Trade-off between NO\textsubscript{x} storage capacity and sulfur tolerance on Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2}/TiO\textsubscript{2}–based DeNO\textsubscript{x} catalysts

Zafer Say\textsuperscript{a}, Oana Mihai\textsuperscript{b,c}, Merve Kurt\textsuperscript{a}, Louise Olsson\textsuperscript{b,⁎,⁎⁎}, Emrah Ozensoy\textsuperscript{a,d,⁎⁎}

\textsuperscript{a} Department of Chemistry, Bilkent University, 06800 Ankara, Turkey
\textsuperscript{b} Chemical Engineering, Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
\textsuperscript{c} Department of Petroleum Processing Engineering and Environmental Protection, Petroleum-Gas University of Ploiesti, 39 Bucuresti Blvd., 100680 Ploiesti, Romania
\textsuperscript{d} UNAM-National Nanotechnology Center, Bilkent University, 06800, Ankara, Turkey

ARTICLE INFO

Keywords:
DeNO\textsubscript{x}
NO\textsubscript{x} storage
FTIR
TPD
SO\textsubscript{x}

ABSTRACT

Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2}/TiO\textsubscript{2} (AZT) ternary mixed oxides functionalized with Pt and BaO were synthesized in powder and monolithic forms and were utilized in NO\textsubscript{x} Storage Reduction/Lean NO\textsubscript{x} Trap (NSR/LNT) catalysis as novel catalytic materials. Adsorption of NO\textsubscript{x} and SO\textsubscript{x} species and their interactions with the catalyst surfaces were systematically investigated via in-situ FTIR technique revealing different NO\textsubscript{x} coordination geometries governed by the presence and the loading of BaO in the powder catalyst formulation. While BaO-free Pt/AZT stored NO\textsubscript{x} as surface nitrates, BaO incorporation also led to the formation of bulk-like ionic nitrate species. NO\textsubscript{x} adsorption results obtained from the current Temperature Programmed Desorption (TPD) data indicated that NO\textsubscript{x} Storage Capacity (NSC) was enhanced due to BaO incorporation into the powder catalyst and NSC was found to increase in the following order: Pt/AZT < Pt/8BaO/AZT < Pt/20BaO/Al\textsubscript{2}O\textsubscript{3} < Pt/20BaO/AZT. Increase in the NSC with increasing BaO loading was found to be at the expense of the formation of bulk-like sulfates after SO\textsubscript{x} exposures. These bulk-like sulfates were observed to require higher temperatures for complete regeneration with H\textsubscript{2}(g). Catalytic activity results at 473 K and 573 K obtained via flow reactor tests with monolithic catalysts suggested that Pt/AZT and Pt/8BaO/AZT catalysts with stronger surface acidity also revealed higher resistance against sulfur poisoning and superior SO\textsubscript{x} regeneration in spite of their relatively lower NSC. Monolithic Pt/20BaO/AZT catalyst revealed superior NSC with respect to the conventional Pt/20BaO/Al\textsubscript{2}O\textsubscript{3} benchmark catalyst at 573 K after sulfur regeneration. On the other hand, this trend was reversed at high-temperatures (i.e. 673 K). Preliminary results were presented demonstrating the enhancement of the high-temperature NSC of AZT-based materials by exploiting multiple NO\textsubscript{x}-storage components where BaO functioned as the low/mid-temperature NO\textsubscript{x}-storage domain and K\textsubscript{2}O served as the high-temperature NO\textsubscript{x} storage domain. Enhancement in the high-temperature NO\textsubscript{x}-storage in the BaO-K\textsubscript{2}O multiple storage domain systems was attributed to the formation of additional thermally stable bulk-like nitrates upon K\textsubscript{2}O incorporation.

1. Introduction

Steady growth of the world population and increasing industrialization of societies cause a constant increase in energy demand. Increasing use of fossil fuels to satisfy the rising global energy demand results in elevated levels of air pollution in both developing and developed countries alike [1]. NO\textsubscript{x} emissions from mobile sources have serious destructive effects on the atmosphere, global ecosystem and particularly on the human health. Therefore, automotive industry must constantly improve novel catalytic abatement technologies to minimize exhaust emission levels by designing novel catalytic materials.

In 1990's, Toyota Motor Company introduced a novel technology for diesel engine tail pipe emission control systems operating in a cyclic mode (i.e. lean and rich), called NO\textsubscript{x} storage and reduction (NSR) or Lean NO\textsubscript{x} Trap (LNT) technology [2]. Conventional after-treatment technology for diesel engine emission systems is the Selective Catalytic Reduction (SCR) technology which selectively reduces NO\textsubscript{x} emissions with additional reducing agents such as urea/NH\textsubscript{3} and/or HC in a non-cyclic manner under continuous lean regime. The LNT can be combined in the tail pipe with diesel oxidation catalysts (DOC) and diesel particulate filters (DPF), which can eliminate HC/CO emissions and particulate matter, simultaneously [3,4]. Tail pipe systems utilizing LNT and SCR systems at the same time may reduce NO\textsubscript{x} emissions and also eradicate ammonia slip as recently demonstrated by Daimler AG [5]. In
this dual-bed catalytic architecture, LNT catalyst is placed upstream in the tail pipe before the SCR catalyst. LNT catalyst serves as the primary NOx storage/reduction material and is followed by the SCR catalyst. SCR catalyst converts the residual NOx slipping into the atmosphere during the lean phase of LNT and simultaneously utilizes the NH3 generated during the LNT rich phase as an external reducing agent in the SCR process [6,7].

