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Nanofibrous Pt-Ba Lean NO_x trap catalyst with improved sulfur resistance and thermal durability

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ABSTRACT

Different LNT catalysts, prepared using γ-Al_2O_3, nanofibrous Al_2O_3 and TiO_2-modified nanofibrous Al_2O_3 supports, with Ba as the storage component and Pt as the oxidation component, have been prepared and NO_x uptake behaviour was examined between 523 and 823 K. The activity study was accompanied by TEM, XRD and H_2 chemisorption characterization. The Pt-Ba nanofibrous Al_2O_3-supported catalyst resulted in the best performance, likely due to better Pt dispersion. This included improved storage capacity as well as more efficient reduction during the regeneration phase. This catalyst also had better performance after identical S exposures and after desulfurization. Ti modification had significant impact on sample thermal durability and general catalyst performance. Results using the Al_2O_3-TiO_2 nanofibrous catalyst reveal that this catalyst has improved thermal degradation resistance properties relative to standard γ-Al_2O_3. Ti incorporation in the nanofibrous Al structure was found to also promote sulfur desorption. Above 1073 K, where complex $Ba_xTi_yO_z$, and/or $Ba_xAl_yTi_zO_n$ structures form, the Ba-Ti interaction was found to have a destabilizing effect on stored nitrites/nitrates.

1. Introduction

NO_x storage/reduction catalysts (NSR or lean NO_x trap – LNT) are being investigated and used to meet current and forthcoming Euro and EPA emission standards for lean-burn engines [1–6]. Since the NSR principle was first reported by Toyota [3,7,8], a large number of studies investigating various NSR catalysts have been published [6,9–12]. One of the most commonly studied NSR catalyst compositions is the Pt-Ba system supported on γ-Al_2O_3, as first discussed by Toyota [12–14]. Many studies have been performed with such a standard formulation; Pt:AE:$Al_2O_3 \approx 1{:}20{:}100$ (AE – alkali or alkaline earth element); however, there is still a need to improve the catalyst's thermal durability and sulfur tolerance, which are primary drawbacks of the NSR catalysts, hindering more widespread commercial application [15].

NSR catalysts normally operate in the 473–673 K temperature range. Above this temperature, the NO_x storage capacity is limited by thermal stability of the trapped nitrites/nitrates [12,16,17]. However, during normal engine operation some event may provoke a sudden, uncontrolled increase in temperature along the catalyst, i.e. combustion of soot accumulated in a diesel particulate filter (DPF) placed upstream with respect to the NSR catalyst, increasing the exhaust gas temperature to induce the onset of soot oxidation if the DPF is downstream, or simply high torque driving conditions. However, due to S accumulation on an NSR catalyst, intermittent high temperature exposure is also required to regenerate the catalyst, i.e. remove the S species for regenerated efficiency. In order to induce S release, the working temperature of the catalyst needs to exceed 873 K for most formulations. Previous data indicate that the high temperatures required for desulfurization result in thermal degradation of NO_x traps [18,19]. Thermal degradation includes precious metal sintering [20,21], trapping material sintering [13], as well as reaction between the trapping material and alumina support [13,18]. Despite the continuous reduction in sulfur concentration in refined fuels and modifications in NSR catalyst formulations, which often target improved sulfur tolerance, sulfur poisoning remains a key issue in NSR application [2,22–25]. Taking into account the stability of sulfates on the NSR trapping component, new NSR formulations need to be developed that are more S resistant or release S at lower temperatures. As an added complication, although not required, when S is released from the catalyst under rich conditions, H_2S formation would be undesired due to the associated odor at rather low concentrations. Furthermore, new formulations that preserve trapping efficiencies at high temperatures would expand their applicability as well as maintain NO_x removal performance during desulfurization events [26].

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There are a few studies directed at high-temperature NSR catalysts, and the possible reactions that may occur between the NO_x storage compound and support at high temperatures, e.g., $BaO + Al_2O_3 \rightarrow BaAl_2O_4$ [26–29]. Enhanced NO_x storage capacity at high temperature has been reported for a Pt-K/$MgAl_2O_4$ catalyst [30]. A novel Pt/$K_2Ti_2O_5$ catalyst has also been reported as a high-temperature NSR catalyst [26]. It was found that the adsorbed NO_x on Pt/$K_2Ti_2O_5$ was much more stable than that trapped over Pt-K/TiO_2. Mechanistic studies revealed that KNO_3-like compounds were formed after NO_x adsorption, and that the NO_x storage and reduction process on $K_2Ti_2O_5$ was accompanied by a structural transformation between $K_2Ti_2O_5$ and $K_2Ti_6O_{13}$. Although K as the trapping component can result in considerable NO_x storage capacity, and TiO_2 is accepted as relatively resistant to sulfur poisoning [12,31], previous studies report better performance using a Ba-based rather than the K-based NSR catalyst [12,31].

In this study, the activity of a novel nanofibrous Pt-Ba/Al_2O_3 catalyst for NO_x removal at high temperature is reported. The aim of the present work is the development of a thermally stable NSR catalyst supported on γ-Al_2O_3 modified with additional components, which may also increase the sulfur tolerance of the material.

