Applied Catalysis B: Environmental 84 (2008) 268–276

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Regenerable ceria-based SO_x traps for sulfur removal in lean exhausts

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ARTICLE INFO

Article history:
Received 18 December 2007
Received in revised form 30 March 2008
Accepted 5 April 2008
Available online 11 April 2008

Keywords:
FTIR spectroscopy
Storage mechanism
CeO_2
Pt
Sulfur oxide

ABSTRACT

Bare and Pt-containing CeO_2, Al_2O_3:MgO mixed oxide and Al_2O_3 have been investigated as potential regenerable sulfur oxides (SO_x) traps. The samples were evaluated by lean SO_x adsorption and temperature programmed desorption using synthetic gas compositions. In addition, combined DRIFT spectroscopy and mass spectrometry were employed to obtain mechanistic information on the adsorption of SO_x. The results suggest Pt/CeO_2 as promising SO_x trap material owing to a high storage capacity at 250 °C in combination with efficient release above 600 °C. The presence of Pt is generally found to enhance the lean SO_x storage capacity at 250 °C for CeO_2-based samples. Lean SO_2 adsorption on CeO_2 is found to proceed via the formation of surface and bulk sulfates, where the latter is formed more rapidly for the Pt-containing CeO_2 sample. Ceria samples pre-exposed to high amounts of SO_2 at 250 and 400 °C show lower SO_x storage capacity and higher SO_x release as compared to fresh samples. This indicates that under the conditions used in this study, a part of the storage sites on CeO_2 are non-regenerable.

1. Introduction

One strategy to reduce CO_2 emissions within the transportation sector is to increase the fuel efficiency by the use of lean-burn or diesel engines [1]. The lean character of the exhausts from these engines requires other aftertreatment concepts than standard three-way technology. One such concept is NO_x storage catalysis which has shown promising characteristics for NO_x reduction under net-lean conditions [2]. This concept is based on temporary storage of NO_x on basic storage sites, usually provided by metal oxides like barium oxide (BaO), during lean periods and release with subsequent reduction of NO_x over noble metals during short periods of rich or stoichiometric conditions. However, one issue regarding this type of catalyst is the sensitivity of the storage material to sulfur, i.e., high affinity towards storage of sulfur oxides (SO_x) under lean conditions and negligible release of sulfur compounds under the NO_x regeneration phase. In course of time, a progressing sulfur poisoning will reduce the NO_x storage capacity and the number of available NO_x storage sites will eventually become critically low, which leads to insufficient NO_x storage and reduction [2–5]. To regenerate the NO_x storage capacity at this stage, thermal decomposition under net reducing conditions by a drastic increase of temperature is essentially the only solution. However, the temperature required for this procedure is too high to guarantee the stability of the catalyst towards thermal deactivation.

Sulfur containing species in the exhausts originate from fuel and lubricants. Even though the content of sulfur in the fuel has been significantly reduced over the years, the presence of sulfur will always lead to reduced NO_x storage capacity. Thus, within the present technology, strategies to handle sulfur in the exhaust are necessary. This can be achieved by increasing the sulfur tolerance of the aftertreatment system or preventing SO_x from reaching the NO_x storage catalyst by using upstream SO_x traps. The sulfur tolerance of the catalyst can be increased by enhancing the release of sulfur species during regeneration and/or by decreasing the sulfur affinity of the storage material. The sulfur release during regeneration can, for example, be facilitated by using thinner washcoat layers [6] or by adding TiO_2 to the Al_2O_3-support of the NO_x storage catalyst [1]. Moreover, the amount of sulfur adsorbed can be decreased by replacing the NO_x storing component with a material with lower affinity towards sulfur compounds [7,8]. A few different SO_x trap strategies have been suggested and materials such as BaO supported on Al_2O_3 [9], Ba/Cu–benzene tricarboxylate [10], $K_xMn_8O_{16}$ [11] and MnO [12] have been proposed as SO_x adsorbents.

In the present work, a series of different materials is evaluated as regenerable SO_x traps. Such traps should, in different temperature intervals, store and release SO_x under lean conditions. During regeneration of the SO_x trap, the exhausts will be by-passed

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doi:10.1016/j.apcatb.2008.04.003

the NO_x storage catalyst to minimize the sulfur exposure. This strategy should be chosen as sulfur species previously have been reported to adsorb on the catalyst under both lean and rich conditions blocking storage and noble metal sites [13]. To our knowledge, this regeneration technique has not previously been suggested in the literature. The desired properties of the SO_x adsorbent are to store SO_x under normal lean exhaust conditions in the temperature interval 200–500 °C and release the stored sulfur species under lean conditions at temperatures slightly above 500 °C. In this way, the fuel consumption required to produce the heat for regeneration is minimized. To avoid permanent sulfur poisoning, we intuitively choose to compare different metal oxides that are sufficiently basic to store SO_x, e.g. CeO_2, Al_2O_3:MgO mixed oxide and Al_2O_3, but less basic than BaO. Ceria is an interesting oxide for many aftertreatment applications. For example, ceria is used as an oxygen storage component in the three-way catalyst and as SO_x traps for stationary applications [14]. It is known that sulfates may form on ceria upon exposure to SO_2 even in the absence of oxygen [15], a property that probably is caused by the high oxygen mobility within the material. Adsorbents based on Al_2O_3:MgO mixed oxides from hydrotalcite precursors have also been suggested as SO_x traps for stationary applications [16]. By using hydrotalcite precursors for the mixed oxide, it is possible to control the basicity of the storage material by varying the Al_2O_3:MgO ratio. Alumina, which is an amphotheric oxide, is the least basic oxide in the present study and is included primarily as reference material. Boehmite is used as binder for the monolith samples which means that all samples contain some Al_2O_3. To investigate the suitability of these metal oxides as SO_x traps, we have employed both kinetic studies in a flow-reactor and mechanistic studies by combined qualitative diffuse reflectance infrared fourier transformed spectroscopy (DRIFTS) and mass spectrometry. The influence of noble metal on the SO_x storage and release properties of the SO_x traps is investigated as well as the stability of the SO_x adsorbent.