SCR and NSR after treatment systems for diesel applications are known to have various drawbacks associated with coke deposition, thermal aging and sulfur poisoning [3,4,8-11]. The temperature in the tail pipe systems can reach high levels for the removal of particulate matter and sulfur regeneration. Thus, catalytic materials are typically exposed to harsh operational conditions resulting in sintering of active sites/promoters/catalytic support materials and loss of specific surface area (SSA) and functionality [12]. Furthermore, since acidic NO(g) and SO2(g) adsorbates compete for similar adsorption sites on the catalyst surface, SOx species gradually accumulate over the BaO NOx-storage components and form BaSO4 which is thermodynamically more stable than Ba(NO3)2 and BaCO3 diminishing the NSC of the LNT catalyst [13-15].

Hence, surface chemistry and the composition of the LNT catalytic materials need to be tailored at the nanometer scale in order to enhance their NSC, thermal stability and sulfur poisoning resistance. For instance, in former studies, CeO2 promotion was found to enhance NOx reduction efficiency under rich conditions while improving the SOx regeneration capability [8,16-18]. We have also demonstrated that TiO2 promotion of BaO/Al2O3 mixed oxides can lead to SOx release from a poisoned LNT catalyst at significantly lower temperatures than that of the unpromoted catalyst [9,19]. However, we have also reported that BaO can diffuse into the TiO2 domains at temperatures higher than 500 °C due to the strong interaction between TiO2 and BaO domains, forming complex BaTiO3 mixed oxides causing thermal aging and de-activation along with a loss in NSC [19-21]. Platinum group metals (PGM) such as Pt, Pd, and Rh serve as the active redox sites in LNT systems. Besides the PGM active sites, nature and the loading of the NOx storage domains and the type of the metal oxide support materials are other critical factors affecting the overall performance and stability of LNT catalysts [22-29].

Novel catalytic mixed oxide architectures can be synthesized with improved material properties by utilizing the well-known stabilizing influence of ZrO2 acting as a diffusion barrier between BaO and TiO2 domains [30-34]. Along these lines, in a recent publication, we reported that incorporation of BaO to the Pt/ZrO2/TiO2 catalyst leads to the formation of ordered BaTiO3 and ZrTiO4 phases rendering a drastic drop in the SSA of the catalytic material from 250 m2/g to 24 m2/g. On the other hand, in the Al2O3/ZrO2/TiO2 (AZT) quaternary mixed oxide system functionalized with BaO, Al2O3 was found to act as a diffusion barrier in between BaO and TiO2 domains of the Pt/BaO/AZT catalyst. This effect leads to the formation of a highly amorphous and thermally stable structure at elevated temperatures as high as 973 K [22]. AZT-based LNT catalysts such as Pt/Rh/Ba/K/AZT and titanium doped-AZT have also been investigated by others in the literature [35,36]. Zou et al. studied the influence of the mass ratio of Al2O3/ZrO2/TiO2 components on the catalytic performance of the Pt/K/AZT system and reported that a mass ratio of 1:1 revealed the best performance after sulfur poisoning [37]. A recent publication by Toyota Motor Company also investigated the nature of BaO domains on the ZrO2/TiO2 and Al2O3 oxides by means of in-situ FTIR studies [38].

In the current manuscript, we focus on the NOx/SOx absorption and desorption characteristics of AZT (ternary mixed oxide) and BaO/AZT (quaternary mixed oxide) systems functionalized with Pt redox active sites in comparison to a benchmark NSR/LNT catalyst (i.e. Pt/BaO/Al2O3) by means of in-situ Fourier Transform Infrared Spectroscopy (in-situ FTIR) and Temperature Programmed Desorption (TPD) techniques. In addition to the analysis of the interactions between the NOx and SOx species with the catalytic surfaces and their transformations under catalytic conditions at the molecular level on powder catalysts in batch mode; we also performed quantitative catalytic performance tests using monolithic catalysts under realistic operational conditions in a flow reactor, in order to determine NSC values at different operational temperatures after sulfur poisoning and subsequent regeneration. We also provide preliminary results regarding how NSC of BaO-based AZT systems can be improved by their incorporation with K2O. Therefore, in the current contribution, we report a holistic investigation of the AZT-based LNT catalysts consolidating surface spectroscopic investigations shedding light on the nature of the reactants/products (e.g. NOx) and poisons (e.g. SOx) on the catalyst surface as a function of catalyst composition and operational conditions (e.g. temperature) and combine these results with realistic catalytic activity/poisoning/regeneration measurements revealing the performance and durability of the currently designed catalytic architectures.

2. Experimental

2.1. Material synthesis

Detailed description of the synthesis procedures for the Al2O3/ZrO2/TiO2 (AZT, Al2O3/ZrO2/TiO2 = 50:35:15, by mass) catalyst and further information regarding all of the chemicals/gases used in the synthesis and in-situ characterization experiments can be found in our former reports [18,39,40]. Pt/BaO/AZT and Pt/BaO/Al catalysts were synthesized with 8 or 20 wt.% nominal BaO loadings (i.e. Pt/8BaO/AZT, Pt/20BaO/AZT, and Pt/20BaO/Al; respectively) and 1 wt.% nominal Pt loading. These particular BaO loadings were chosen in order to be comparable with the former reports in the literature on the conventional Pt/BaO/Al LNT catalyst, where 8 wt.% BaO loading corresponds to a nominal BaO surface coverage of ca. 1.0 monolayer (ML) on γ-Al2O3 resulting in the formation of predominantly 2D-BaO islands and small BaO particles, and higher BaO loadings (i.e. 20 wt.%) with a nominal surface coverage greater than 1.0 ML leads to the formation of mostly bulk-like 3D-BaO structures on γ-Al2O3 along in addition to smaller BaO particles [41]. Moreover, physically mixed hybrid catalyst was prepared by mixing 50 wt.% of each Pt/5.4 K2O/AZT and Pt/8BaO/AZT.

