higher CO_2 and/or steam concentrations during aging). Particle aggregation is a major factor responsible for the deactivation of the aged Ba/Ce-based NSR catalysts.

1. Introduction

Lean NO_x trap (LNT), also known as NO_x storage reduction (NSR), has drawn wide attention as an advanced exhaust control technology to reduce NO_x emissions from lean-burn engines [1]. A typical NSR catalyst formulation contains basic NO_x storage components (mostly barium species), noble metals (NM, such as Pt, Rh, Pd), and support oxides. The combined effects of these three components efficiently remove NO_x from vehicle exhaust through the periodic operations of NO_x oxidation, NO_x sorption, NO_x release, and NO_x reduction [2,3].

Ceria-based materials have been shown to be beneficial for NSR catalysts. They maintain higher metal dispersions [4], provide surface basicity to benefit the formation of carbonates [5], promote the water–gas shift (WGS) reaction and the reduction of NO_x at anionic vacancies [6], and release lattice oxygen, which modifies the redox process [7]. Many current commercial samples have already incorporated ceria into NO_x traps. Several research articles have reported the outstanding performance of Ba/Ce-based NSR catalysts compared to the catalysts with other oxide supports (Al, Si, or Zr), although ceria-based materials are admitted to have several drawbacks [3,8,9]. Not only do ceria-based materials sinter at relatively low temperatures [3], they also maintain the oxidation states of NM during rich periods [10], and their surface basicity is negative for NO oxidation in lean conditions [11].

Thermal deterioration, especially with concern to the modification of NO_x storage components [12], is one of the main reasons for the deactivation of NSR catalysts [2]. Besides several recent studies focused on the Pt–Ba interactions [13,14], much emphasis is put on the barium-based components modified by the Ba-support interactions [2,3]. The formation of $BaCeO_3$, $BaAl_2O_4$, and $BaZrO_3$ in Ba/Ce, Ba/Al, and Ba/Zr systems is well documented, and these compounds are known to decrease the NO_x storage efficiency [9,15]. Additionally, investigations into the regeneration of thermal-aged NSR catalysts have been reported [12,15]. In general, treatments in an acidic liquid (water) or a 300–800 °C acidic atmosphere, in which H_2O, NO_x, and CO_2 are applied at concentrations much higher than those in the exhaust, are required for the regenerations. Therefore, it is desirable to develop a heterogeneous NSR catalyst that does not form the inactive phases during the aging treatment or readily regenerates the deactivated phases under realistic conditions in vehicle exhaust [2]. Regeneration of $BaCeO_3$ is more likely when compared with that of $BaAl_2O_4$ and $BaZrO_3$ [15]. However, the possibility of $BaCeO_3$ formation under realistic applications was questioned due to the lower concentrations of CO_2 and H_2O

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doi:10.1016/j.jcat.2010.01.018

Table 1
Descriptions of the different aging treatments.

Names of the treatments	Brief description (for 0–18 h aging)
Fresh	As-prepared samples
Thermal	Samples treated in 800 °C air
Hydrothermal	Samples treated at 800 °C in 10% steam (air balance)
5%* CO_2 thermal	Samples treated at 800 °C in 5% CO_2 (air balance)
10% CO_2 thermal	Samples treated at 800 °C in 10% CO_2 (air balance)
5% CO_2 hydrothermal	Samples treated at 800 °C in 5% CO_2 + 10% steam (air balance)
10% CO_2 hydrothermal	Samples treated at 800 °C in 10% CO_2 + 10% steam (air balance)

* All percentages presented stand for gaseous percentages in volume.

(NO_x can be eliminated) found in lean-burn exhaust [12]. It is not clear whether the decent activity of Ba/Ce-based NSR catalysts is due to the higher NO_x storage capacity (NSC) of $BaCeO_3$, or the improved maintenance of active phases against $BaCeO_3$.

The performance of the aged NSR catalysts strongly depends on the real operation conditions; and therefore, the lab aging strategies should be careful examined. Even at similar temperatures, different atmospheric compositions during the aging treatments will have a significant impact on the aged catalyst performance [5,16]. In contrast to the periodically varying NO_x concentrations (eliminated at most of the time), the concentrations of CO_2 and steam are kept almost at a constant level during the lean–rich cycles. Their continuous effects of modifying NSR materials should be studied.

Temperature-dependent effects of steam and CO_2 during NSR reactions have been systematically studied [5,16], but their influences during long time aging have yet to be thoroughly investigated. In the present work, the effects of CO_2 and steam on the morphological and chemical properties of Ba/Ce-based NO_x NSR materials during the aging treatments were studied through surface/bulk analysis and activity tests. Since there is little evidence that noble metals change the Ba-support interaction [13,17], the NM-related interactions have been decoupled from the Ba–Ce contact for most of the samples we investigated.

