Applied Catalysis B: Environmental 102 (2011) 620–626

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Improvement in sulfur desorption of NO_X storage and reduction catalysts using a Ba–Ti composite oxide

Toshiyuki Tanaka[a,*], Ichirou Tajima[a], Yuichi Kato[a], Yasushi Nishihara[b], Hirofumi Shinjoh[a]

[a] *Toyota Central Research and Development Labs., Inc., Nagakute-cho, Aichi 480-11, Japan*
[b] *Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushimanaka, Kita-ku, Okayama, 700-8530, Japan*

ARTICLE INFO

Article history:
Received 15 November 2010
Received in revised form
23 December 2010
Accepted 4 January 2011
Available online 8 January 2011

Keywords:
NSR catalyst
Desulfation
Barium sulfate
Titanium oxide
Citric acid

ABSTRACT

A Ba–Ti composite oxide was formed on a NO*x* storage and reduction catalyst via impregnation of a Ba–Ti precursor solution composed of H_2O_2 added to a complex prepared using the citric acid method. The structure of the Ba–Ti composite in solution was analyzed by chemical composition analysis and FT-Raman and UV–vis spectroscopy. MM2 calculations were performed to propose its chemical structure. Both Ba and Ti together were found to form a composite molecule in the solution. Furthermore, TEM-EDX and XRD analyses of the Ba–Ti composite oxide on the catalyst prepared by impregnation with the Ba–Ti composite aqueous solution revealed that Ba and Ti in the catalyst were highly dispersed at the nm scale. The formation of the Ba–Ti composite oxide on the NSR catalyst enhanced sulfur desorption efficiency and led to high-performance NO_X conversion as a NO_X storage and reduction activity catalyst after desulfation treatment. It was assumed that the existence of nano-scaled Ba compounds combined with Ti was efficient for the inhibition of the sintering of barium sulfate and its facile decomposition. It was found that dispersion of Ba compounds for NO_X storage materials using a Ba–Ti complex solution is an efficient way to improve the durability of NSR catalysts.

1. Introduction

Curbing CO_2 emissions and improving the fuel efficiency and clean-up of automobile exhaust gases are required for global environmental protection. Lean-burning gasoline and diesel engines achieve high fuel economy using higher air/fuel ratios (A/F). It is difficult, however, to remove the NO_X in exhaust gases from these engines under excess oxygen conditions. Some NO_X purifying systems such as selective NO_X reduction by hydrocarbons [1–3], NH_3 (urea) [4], H_2 [5] and CO [6] have been researched, with a few of them developed for commercial use.

A NO_X storage and reduction (NSR) catalyst system is one of the most efficient ways to achieve NO_X purification [7,8]. In the NSR system, NO_X (NO) is oxidized to NO_2 over precious metals in the catalyst, then combined with NO_X storage materials and finally stored as nitrate ions. In the following reduction stage, under a stoichiometric or reductive atmosphere (rich), the stored nitrate ions are released as NO_X (NO or NO_2) from the NO_X storage materials and then reduced to nitrogen. The NSR catalyst system has the advantages of high performance and feasibility for purifying NO_X compared with other methods.

Unfortunately, NSR catalysts deactivate due to sulfur poisoning and/or thermal deterioration. Sulfur deactivation in particular is the most important problem to be solved. The sulfur poisons the precious metals [9,10], supports [11] and NO_X storage materials [8,9]. Furthermore, sulfur poisoning strongly influences the NO_X storage ability of the system. NSR catalysts include some alkali metals or alkali earth metals that produce stable sulfates (SO_X) when exposed to exhaust gases. It has been confirmed that the adsorbed sulfur transforms the NO_X storage materials into sulfates [8–10]. The formation of nitrate on the storage compound is inhibited and thus the NO_X storage ability deteriorates. Consequently, the deactivation of NSR catalysts depends on the amount of sulfur poisoning of the catalyst [12]. Sulfur deactivation also depends on the particle size of the sulfate produced by the NSR catalyst [13]. It has been reported that the decomposition temperature of sulfates decreases if the $BaSO_4$ particles in the catalyst are kept under 3 nm in size [14].

There have been several reports about improving the sulfur tolerance of NSR catalysts based on the above research. One of the methods involved the usage of TiO_2 [15]. The decomposition temperature of sulfates on a TiO_2 support was found to be lower than that on an Al_2O_3 support under reducing conditions. By blending TiO_2 with Al_2O_3 [16], sulfur deposition was simultaneously suppressed and enhanced the NO_X storage of the sulfur-aged catalyst. The tolerance of the NSR catalyst against sulfur poison-

---

[*] Corresponding author. Tel.: +81 561 636140, fax: +81 561 636150.
E-mail address: e0924@mosk.tytlabs.co.jp (T. Tanaka).

0926-3373/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2011.01.002

Table 1
Catalyst formulations.

Catalyst	Support	Pt (g/L)	Rh (g/L)	Ba (mol/L)	Ti (mol/L)	K (mol/L)	Li (mol/L)
BaTi-A	γ-Al_2O_3	2	–	0.2	0.2	–	–
BaTi-B	Mixed oxides	2	0.5	0.2	0.2	0.15	0.1
Ba-A	γ-Al_2O_3	2	–	0.2	–	–	–
Ba-B	Mixed oxides	2	0.5	0.2	0.2	0.15	0.1

ing was successfully improved by the use of fine TiO_2 particles [17–20]. The decomposition temperature of titanium sulfate is known to be 150 °C in the static condition, and is considerably lower than that of aluminum sulfate (770 °C) and cerium sulfate (900 °C) [21]. Although this decomposition temperature changes including reducing gases such as H_2, titanium sulfate that forms under exhaust gases including SO_X is assumed to be decomposed easily and release SO_X more readily compared with other oxides.