2.2. In-situ FTIR and TPD measurements

Transmission mode in-situ FTIR measurements were performed in a custom-designed batch-type spectroscopic reactor coupled to an FTIR spectrometer (Bruker Tensor 27) and a quadruple mass spectrometer (QMS, Stanford Research Systems, RGA 200) for TPD analysis [39]. All of the FTIR spectra were acquired at 323 K using the powder form of the catalysts.

Stepwise NOx adsorption experiment series were performed by flushing the material surfaces with 1.0 Torr of NOx(g) for 5 min and subsequent annealing to 973 K with a 12 K/min heating rate under vacuum in order to remove all of the adsorbed contaminants and water on catalyst surfaces. Then, material surfaces were gradually exposed to NOx(g) at 323 K in a stepwise fashion from low to higher pressures where each exposure step took 1 min. Finally, surface saturation was achieved via the introduction of 5.0 Torr NOx(g) over the catalyst surfaces for 10 min at 323 K followed by evacuation to a pressure lower than 10−2 Torr.

In-situ CO adsorption experiments were carried out using FTIR technique by exposing the fresh and spent catalyst surfaces to 10.0 Torr of CO(g) for 10 min at 323 K. Prior to analysis of fresh catalyst (calcined powder), material was pre-treated by exposing to 10.0 Torr of H2 at 773 K for 10 min. CO adsorption experiment was also applied to the spent catalyst in the powder form that was scraped from the spent monolith after poisoning and high temperature regeneration.

Sulfur desorption/regeneration characteristics of each material was investigated by exposing the pre-poisoned (2.0 Torr SO2 + O2 gas
mixture, SO₂:O₂ = 1:10, at 673 K for 5 min, SO₂ purity > 99%, Air Products, O₂ purity > 99.999%, Linde GmbH) catalyst surfaces to 15.0 Torr of H₂ (H₂ purity > 99.999%, Linde GmbH) at 323 K. Next, catalyst surfaces were annealed at 773 K in the presence of H₂ for 5 min. Finally, the catalysts were cooled to 323 K in the reducing gas environment and FTIR spectra were acquired.

NOₓ storage and desorption on powder catalysts were also subsequently followed by TPD analysis. In TPD runs, NO₂-saturated catalysts were heated up to 973 K with a linear heating rate of 12 K/min in vacuum. FTIR spectra of the corresponding surfaces were also recorded before and after the TPD experiments.

2.3. Catalytic reactions

NOₓ storage characteristics of the synthesized materials before and after sulfur poisoning and regeneration were studied in detail using monolithic samples in a flow reactor system. The monoliths (length = 20 mm, diameter = 21 mm, cell density of 400 cpsi) were then wash-coated with the powder catalysts of Pt/AZT, Pt/8BaO/AZT, Pt/20BaO/AZT and Pt/20BaO/Al. Details regarding the monolith preparation can be found elsewhere [40]. The washcoat consisted of 5 wt. % boehmite as a binder and 95 wt.% powder catalyst. The washcoated monoliths were finally calcined at 923 K for 2 h.

The sulfur poisoning, regeneration and the storage/reduction cycles were carried out in a horizontally mounted quartz tube flow reactor [40]. The temperature was regulated using a thermocouple placed about 10 mm in front of the monolith, and in addition the temperature was measured by another thermocouple in a center channel. The inlet gas feed, including water vapor, was regulated using several Bronkhorst mass flow controllers and a CEM system (controlled evaporation and mixing system from Bronkhorst Hi-Tech). All lines were heated and maintained at 473 K in order to prevent water condensation. The gases coming out of the reactor were analysed by a gas phase FTIR spectrometer (MKS Instruments, MultiGas 2030) with the gas cell heated to 464 K.

The calcined monoliths were first degreened at 923 K in order to stabilize the samples. During degreening, the samples were exposed to 1% H₂ for 30 min at 923 K; then the samples were flushed with Ar for 5 min at 923 K, and then using an additional gas mixture (500 ppm NO, 5% O₂, 5% CO₂, 5% H₂O), balanced with Ar at 923 K for 2 h. The stability of the samples was examined by conducting experiments at 573 K with ten successive lean/rich cycles (7 cycles with NO in the feed and 4 cycles with NO₂ in the presence of 5% CO₂, 5% H₂O and 10% O₂) (for lean step during 4 min) and 1% H₂ (for rich step during 1 min). The cycles described above were denoted in this study as a single set of stability test and before each stability test a pre-treatment, described in the following section, was performed. This set was repeated three times for Pt/20BaO/Al, Pt/20BaO/AZT and Pt/AZT. Moreover, Pt/8Ba/AZT catalyst was subjected to three additional stability sets, since it was not completely stable after three sets.

After the stability tests, the samples were subjected to NOₓ experiments where successive lean/rich cycles (seven cycles with NO in the feed and four cycles with NO₂) at three different temperatures of 673 K, 573 K and 473 K were performed. Before each experiment at each temperature the catalysts were pretreated at 773 K with 1% H₂, 5% CO₂ and 5% H₂O for 15 min, which was followed by exposing the sample to 5% CO₂, 5% H₂O and Ar for 5 min and finally an oxidation step with 5% O₂, 5% CO₂ and 5% H₂O for 15 min.

