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Influence of Pt location on $BaCO_3$ or Al_2O_3 during NO_x storage reduction

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ABSTRACT

Catalysts for NO_x storage–reduction (NSR) were made selectively with Pt on either the Al- or the Ba-components without altering significantly the Al_2O_3 or $BaCO_3$ crystal sizes, Al/Ba weight ratio, specific surface area, porosity, and Pt dispersion using a two-nozzle flame spray pyrolysis (FSP) unit. The NO_x storage performance at 300 °C was best for Pt located near Al_2O_3 as it facilitates the oxidation of NO to NO_2 during the fuel lean period but the reduction rate during the subsequent short fuel rich period was much slower resulting in incomplete regeneration. This contributed to a gradual decrease of the NO_x conversion at increasing cycling. In contrast, Pt on $BaCO_3$ resulted in an initially lower NO_x storage rate but during ten storage–reduction cycles a stable NO_x conversion of about 50% was reached. When using NO_2 instead of NO or higher NO_x oxidation-reduction temperatures (e.g. 350 °C) the Pt location did not affect the NSR performance of the Pt/Ba/Al_2O_3 catalysts.

1. Introduction

Anthropogenic NO_x is formed typically during fuel combustion contributing to smog formation and acid rain [1,2]. New catalysts are needed to meet stricter emission limits, especially to remove NO_x under oxygen rich conditions of lean fuel and direct injection engines. Among these catalysts, the ones for NO_x storage–reduction (NSR) can trap exhaust NO_x on an alkali- or alkaline earth metal (typically Ba or K) in the form of metal-nitrates [3] without requiring an additional reducing agent, as NH_3 or urea in selective catalytic reduction (SCR). During a subsequent fuel rich period the stored metal-nitrates are reduced to harmless N_2 over a noble metal (typically Pt or Pd) [4]. The storage and the noble metal are supported on a thermally stable carrier material, usually Al_2O_3 or CeO_2 [5]. Pt-free BaO/Al_2O_3 mainly stored NO_2, whereby releasing one NO for three NO_2 stored [6]. In the presence of Pt, NO is oxidized to NO_2 resulting in higher storage capacity and faster NO_x uptake [7], involving NO_2 spillover from the Pt to the Ba sites as proposed from simulations [8] and experimental investigations [9]. Already in 1995 the proximity of Pt to the storage component of NSR catalysts was proposed to strongly influence the performance [10] and was recently investigated by comparing ternary Pt/Ba/Al_2O_3 catalysts with binary mixtures of Pt/Al_2O_3 and Ba/Al_2O_3 [11]. For Pt in close contact with Ba a 5-times higher isotopic exchange rate between ^{15}NO was measured, indicative of NO_x forward and reverse spillover from Pt to Ba [11].

In contrast to storage, the reduction (regeneration) is less understood mainly due to parallel occurring phenomena such as the desorption of gaseous NO_x at high temperature [12] and the reaction of the stored nitrate with CO_2 [13,14]. Nova et al. [15] showed that the reduction of nitrates occurs by Pt-catalyzed surface reactions involving (reverse) spillover processes and concluded that a close proximity of Ba and Pt would be necessary to increase the Ba-nitrate decomposition. Physical (mechanical) mixtures of Pt/Al_2O_3 and $BaCO_3$, Al_2O_3 and Pt/$BaCO_3$ have been used to investigate the influence of the NO_x spillover distance [11,15,16]. The multiple impregnation steps employed in these studies, however, made difficult to maintain constant material characteristics for different catalyst compositions.

Here, we investigated the importance of Pt being located close to Ba or to Al on NSR catalyst performance. The catalysts were prepared by a two-nozzle flame spray pyrolysis unit as already applied for NSR catalysts [17] with high storage capacity [18]. By this procedure, Pt can be deposited preferentially on Al_2O_3 and/or $BaCO_3$ without altering their structural properties.