2. Materials and methods

2.1. Catalyst preparation and characterization

Synthesized nanostructured γ-Al_2O_3 (denoted Al_{NF}) and nanostuctured γ-Al_2O_3-TiO_x (denoted Al-Ti) were used as supports. The preparation procedure has been described in detail elsewhere [32,33]. An aqueous $NaAlO_2$ solution was added dropwise to a 5 N acetic acid solution. The obtained precipitate was decanted, filtered and washed with water. The resulting powder was dried overnight at 373 K and subsequently mixed with a non-ionic surfactant, Tergitol (15-TS-5, Sigma), using a Tergitol/Al ratio of 0.5. The mixture was kept in an autoclave for 72 h at 373 K and later calcined at 773 K for 20 h. The same preparation procedure was applied to obtain nanostructured Al-Ti, but with the addition of $TiCl_3$ as a precursor (12% $TiCl_3$ in hydrochloric acid, Sigma). Both, Al- and Ti-precursors were added dropwise simultaneously to the acetic acid solution. The Tergitol/(Al + Ti) ratio was 0.5. The autoclaved mixture was calcined at 623 K for 2 h and the temperature was then increased at 5 K min^{-1} to 773 K and maintained at 773 K for 18 h. In case of sample treated at 1073 K or 1273 K, the additional calcination was performed with a previous calcined catalyst sample for 1 h.

The Pt and Ba components were added via the incipient wetness impregnation method using diamminedinitroplatinum (II) ($Pt(NH_3)_2(NO_2)_2$, Aldrich) and barium acetate ($Ba(CH_3COO)_2$, MERCK) as precursors. The catalyst formulations are summarized in Table 1. The metal loading is expressed as formal surface atomic density (atoms per nanometer square, at nm^{-2}) for comparison in terms of surface coverage. First Pt (0.4 at nm^{-2}; 0.4Pt/Al_{NF}, 0.4Pt/Al-Ti) catalysts were prepared by impregnation of the Al_{NF} and Al-Ti supports with an aqueous solution of Pt, drying overnight at room temperature and calcination for 3 h at 648 K in air. These were then impregnated with Ba (4 at nm^{-2} of Ba) to obtain the final formulations (0.4Pt-4Ba/Al_{NF}, 0.4Pt-4Ba/Al-Ti). The final calcination was performed for 5 h at 798 K in air.

The Pt-Ba/Al-Ti_{MF} physical mixture was prepared by mixing the prepared 0.4Pt-4Ba/Al_{NF} catalyst with rutile TiO_2 powder (Sigma–Aldrich, 99.7% purity, used as received) in a 9:1 ratio. The standard Pt-Ba/Al_2O_3 catalyst, denoted as Pt-Ba_{ST}, has been described in detail elsewhere along with its preparation procedure [12].

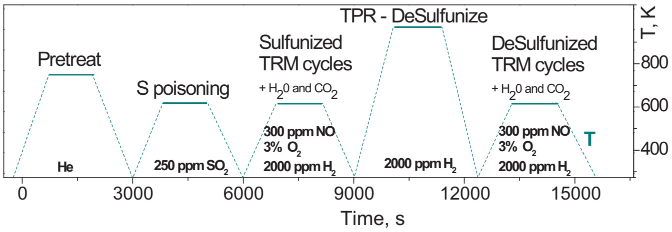

Fig. 1. S poisoning experiment scheme.

The TEM images of powder samples deposited onto a copper mesh grid coated with a carbon film were taken with a Philips CM200 (200 kV) microscope equipped with an EDX (energy dispersive X-ray) detector. The XRD patterns of the powder samples were recorded with a Siemens D-501 goniometer equipped with a Johansson type monochromator with a Ge(111) crystal. During measurement, Cu Kα1 radiation and a fixed power source (45 kV and 35 mA) were used.

N_2 adsorption–desorption isotherms for the Al_{NF} and Al-Ti supports were obtained at 77 K using a Beckman Coulter SA3100 Surface Area Analyzer. Before the analysis, the samples were outgassed in vacuum (1×10^{-3} Pa) for 5 h at 453 K. The specific surface area was obtained by the BET isotherm equation and the pore volume by the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm.

H_2 chemisorption experiments were carried out in the pulse mode in a Hiden CATLAB microreactor module connected to a Hiden QIC-20 gas analysis system. Prior to H_2 chemisorption, each sample was heated from room temperature (RT) to 723 K in the presence of H_2 (5% H_2 in He). The sample was then reduced in this mixture at 723 K for 30 min, and then purged in a He flow. Next, the temperature was decreased to RT and the chemisorption measurements were performed at ca. 310 K. For each experiment, 27 pulses of H_2-containing gas were injected into the reactor (100 μl of 5% H_2 in He each pulse). For calculation purposes, a stoichiometry relation of two platinum sites per one H_2 molecule was used [34].

2.2. Transient response method (TRM)

TRM runs were performed in a quartz tube reactor connected to a Pfeiifer Prisma^{TM} QMS 200 mass spectrometer or in a CATLAB microreactor module connected to a Hiden QIC-20 gas analysis system. The method was used to study the NO_x storage–reduction process over the catalysts between 473 and 773 K with a total gas flow of 100 ml min^{-1} using 60 or 40 mg of catalyst (GHSV = 1.5×10^5 (or 1×10^5) h^{-1}, at 1 atm and 293 K). A rectangular pulse of NO (1000 ppm or 300 ppm) + O_2 (3%) in He flow followed by a H_2 (2000 ppm) in He flow were fed during the oxidation and reduction steps, respectively. For experiments with H_2O and CO_2, 2.5% H_2O and 5% CO_2 were continuously fed to the microreactor. For all experiments, the N-balance closed with a deviation between 4% and 5%.

2.3. Sulfur poisoning study

The sulfur poisoning study was performed in the CATLAB microreactor system. The general experiment scheme is presented in Fig. 1. First, catalyst sulfation was carried out at 623 K for 30 min with a gas mixture containing 250 ppm SO_2, 5% O_2 and a He balance. Then the catalyst was cooled to RT in He and afterwards NO_x storage–reduction measurements and analysis of sulfur-poisoned catalysts were performed using a conventional TRM protocol. The content of H_2O and CO_2 in the gas stream during TRM cycles was 2.5 and 5%, respectively. Next, temperature-programmed reduction