SO₂ poisoning was investigated by exposing the samples to sulfur-containing gas mixture where lean and rich cycles were alternated. For the SO₂ poisoning tests, the temperature was decreased to 573 K after pre-treatment at 773 K and ten successive lean/rich cycles were conducted according to the following procedure: (1) lean cycle: 30 ppm SO₂, 500 ppm NO, 10% O₂, 5% CO₂ and 5% H₂O for 4 min; (2) rich cycle: 30 ppm SO₂, 500 ppm NO, 1% H₂, 5% CO₂ and 5% H₂O for 1 min. Thereafter, the same lean-rich cycling was repeated at the respective temperature without sulfur to study the activity of the catalyst after sulfur poisoning. It should be noted that pre-treatment was always conducted before each experiment at each temperature.

Sulfur regeneration of the catalysts was also investigated and the samples were regenerated at 773 K and 973 K, respectively, in a gas mixture of 1% H₂, 5% CO₂ and 5% H₂O for 1 h. After the regeneration, the samples were pre-treated (as reported above) and subjected to seven lean/rich cycles at 573 K contained NO + O₂ + CO₂ + H₂O (during lean) and NO + H₂ + CO₂ + H₂O (during rich), followed by four cycles with NO₂. For all catalytic reactions, flow rate was set to 3 L/min.

NH₃-TPD measurements were performed in a Setaram Sensys Digital Scanning Calorimeter (DSC), combined with an Hiden HPR-20 QUI mass-spectrometer using powder samples (about 60 mg). After degreening of the powder at 923 K (0.9% H₂ for 30 min; Ar 5 min; 474 ppm NO, 4.5% O₂, 4.8% CO₂ for 2 h) and pre-treatment (8% O₂ for 30 min and 0.9% H₂ for 1 h) the catalyst was exposed to 2000 ppm ammonia at 323 K for 8 h. Next, the samples were treated with Argon for 30 min, and the temperature was increased to 1073 K with a heating rate of 5 °C/min in the presence of Ar (g) flow. Further details regarding the NH₃-TPD measurements can be found elsewhere [40].

3. Results and discussion

3.1. NOₓ adsorption and desorption nature of AZT-based NSR/LNT materials

Fig. 1 illustrates the in-situ FTIR spectra corresponding to NO₂(g) adsorption at 323 K on (a) Pt/AZT, (b) Pt/8BaO/AZT, (c) Pt/20BaO/AZT and (d) Pt/20BaO/Al₂O₃ starting from low pressures up to saturation (5.0 Torr NO₂ for 10 min). Each material exhibits highly convoluted features in the spectral range of 1800–1000 cm⁻¹ including well-known oxides coordinated nitrate and nitrite functional groups reported in literature such as in our former studies [18,20,39,42–46]. In Fig. 1a, there are five main vibrational stretchings located at 1640, 1582, 1561, 1324 and 1234 cm⁻¹ on BaO-free Pt/AZT material. While features at 1640 and 1238 cm⁻¹ can be attributed to bridging nitrates, other three frequencies at 1582/1283 and 1561 cm⁻¹ are associated with bidentate and monodentate nitrates; respectively [39,47]. It is worth mentioning that highly convoluted spectral line characteristics renders assignment of nitrate/nitrite features rather difficult. Incorporation of BaO domains leads to a different spectral line shape as demonstrated in Fig. 1b and c for Pt/8BaO/AZT and Pt/20BaO/AZT; respectively. Fig. 1b–d shows that NO₂ adsorption on each material generates six main vibrations located at ca. 1628, 1570, 1480, 1436, 1324 and 1234 cm⁻¹. In addition to the surface nitrate/nitrite groups, formation of bulk/ionic type of nitrate groups which are apparent by the features located at ca. 1480, 1437 and 1322 cm⁻¹ are observed as well. For all of the sample surfaces in Fig. 1, it is apparent that NO₂ molecules are initially adsorbed as nitrates evident by the feature located at 1211 cm⁻¹ and are subsequently oxidized to nitrate functional groups.

It is also visible in Fig. 1b and c that the absorbance intensity of the spectrum corresponding to NO₂-saturated Pt/20BaO/AZT (top-most red spectra in Fig. 1c) is clearly higher than that of Pt/8BaO/AZT (Fig. 1b). These findings imply a higher amount of NO₂ adsorption on Pt/20BaO/AZT as compared to Pt/AZT and Pt/8BaO/AZT at 323 K. However, deduction of quantitative information regarding adsorbate coverages solely from FTIR absorption intensities could be misleading due to variations in IR absorption cross sections. Thus, a more accurate and a quantitative comparison of NSC was also performed via TPD experiments on powder catalysts in batch mode and flow-mode reactor studies on monolithic catalysts which will be described in the upcoming sections demonstrating good correlation between batch-mode and flow-mode experimental findings.

NO₂ adsorption and desorption properties of the synthesized powder catalysts via in-situ FTIR analysis in batch-mode yield mostly...
qualitative information. Hence, FTIR experiments were complemented with batch-mode TPD experiments in order to gather semi-quantitative information regarding the total NOx adsorption quantities and thermal stabilities of adsorbed nitrate/nitrite species as well as their decomposition pathways.