2. Experimental

2.1. Apparatus and preparation

With an internozzle distance, d, of 6 cm and an angle, φ, of 160° between the two nozzles (Fig. 1), the mixing distance (m) was calculated to be 34 cm above the nozzles ($m = d\tan(\varphi/2)$) assuring complete particle formation (Pt, $BaCO_3$ and Al_2O_3) at this point [19]. The individual spray nozzles were described previously

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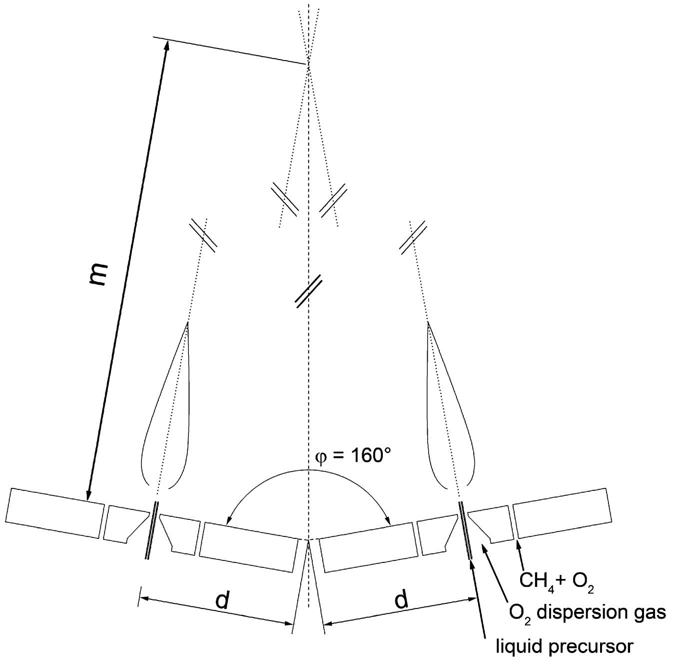

Fig. 1. Schematic of the 2-nozzle FSP unit where Al- and Ba-precursor solutions are sprayed separately. The Pt precursor is added to the Al- or Ba-precursor solutions resulting in preferential deposition of Pt-clusters on each component of the product catalyst particles. The mixing distance, *m*, is the distance from the burner to the crossing point of the two flame axes.

in detail [20]. The Al-precursor solution consisted of aluminum-tri-*sec*-butoxide (Fluka, 95%) dissolved in a 2:1 vol% mixture of diethylene glycol monobutyl ether (Fluka, 98%) and acetic anhydride (Riedel-de Haën, 99%). The aluminum concentration was kept constant at 0.5 mol/L. The Ba-precursor, barium 2-ethylhexanoate (Aldrich, 98%) was dissolved in 1:1 vol% toluene (Riedel-de Haën, 99%) and 2-ethylhexanoic acid (Riedel-de Haën, 95%) for a Ba concentration of 0.06 mol/L. The Pt-precursor platinum(II) acetylacetonate (STREM, 98%) was added either to the Ba or Al precursor solutions, while for an equal distribution of Pt on Al_2O_3 and $BaCO_3$ half of the platinum(II) acetylacetonate was added to each precursor solution.

For the nomenclature of all $Pt/Ba/Al_2O_3$ catalysts, the Pt is written next to the element with which it was fed to the FSP unit and precipitated on: therefore a catalyst with Pt deposited on Al_2O_3 is referred as PtAl–Ba, with Pt on $BaCO_3$ as Al–BaPt, and with Pt both on Al_2O_3 and $BaCO_3$ as PtAl–BaPt. The Ba precursor was fed at 3 mL/min through the first nozzle and the Al-precursor was fed at 5 mL/min through the second nozzle. The concentration of the metals in the precursors was chosen to result in a nominal $Pt:Ba:Al_2O_3$ weight ratio of 1:20:100. Each solution was dispersed with 5 L/min oxygen (PanGas, 99.95%) and ignited by a supporting premixed methane/oxygen flame with 3 L/min total gas flow rate and a CH_4/O_2 molar ratio of 0.5. The product powders were collected on a glass fiber filter (Whatman GF6, 25.7 cm in diameter) with the aid of a vacuum pump (Busch, Seco SV 1040C).