2. Experimental considerations

2.1. Sample preparation and characterisation

The metal oxides used as SO_x adsorbents were; CeO_2 (99.5 H.S.A. 514, Rhône-Poulenc), Al_2O_3:MgO (30:70 wt.%) mixed oxide prepared from a hydrotalcite precursor (Condea) and Al_2O_3 (Puralox SBa-200, Sasol). All samples were pre-treated in air at 750 °C for 2 h. The Pt-containing powder samples were prepared by wet impregnation of Al_2O_3 and CeO_2 using $Pt(NO_3)_2$ (Hereaus) as precursor. Due to different point of zero charge for the oxides, the impregnation was performed at pH 2 and 3 for the Al_2O_3 and CeO_2 sample, respectively. After impregnation, the slurries were instantly frozen with liquid nitrogen and freeze-dried. The resulting powder samples were finally calcined in air at 600 °C for 1 h (heating rate of 4.8 °C/min from 25 to 600 °C). Surface area measurements of the powder samples were performed by N_2-physisorption at 77 K using a Micromeritrics Tristar instrument. For a few selected samples, the specific surface areas, calculated using the BET-method [17], are summarised in Table 1.

Table 1
Specific surface area of Al_2O_3 and CeO_2-based powder samples

Sample	Specific surface area (m^2/g)	Comment
CeO_2	254	Fresh
CeO_2	82	Air, 750 °C, 2 h
5 wt.% Pt/CeO_2	78	CeO_2 treated in air, 750 °C, 2 h and impregnated with Pt
Al_2O_3	203	Fresh
Al_2O_3	187	Air, 750 °C, 2.5 h
5 wt.% Pt/Al_2O_3	174	Al_2O_3 treated in air, 750 °C, 2.5 h and impregnated with Pt

Monoliths samples (Ø = 20 mm and length = 20 mm) were cut from a commercial honeycomb cordierite structure with 400 cpsi. The monoliths were coated with the SO_x adsorbent material following the procedure described in Ref. [18]. As a binder for the adsorbent material, Boehmite (Disperal SOL P2, Condea) was used in all samples (20 wt.% of the dry material in the slurry). After coating, all monolith samples were calcined in air at 650 °C for 3 h. The Pt-containing samples were prepared by impregnation of the coated monoliths using $Pt(NO_3)_2$ as platinum precursor for the Al_2O_3 and CeO_2 samples and $Pt(NH_3)_2(NO_2)_2$ (Johnson Matthey) for the Al_2O_3:MgO sample. The impregnation was performed at pH 2, 3 and 8 for the Al_2O_3, CeO_2 and Al_2O_3:MgO sample, respectively. After impregnation, the monolith samples were dried in air at 80 °C for 12 h. The temperature was thereafter gently increased by 4.3 °C/min to 600 °C and the samples were finally calcined in air at this temperature for 1 h.

2.2. Isothermal SO_2 adsorption followed by temperature programmed desorption

The flow-reactor experiments with monolith samples were performed using a quartz tube reactor equipped with a gas mixer unit (Environmentics 2000) for control of the inlet gas composition, and a surrounding metal coil for resistive heating of the reactor tube. A thermocouple (type K, Pentronic) placed 10 mm upstream of the monolith was used together with a Eurotherm regulator to control the inlet gas temperature. A second thermocouple was positioned inside the monolith, about 2 mm from the end of the sample, to measure the sample temperature. To facilitate the analysis of the total SO_x outlet concentration, the experimental method previously reported by McLaughlin et al. [19] was used. Following this method, the outlet gas flow was first passed over an oxidation catalyst before introduced to the SO_2 analyser (non-dispersive IR, Maihak UNOR 610). For further information about the experimental method see Appendix A.

For all experiments, the total flow was 3500 ml/min, which corresponds to GHSV = 33 400 h^{-1}, and Ar was used as balance. Prior to each experiment, the samples were treated in 7% O_2 for 10 min at 500 °C. The temperature was thereafter decreased and lean SO_x adsorption was performed (100 ppm SO_2 and 7% O_2 in Ar) at 250 or 400 °C for 1 h. The high SO_2 concentration in these experiments was used to assure measurement accuracy rather than mimicking real lean exhaust conditions. After the SO_2 exposure, temperature programmed desorption (lean SO_x-TPD) was performed by increasing the temperature by 10 °C/min to 700 °C in 7% O_2. The temperature was kept constant at 700 °C for 20 min before cooling in Ar.

2.3. DRIFT spectroscopy measurements

FTIR measurements were performed with powder samples in diffuse reflectance mode using a Bio-Rad FTS6000 spectrometer equipped with a Harrick Praying Mantis DRIFTS cell and a MCT detector. The resolution was 1 cm^{-1} and the number of scans per spectrum was set to 20. All experiments were performed with fresh samples using a total gas flow of 100 ml/min and Ar as balance. Prior to each experiment, the sample was treated in 20% O_2 at 500 °C for 10 min followed by cooling in 7% O_2 to the temperature to be studied, i.e., 250 or 400 °C. Because the windows in the reactor dome absorb IR radiation in the same wavenumber