Prior to TPD experiments, materials were saturated with 5.0 Torr NO2(g) for 10 min at 323 K, followed by vacuum annealing up to 973 K. Fig. 2a–d illustrates the TPD profiles obtained after NO2(g) adsorption over Pt/AZT, Pt/8BaO/AZT, Pt/20BaO/AZT and Pt/20BaO/Al2O3 materials; respectively. Thermal decomposition of adsorbed nitrate species on Pt/AZT and Pt/8BaO/AZT exhibits relatively similar characteristics as shown in Fig. 2a and b; respectively. It is clear that NO desorption signal (m/z = 30) revealed two main desorption maxima at 645 and 740 K. Nitrate decomposition produces desorption channels of NO (m/z = 30), NO2 (m/z = 46) and O2 (m/z = 32) at low temperatures (i.e. 645 K), while the major desorption channels are primarily NO (m/z = 30) and O2 (m/z = 32) for high temperatures (i.e. 740 K). Identical TPD experiments were also performed for the catalysts with higher BaO loadings (i.e. wt.% 20 BaO). Thermal decomposition of nitrate species on Pt/20BaO/AZT and Pt/20BaO/Al2O3 surfaces are illustrated in Fig. 2c and d; respectively. As compared to the TPD results for Pt/AZT and Pt/8BaO/AZT (Fig. 2a and b), Fig. 2c and d clearly indicates that the desorption channels related to NO (m/z = 30) and O2 (m/z = 32) are more pronounced at higher temperatures (i.e. 750 K). Increase in BaO loading from 8 wt.% to 20 wt.% leads to formation of a greater extent of bulk like nitrate species which is consistent with the observation of stronger high temperature (i.e. 750 K) NO and O2 desorption signals.

In addition to the mechanistic information discussed above, one can also obtain quantitative knowledge from the TPD results regarding the relative NOx adsorption capabilities of different catalysts by integrating each of the N-related desorption channels (i.e. N2, NO, N2O, and NO2) by considering particular QMS fragmentation patterns of all of the desorbing species. More details regarding fragmentation calculations can be found elsewhere [39]. In such a semi-quantitative analysis, it is also important to make sure that all of the NOx species are completely removed from the surfaces at the end of TPD experiments. In order to verify this point, in-situ FTIR data corresponding to the surfaces before and after TPD runs were acquired as shown in the insets of Fig. 2. These in-situ FTIR results clearly illustrate that materials were completely regenerated after TPD experiments (i.e. annealing under vacuum at 973 K).

Table 1 shows the total NOx desorption from investigated catalyst normalized by either mass or SSA of the catalysts. Calculated numbers clearly suggest that NOx adsorption capability of Pt/AZT is only slightly affected by the addition of 8 wt.% BaO. However, a higher BaO loading (i.e. 20 wt.%) onto Pt/AZT leads to a drastic change where total NOx release increased by about 58%. Another striking aspect of Table 1 is the fact that total NOx release of Pt/20BaO/AZT is 19% higher than that of benchmark Pt/20BaO/Al2O3 catalyst. This latter finding clearly emphasizes the relatively better NOx storage performance of the AZT support material in comparison to the conventional γ-Al2O3 support (i.e. annealing under vacuum at 973 K).

Moreover, calculated NOx adsorption quantities can also be assessed by considering their specific surface areas (SSA). SSA-normalized NOx release values increase in the following order: Pt/AZT < Pt/8BaO/AZT < Pt/20BaO/Al2O3 < Pt/20BaO/AZT. Here, it should be mentioned although these results are informative, they correspond to batch mode experiments on powder catalysts where initial adsorption was performed at 323 K. Thus, for a more accurate evaluation of NSC values, flow-mode NOx adsorption and release experiments were performed on monolithic catalysts under operationally-relevant conditions as discussed in depth in the next section.

3.2. Quantitative NSR performance analysis

In order to evaluate the NOx storage reduction (NSR) performance of the synthesized materials under more realistic conditions in the form of wash-coated monoliths before and after exposure to SOx as well as after SOx regeneration at 773 and 973 K, flow reactor measurements...
were carried out as described in the experimental section. NSC were calculated by integration of the outlet NO concentrations with respect to the inlet concentration and the obtained NSC results are depicted in Figs. 3 and 4, for experiments conducted at 473 and 573 K, respectively.

Fig. 3 illustrates the NSC values at 473 K for fresh (F), sulfur-poisoned (S), regenerated at 773 K (R) catalysts in terms of mmol/gcat (Fig. 3). These results clearly point out the fact that Pt/AZT and Pt/8BaO/AZT revealed superior resistance against sulfur poisoning at 473 K, where NSC values remain practically invariant for fresh, SOx-poisoned and regenerated catalysts at 773 K (R'). It should be noted that the for the SOx-poisoned catalyst lean-rich cycling was conducted after the sulfur poisoning in addition to pre-treatment steps conducted before each experiment at each temperature. Interestingly, high temperature regeneration of these catalysts at 973 K (R') leads to an apparent increase in NSC due to change in material morphology under the severely reducing regeneration conditions which will be discussed further in the text below.

On the other hand, increase in the loading of the basic storage domain (i.e. BaO) significantly alters the performance characteristics of Pt/20BaO/AZT in the presence of sulfur-poisoning (Fig. 3). Although fresh Pt/20BaO/AZT catalyst exhibits comparable NSC to the fresh Pt/AZT and fresh Pt/8BaO/AZT, its NSC is significantly influenced by the SOx exposure, resulting in ca. 40% decrease. Among all of the investigated materials, benchmark Pt/20BaO/Al was found to have the most severe relative attenuation in NSC upon sulfur poisoning (i.e. 52% loss in NSC with respect to its fresh form). Moreover, comparison of the Pt/20BaO/AZT and Pt/20BaO/Al materials provides an insight regarding the influence of the support material (AZT vs. γ-Al2O3) on the sulfur regeneration performance. While the NSC after thermal regeneration at 773 K was found to be ca. 73.6% of the NSC of fresh Pt/20BaO/AZT, this was limited to only 52% for the conventional Pt/20BaO/Al benchmark catalyst. Differences in the percent regeneration capabilities of AZT and γ-Al2O3 supported materials after sulfur poisoning becomes even more evident after the regeneration at 973 K (Fig. 3). While Pt/20BaO/AZT catalyst could recover ca. 100% of its original NSC after regeneration at 973 K, Pt/20BaO/Al could only recover 76% of its NSC.