2.2. Materials characterization

The specific surface area (SSA) of the as-prepared powders was determined by a 5-point nitrogen adsorption isotherm at 77 K using the BET method, and a full adsorption isotherm of the as-prepared powder was measured (Micrometrics Tristar). X-ray diffraction (XRD) patterns were recorded (Bruker D8 Advance, 40 kV, 40 mA, $\lambda = 1.54$ nm) at a scan speed of 0.5°/min at $10° < 2\theta < 70°$. The effective chemical composition of pelleted powder was determined by laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [21]. The Pt dispersion was measured by CO-pulse chemisorption at 40 °C on a Micromeritics Autochem II 2920. Samples were pretreated by heating in 10% O_2/He up to 500 °C ($10\,°C\,min^{-1}$) and maintained for 30 min at 500 °C, then cooled in He to 350 °C where they were reduced in 5% H_2/Ar for 30 min. Subsequently, the samples were kept for another 30 min at 350 °C under flowing He before cooling to 40 °C. Pulses of 0.35 mL 10% CO/He were injected in 10% H_2/Ar and the CO concentration in the off gas was recorded using a mass spectrometer (Pfeiffer Vacuum, ThermoStar) [18].

For scanning transmission electron microscopy (STEM), the catalyst material was dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid (Okenshoji Co. Ltd.). The STEM images were obtained with a high-angle annular dark-field (HAADF) detector attached to a Tecnai 30F microscope (FEI; field emission cathode, operated at 300 kV), showing the metal particles with bright contrast (Z contrast). For qualitative analysis, the electron beam was set to selected areas in the STEM images and the signal was measured by energy dispersive X-ray spectroscopy (EDXS; detector: EDAX).

The NO_x storage–reduction (NSR) measurements were performed with 20 mg catalyst in a fixed-bed reactor (with an inner diameter of 4 mm). The reactor was connected to a valve allowing rapid switching between oxidizing and reducing conditions [22]. The NO and NO_2 concentrations in the effluent gas were monitored using a chemiluminescence detector (ECO Physics, CLD 822S). The NO_x conversion for a full cycle (one storage and one reduction) was derived from the corresponding NO_x outlet concentration according to:

$$NO_x \text{ conversion} = \frac{NO_{x,\text{in}} - NO_{x,\text{out}}}{NO_{x,\text{in}}} \times 100\%. \tag{1}$$

The presence of N_2O was neglected here as at 300–350 °C its formation is very low [23]. The dynamic NSR behavior of as-prepared powders was measured at 300 and 350 °C by switching 10 times between oxidizing (3 min in 667 ppm NO and 3.3% O_2 in He) and reducing atmospheres (1 min in 667 ppm NO, 1333 ppm C_3H_6 in He). The total gas flow rate for all experiments was 60 mL/min corresponding to a space velocity of 72,000 h^{-1}. Complete storage and reduction tests were performed at 300 °C. The catalysts were heated to this temperature and reduced for 30 min (C_3H_6 2000 ppm, He). Then storage was recorded for 180 min with 667 ppm inlet NO or NO_2 (in He containing 3.3 vol% O_2).

3. Results and discussion

3.1. Structural properties

Preferential Pt deposition on alumina and the Ba component was confirmed by STEM combined with EDX analysis of the indicated area as shown in Fig. 2 for PtAl–Ba (A) and Al–BaPt (B) catalysts. Clusters of Pt appear as bright, spherical dots. The gray particles are assigned to Al_2O_3 as they are much smaller than the brighter, non-spherically shaped $BaCO_3$ particles [17]. Fig. 2A shows Pt clusters on Al_2O_3 corroborated by the corresponding EDX analysis detecting predominately Al and Pt and hardly any Ba (C and Cu peaks resulted form the TEM-grid). Similarly Fig. 2B illustrates the proximity of Pt on $BaCO_3$-particles with a strong Ba signal in the EDX spectra, also Al-peaks can be detected given the high Al-concentration in these $Pt/Ba/Al_2O_3$ catalysts (1:20:100). The presence of Pt did not influence measurably the characteristics of γ-Al_2O_3 or $BaCO_3$ as has been shown for TiO_2 [19]. All catalysts had a specific surface area (SSA) of about 140 m^2/g, while pure γ-Al_2O_3 had 148 m^2/g and pure $BaCO_3$ had 20 m^2/g, and