2. Experimental

2.1. Sample preparation

For the supported samples, Pt and BaO were loaded by wet impregnation, using $Pt(NO_3)_2$ and $Ba(Ac)_2$ solutions, respectively. CeO_2, Al_2O_3, and ZrO_2 support oxides were from Aldrich. The impregnated materials were calcined in air at 500 °C for 5 h to obtain the fresh samples. Only the BaO/CeO_2 parts were treated under different aging conditions, and they were mixed with the fresh 2 wt.% Pt/Al_2O_3 in the weight ratio of 6:4 right before the catalytic tests. For comparison, 2 wt.% Pt/30 wt.% BaO/CeO_2 samples and 30 wt.% BaO/2 wt.% Pt/CeO_2 samples were also prepared (Pt and Ba impregnated with reverse sequences), in which the NM and barium species were loaded on the same support oxide in reverse sequences. Descriptions of the different treating strategies are listed in Table 1.

Pertaining to the impregnated BaO/CeO_2 samples, the contact between barium species and ceria takes place on the interface where the barium salts were wet-impregnated. According to our X-ray diffraction and thermogravimetric data, the insufficient close Ba–Ce contact and less barium content make the quantification of the major phases and the tracking of the minor intermediate species difficult. Therefore, co-precipitated Ba/Ce (molar ratio 1:1) mixed compounds magnifying the Ba–Ce close contact, designated as BaCe11, were used in the study for comparison. The BaCe11 samples were prepared by adding $Ce(NO_3)_3 \cdot 6H_2O$ and $Ba(NO_3)_3$ into a NH_4HCO_3 precipitator. Additional basic solutions were added until pH = 9 (200% in excess). The precipitates were stirred at room temperature (RT) for 30 minutes and stabilized at 60 °C for 12 h. After being filtered and washed with de-ionized water till pH = 7, the products were dried at 100 °C for 12 h. Fresh powders were obtained after the subsequent calcination in air at 500 °C for 5 h. The majority of fresh powder is able to be converted into $BaCeO_3$ crystallites after 4 h calcination at 1100 °C according to XRD analysis [18,19].

2.2. Characterization and model reaction

The XRD patterns were acquired using X'Pert Pro diffractometer operating at 30 kV and 30 mA with nickel-filtered Co Kα radiation, at a 0.02° step size. For *in situ* experiments, the heating rate from RT to the target temperature was 10 °C/min, and the space velocity was 10,000 h^{-1}. Percentages of detected crystallites in samples were estimated by comparing the obtained XRD patterns with the monocomponents patterns of standardized crystallites in HIGHSCORE software database. Crystal sizes are calculated by JADE 5. Thermogravimetric experiments were conducted on METTLER TOLEDO TGA/DSC 1. Approximately, 20 mg of fresh sample was heated in a gas flow (50 ml/min) at a heating rate of 5, 10, and 15 °C/min, respectively.

BET surface areas were measured using N_2 adsorption with a Quantachrome NOVA 1200. Scanning electron microscopy (SEM) of the samples coated with Au–Pd was measured on a HITACHI S4800 field emission microscope. X-ray energy dispersive spectroscopy (EDS, NORAN System 7) results indicated that the enrichment of $BaCO_3$ generally shows deep color, CeO_2 the intermediate, and $BaCeO_3$ the light color.

In situ DRIFTS of NO_x isothermal adsorption and temperature programmed desorption were performed on a NICOLET 6700 FT-IR equipped with a commercial reaction chamber (Thermofisher) at the resolution of 1 cm^{-1}. Ten scans were operated for each spectrum. Powder samples were purged in 0.3% O_2/N_2 balance from RT to 500 °C. The sample cell was then cooled to 350 °C under the same atmosphere. NO_x adsorption measurements were conducted by introducing freshly mixed 0.075% NO/0.3% O_2/N_2 balance to the chamber at 350 °C. After the saturation of NO_x adsorption, which was judged by the invariant IR spectra, the sample was purged by N_2 at 350 °C till no changes happen to the IR spectra with the increasing time. The sample cell was subsequently heated to 500 °C at 10 °C/min, and NO_x desorption behaviors were recorded. The gas flow rate in all circumstances was 200 ml/min, and the tiny IR interference from gas molecules was subtracted.

In NSR activity tests, 0.5 g catalyst (0.2 g of 2 wt.% Pt/Al_2O_3) was mixed with quartz sand in a volume ratio of 1:3. The total flow rate is 1 L/min, with the space velocity of 30,000 h^{-1}. A NICOLET 380 FT-IR equipped with a 2-m gas cell was used to detect the outlet concentrations of NO, NO_2, NH_3, N_2O, CO, CO_2, and H_2O (g) at 4 s intervals. IR spectra of the multiple gases were collected at the same time. These spectra were automatically quantified by comparing them with the standardized spectra of diluted monocomponent gases at different concentrations, which were already set into mathematical functions as a method file. Home-developed software, OMINIC, TQ Analyst, and Macros Basic were connected to effectuate the calculations. A set of 1 min (lean)–1 min (rich) experiments and another set of 10 min (lean)–1 min (rich) experiments were conducted. The inlet gas concentrations are listed in Table 2. Calculations were made based on the reproducible concentration curves for at least 3 cycles (usually 5–6 cycles were required before stabilization). NO_x-TPD experiments were conducted on the same equipment with the same flow rate. Powder samples were pre-treated in 7.5% O_2/N_2 at 500 °C for 20 min, and