Further experiments were also carried out in order to investigate the effect of temperature on NSC as shown in Fig. 4. It is seen that NSC of BaO-free Pt/AZT decreases to some extent at 573 K as compared to that of 473 K. However, it should be noted that although NSC of fresh Pt/AZT at 573 K is almost one third of Pt/20BaO/Al, it demonstrates a striking resilience against sulfur poisoning, preserving ca. 96% of its original NSC at 573 K (i.e. 0.024 vs 0.022 mmol/gcat) after poisoning. Thus, AZT support has poor NOx and SOx storage. In order to utilize the full potential of the AZT material, it should be combined with a storage component such as barium. It is also apparent that fresh Pt/20BaO/AZT...
exhibits ca. 38% higher NOx storage at 573 K than that of Pt/20BaO/Al benchmark catalyst. Indeed, NSC performance of Pt/20BaO/AZT at 573 K after high temperature regeneration (R') is the highest among all of other investigated catalyst (i.e.52% higher than that of Pt/20BaO/Al). It should also be noted that Pt/8BaO/AZT exhibited comparable NSC at 573 K to the benchmark Pt/20BaO/Al catalyst after regeneration at 973 K.

The increase in NSC at 573 K after regeneration at 973 K (Fig. 4) deserves more attention. It is seen that regeneration at elevated temperatures under a severely reducing environment not only facilitates the sulfur regeneration, but leads to increased NOx storage, which could be due to structural changes in the materials. This can be tentatively attributed to the enhancement of the dispersion of BaO and AZT support upon high temperature regeneration. This is also in very good agreement with one of our recent reports, indicating enhanced BaO dispersion on ZrO2/TiO2 as compared to γ-Al2O3 [38]. Enhanced BaO dispersion was also demonstrated on the TiO2/Al2O3 support material [21].

In order to shed light on the changes in Pt sintering due to aging, poisoning and regeneration, we performed in-situ FTIR spectroscopy experiments and followed CO adsorption characteristics of Pt sites on fresh Pt/20BaO/AZT powder directly after calcination and spent Pt/20BaO/AZT catalysts scraped of washcoat from the sulfur regenerated Pt/20Ba/AZT monolith as shown in Fig. 5. In-situ FTIR spectrum in...
Fig. 5 for the fresh catalyst (black spectrum) revealed a main feature at 2052 cm$^{-1}$ which can be ascribed to linear (atop) Pt$^0$-CO species [48–50]. For the spent catalyst (red spectrum) this peak was observed to shift to a higher frequency of 2059 cm$^{-1}$ with a distinguishable tail towards lower frequencies, exhibiting a shoulder at 1966 cm$^{-1}$. The blue shift in the linear (atop) Pt$^0$-CO species in the spent catalyst can be readily ascribed to sintering and Pt particle size growth and increase in the extension of the Pt(111) facets/terraces on Pt nanoparticles. This argument is in good agreement with the observation of the shoulder at 1966 cm$^{-1}$ for the spent catalyst which can be attributed to bridging CO species on Pt$^0$ sites located on the sintered Pt nanoparticles [48–50].

The NO oxidation is known to be important for NO$_3^-$ storage when using NO as inlet feed. The NO oxidation is both a function of the amount of active sites, but it is also a structure-sensitive reaction, where larger Pt particles are more active for NO oxidation [51,52]. Moreover, Olsson and Fridell [52] found that sulfur poisoning followed by sulfur regeneration with hydrogen significantly improved the NO oxidation. In Fig. 6, the NO oxidation to form NO$_2$ at 573 K during the last NO cycle for fresh, sulfur poisoned, 773 K-regenerated at and 973 K-regenerated catalysts for a) Pt/AZT, b) Pt/8Ba/AZT, c) Pt/20Ba/AZT and d) Pt/20Ba/Al.

Fig. 6. NO oxidation to form NO$_2$ at 573 K during the last NO cycle for fresh, sulfur poisoned, 773 K-regenerated at and 973 K-regenerated catalysts for a) Pt/AZT, b) Pt/8Ba/AZT, c) Pt/20Ba/AZT and d) Pt/20Ba/Al.

In Fig. 6 for the fresh catalyst (black spectrum) revealed a main feature at 2052 cm$^{-1}$ which can be ascribed to linear (atop) Pt$^0$-CO species [48–50]. For the spent catalyst (red spectrum) this peak was observed to shift to a higher frequency of 2059 cm$^{-1}$ with a distinguishable tail towards lower frequencies, exhibiting a shoulder at 1966 cm$^{-1}$. The blue shift in the linear (atop) Pt$^0$-CO species in the spent catalyst can be readily ascribed to sintering and Pt particle size growth and increase in the extension of the Pt(111) facets/terraces on Pt nanoparticles. This argument is in good agreement with the observation of the shoulder at 1966 cm$^{-1}$ for the spent catalyst which can be attributed to bridging CO species on Pt$^0$ sites located on the sintered Pt nanoparticles [48–50].

After sulfur poisoning. It should be remembered that in all these experiments lean-rich cycling was conducted after the sulfur poisoning. This means that the catalyst during the cycling was exposed to hydrogen in the rich phase and in addition to hydrogen during the pretreatment (at 773 K with 1% H$_2$, 5% CO$_2$ and 5% H$_2$O for 15 min) which was conducted before experiment at each temperature, which will remove some of the sulfur from the noble metal sites, and thereby facilitate the NO oxidation. Interestingly, the NO oxidation is quite different after sulfur regeneration at 973 K between the samples. For Pt/8BaO/AZT the NO$_2$ formation is significantly increased compared to all samples. This could be due to sintering and that larger Pt particles are more active compared to small Pt particles [53]. This increased NO$_2$ production can explain the larger NO$_3^-$ storage observed after sulfur regeneration (see Fig. 4). However, for the Pt/20BaO/AZT and Pt/20BaO/Al, the NO oxidation activity went down after the 973 K regeneration and the reason for this could be that even though the larger Pt particles are more active, sintering is also decreasing the amount of active sites. These results clearly show that the noble metal activity for NO oxidation cannot explain the increase in NO$_3^-$ storage for the sulfur regenerated samples at 973 K.