In conventional NSR catalysts, some alkali materials such as Ba and K compounds are supported on porous oxide supports such as Al_2O_3. The co-existence of both Ba and K is effective for expanding the active temperature range. The NO_X storage amount for the K containing NSR catalyst is higher than that of the Ba containing catalyst at high temperatures (over 450 °C and lower at low temperatures (under 450 °C). For this reason, both Ba and K are used [22]. While the utilization of Ba compounds for the NSR catalyst is very important for NO_X storage performance, it also inhibits sulfur deterioration. Ba sulfate is more stable than other alkali sulfates [16], and thus more sulfur residue exists after desorption treatment on the Ba compounds in an NSR catalyst compared to the K compounds. Accordingly, desulfation of Ba containing NSR catalysts is the most important subject to address in order to prepare highly durable NSR catalyst systems.

Based on the above information, we felt that the most effective way to realize improvement of sulfur desorption from NSR catalysts would be to make highly homogeneous fine particles of Ba and Ti compounds on a high surface area support such as Al_2O_3. One of the most simple and effective methods for achieving this aim is to disperse a composite aqueous complex solution including both Ba and Ti on the high surface area support. Citrate complexation is an efficient precursor method for producing fine and homogenous Ba–Ti composite oxides such as perovskite type $BaTiO_3$ [23–25]. In this method, however, the complex in solution tends to polymerize and produce a precipitate, which makes it difficult to use for impregnation on support oxides. However, we found that the addition of H_2O_2 is effective for keeping the solution stable [26]. In this study, we prepared NSR catalysts using a Ba–Ti composite oxide dispersed on the support surface and examined their structures and catalytic performance.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of Ba–Ti composite solution

The preparation method is described as follows. Citric acid was first dissolved in water at 75 °C followed by addition of Ti(i-PrO)$_4$ (Wako Co.) with continuous stirring. After stirring at 75 °C for 5 h, the solution transformed to a light yellowish transparent state without any precipitates. The solution was then cooled at room temperature and 30% aqueous H_2O_2 solution (Wako Co.) was added, resulting in a change of color from light yellow to red. Finally, aqueous $Ba(CH_3COO)_2$ (Wako Co.) was added to the transparent red solution to obtain the Ba–Ti composite solution as the precursor of the Ba–Ti composite adsorbent. We found that addition of H_2O_2 inhibited precipitation, making the Ba–Ti precursor solution more stable than when no additives were used. The prepared composite solution was suitable for impregnation on various oxide supports.

2.1.2. Catalyst preparation

Four catalyst formulations, BaTi-A, BaTi-B, Ba-A and Ba-B, as summarized in Table 1, were prepared in this study. Cordierite substrates (cylindrical, $\varphi = 30$ mm, $L = 50$ mm, 400 cells per square inch) were first coated with two types of metal oxides: (1) 7 g γ-Al_2O_3 (170 m^2/g) for characterization and (2) 9.45 g mixed oxides including γ-Al_2O_3, ZrO_2 and TiO_2 for estimation of catalytic activity. The wash coat was deposited by first immersing the substrate in an aqueous slurry of the above oxides. The excess slurry was gently removed by blowing air through the monolith channels. The samples were then dried and subsequently calcined. The coating procedure was repeated until the desired amount of alumina was deposited and the samples were then calcined for 1 h at 500 °C in air. Catalysts were prepared by impregnating $Pt(NH_3)_2(NO_2)_2$ and $Rh(NO_3)_3$ (Tanaka Precious Metals) followed by drying at 110 °C for 12 h and then calcining at 300 °C for 3 h in air. The amount of Pt and Rh loading was 2 and 0.5 g/L, respectively. The monolith obtained was then added to an aqueous solution containing Ba to form the storage material. The BaTi-A and BaTi-B catalysts were prepared using the Ba–Ti composite solution prepared above. The Ba-A and Ba-B catalysts were prepared using $(CH_3COO)_2Ba$. Finally, an aqueous solution containing CH_3COOK and CH_3COOLi (Wako Pure Chemical Industries) was impregnated on the monolithic samples containing Pt and Rh, such as BaTi-B and Ba-B. The loading amounts of Ba, K and Li were 0.2, 0.15 and 0.1 mol/L, respectively. After the catalysts were dried at 110 °C for 12 h, they were calcined at 300 °C for 3 h in air.

2.2. Characterization of the Ba–Ti composite precursor solution

The structure of the Ba–Ti composite in solution was analyzed by chemical composition analysis and FT-Raman and UV–vis spectroscopy. Chemical composition analysis was performed on the solid obtained by accumulating the red colored fraction separated by silica gel column chromatography using water as a solvent. The content of Ba and Ti were analyzed by ICP (SSI Nano-TEC SPS4000) and the content of C was analyzed by the combustion infrared absorption method (Horiba Co. EMIA810). The chemical structure of the Ba–Ti composite in solution was proposed by performing an optimized geometry calculation in mechanics using CAChe and SCiGRESS software (FUJITSU Limited) with augmented MM2 parameters based on the results of the above analyses.

2.3. Characterization of the catalysts

XRD patterns were recorded using an X-ray diffractometer (Cu Ka radiation $l = 1.5418$ Å, 40 kV, 30 mA) (Rigaku, RINT-1500 V). Samples of catalyst powders were pressed into wafers and affixed to standard sized microscope slides. The particle size of Pt was calculated using Scherrer's formula.

The ratio of Ti to Ba in the BaTi catalyst powder was analyzed using an energy-dispersive X-ray (EDX) analyzer equipped with a field-emission transmission electron microscope (Hitachi, HF-