In order to further elucidate the effect of high temperature sulfur
regeneration with hydrogen, the NOX storage for the four catalysts when using NO2 as inlet NOX source is displayed in Fig. 7. In general, the NOX storage is higher for the case with NO2 in the inlet feed (compare Figs. 4 and 7), which is also observed at 573 K by Fridell et al. [54]. When using NO2 in the feed the NOX can store directly on the storage sites [55]. Interestingly, also for the case with NO2 in the inlet feed the NOX storage is higher after sulfur regeneration at 973 K for all barium containing catalysts, thus we suggest that there are morphological changes in the surface structure of the BaO/AZT mixed oxide system and Ba/Al system after sulfur poisoning and high temperature regeneration.

As discussed in detail in one of our recent reports, some of the trends in the NSC presented in Figs. 3 and 4 can be explained in the light of the relatively higher surface acidity of the AZT-supported materials as compared to the Pt/20BaO/Al benchmark catalyst. This is in agreement with the NH3 uptake data as shown in Fig. 8 revealing ammonia storage quantities of 0.67, 0.58, 0.46 and 0.35 mmol/gcat for Pt/AZT, Pt/8BaO/AZT, Pt/20BaO/AZT, and Pt/20BaO/Al, respectively [40]. These results are in very good accordance with the former pyridine adsorption FTIR experiments which revealed a higher surface concentration of Lewis acid sites for AZT-supported materials as compared to other Al2O3-based counterparts [40].

Relative changes in NSC values upon SOX poisoning and subsequent regeneration for all of the investigated materials as compared to their fresh forms are summarized in Table 2. These results suggest that regenerated Pt/8BaO/AZT catalyst reveals promising performance both at low (i.e. 473 K) and moderate (i.e. 573 K) temperatures surpassing the conventional Pt/20BaO/Al2O3 benchmark catalyst.

In-situ FTIR experiments were also performed in batch-mode on powder catalysts in order to investigate the relative extent of residual SOX species remaining on the catalyst surfaces after SOX poisoning and subsequent regeneration with H2 (Fig. 9). These experiments reveal...
Z. Say et al.

revealing acidic-enough character (Fig. 8) to enable emission from the more acidic surfaces (Pt/AZT and Pt/8BaO/AZT) which significantly decreases on after regeneration with H2. However, these latter catalysts, in turn, suffer from limited NSC due to their higher acidity. It is worth mentioning that all of the investigated catalysts including Pt/AZT and Pt/8BaO/AZT uptake different extents of SO2 species upon SO2 + O2 adsorption as described in detail in one of our former reports [40]. Along these lines, Pt/20BaO/AZT catalyst seems to possess a more favourable trade-off between NSC (Figs. 3 and 4) and sulfur tolerance (Fig. 9), revealing acidic-enough character (Fig. 8) to enable efficient sulfur regeneration without experiencing a severe suppression in NSC.

NSC measurements performed at high temperatures such as 673 K (Fig. 10) illustrate that, stability of nitrates significantly decreases on the more acidic surfaces (Pt/AZT and Pt/8BaO/AZT) which significantly suffer from loss of NSC. Fig. 10 clearly highlights the need for the improvement of the NSC of AZT-based catalysts at elevated temperatures so that they can surpass the performance of conventional Pt/20BaO/Al benchmark catalyst.

Integrated ammonia production from the cycling experiments are shown in Fig. 11, for 473, 573 and 673 K. Ammonia production during rich conditions could be beneficial, if it is used in combination with an SCR unit [56]. For example, during vehicle chassis dynamometer experiments performed by Volvo Cars an SCR catalyst was used downstream of the LNT [57].

These corresponding results in general lead us to conclude that ammonia production over fresh materials increases along with the increase in temperature. Ammonia production over platinum in Pt/SiO2 was previously found to increase with temperature [58], which is in line with our results. However, this general trend was not applicable for both Pt/8BaO/AZT and Pt/20BaO/AZT samples at 673 K. This is because ammonia production over NOx storage materials is very complex. It mainly relates to three parts: (i) formation of ammonia from the inlet NOx over the Pt sites, (ii) formation of ammonia from the stored NOx, which is being released in the rich phase and (iii) consumption of ammonia due to SCR reaction with the stored NOx, which will lower the amount of ammonia after the catalyst [59,60]. This means that the stored NOx can increase the ammonia formation because of increased availability of NOx, but also decrease the ammonia production due to the SCR reaction. The selectivity between these two reactions depend on the catalyst material, such as proximity between the noble metal and storage component, noble metal particle activity, etc. For the Pt/20BaO/Al2O3 material the ammonia production increases for all temperatures. Figs. S1, Supplementary material shows the ammonia profile. At 473 K, there is a sharp and quite small ammonia peak when switching to rich conditions, which is due to small amounts of stored NOx. Quickly, the ammonia peaks levels off to close to 500 ppm which is the inlet NO level. These results show that a clear limiting factor is the supply of NOx. When increasing the temperature using NO in the inlet feed, the ammonia production is increasing due to increased conversion of the stored NOx to ammonia. Indeed, the NOx storage is higher for 673 K compared to 573 K and compared to 473 K (compare Figs. 10, 4 and 3). This means that the ammonia production from the released NOx is increasing more compared to the SCR reactions (which also are increasing with temperature), resulting in increased selectivity for ammonia.

For Pt/20BaO/AZT, the ammonia production decreases at the highest temperature (673 K), see Figs. 11 and S2, Supplementary material. The reason for this is that the NOx storage is quite similar at 673 K and 573 K for this material and the increased temperature increases the rate for the SCR reaction more, which resulted in less ammonia in the outlet. For the Pt/BaO/Al2O3 on the other hand, the NOx storage was substantially increased at 673 K, which resulted in much larger availability of NOx and resulted in an overall increased ammonia concentration even though SCR rate was faster.

Examining the results for sulfur poisoning and regeneration at 473 K (see Fig. 11a) the ammonia production for fresh and sulfur poisoned catalysts is quite similar, except for the Pt/20BaO/Al2O3 sample, where a significant decrease is seen. For the Pt/20BaO/Al2O3 catalyst, most of the ammonia production could be regenerated, but it required high temperature (973 K). At 573 K (see Fig. 11b), the sulphur poisoning results in lower ammonia production, but most of it could be regained after regeneration. Also at 673 K, sulphur poisoning was clear (see Fig. 11c), however the ammonia production capacity could not be fully regained. At 673 K, the NOx storage capacity is not either fully regained after the 973 K regeneration, which means that there is less stored NOx on the catalysts, and thereby less available NOx for the ammonia production and this can explain why the ammonia production could not be fully regained after the regeneration.

Interestingly, the ammonia production was higher for the AZT containing samples after sulfur regeneration compared to fresh material. These results are in line with the NOx storage results presented in Figs. 3 and 4 and the reason for this could be structural changes in the materials after sulfur poisoning followed by regeneration in the presence of hydrogen at high temperatures.

The N2O production is shown in Fig. 12 for the three temperatures. It is observed that the N2O production is significantly higher at low temperature, which is in line with the study by Lindholm et al. [61]
Interestingly, the fresh Pt/BaO/AZT materials showed lower N₂O formation compared to Pt/BaO/Al₂O₃ at 573 K, which is very beneficial. Simultaneously, the Pt/BaO/AZT produced more ammonia, and the lower N₂O formation for Pt/BaO/AZT is likely related to higher selectivity for the formation of ammonia compared to N₂O. Moreover, at 473 K (see Fig. 12a) there is a clear poisoning effect of the N₂O formation for all barium containing samples and most of the N₂O production could be restored after regeneration. At 573 K, poisoning was also observed, but the regeneration capability varied between the samples. However, at the highest temperature (i.e. 673 K) the N₂O production was between 38 and 86 times lower compared to at 473 K and due to this low amount, no clear trends could be visible.

We also performed preliminary experiments in order to demonstrate that high-temperature NSC of AZT-based materials can be improved further by utilizing multiple NOₓ-storage components where one of these components provide efficient NSC at T ≤ 573 K, while the second component enables NSC at elevated temperatures (i.e. 673 K). K₂O is a versatile NOₓ storage component used in NSR/LNT catalysts at high temperatures [62,63]. Therefore, currently observed NSC loss at high temperatures, particularly for Pt/8BaO/AZT could be alleviated by incorporating a high-temperature NOₓ storage functionality (i.e. K₂O) to the catalyst formulation as shown in Fig. 13. Fig. 13 shows NSC for

![Fig. 11. Ammonia production for Pt/AZT, Pt/8BaO/AZT, Pt/20BaO/AZT and Pt/20BaO/Al monolithic catalysts at a) 473 K, b) 573 K and c) 673 K obtained in a flow-reactor using an inlet gas feed of 500 ppm NO, 5% O₂, 5% CO₂, 5% H₂O, balanced in Ar. F = fresh, S = SOx poisoned, R’ = regenerated at 773 K after SOx poisoning and R” = regenerated at 973 K after SOx poisoning (see text for details).](image-url)
monolithic catalysts in their fresh forms which only contained K₂O (Pt/5.4 K₂O/AZT) or BaO (Pt/8BaO/AZT) as storage domains as well as a hybrid catalyst comprised of a physical (50 wt.%) mixture of Pt/5.4 K₂O/AZT – Pt/8BaO/AZT. Preliminary results in Fig. 13 clearly indicate that NSC of the fresh Pt/8BaO/AZT can be improved at all of the investigated temperatures (i.e. 473–673 K) by physically mixing it with Pt/5.4 K₂O/AZT. In our forthcoming studies, this strategy will be applied to other AZT-based LNT catalysts (including Pt/20BaO/AZT) in order to present a comprehensive report on the catalytic behaviour and the surface chemistry of the NOₓ/SO₃ species on these advanced hybrid catalytic architectures.

Fig. 13, we performed in-situ FTIR experiments and investigated NO₂ adsorption on Pt/8BaO/AZT, (b) Pt/5.4 K₂O/AZT – Pt/8BaO/AZT (physical mixture), and Pt/5.4K₂O/AZT powder catalysts as illustrated in Fig. 14. While the majority of the adsorbed NOₓ species on Pt/8BaO/AZT corresponded to surface nitrates and nitrites (evident by the IR vibrational frequencies located at 1609, 1575, 1460, 1298 and 1241 cm⁻¹), K₂O incorporation significantly altered the nature of the existing NOₓ species, favouring the formation of bulk-like nitrates on K₂O domains characterized by IR features at 1396 and 1369 cm⁻¹ as well as the surface-like nitrates [64–66]. These interesting in-situ FTIR results are consistent with the fact that incorporation of K₂O domains extends of the operational temperature window towards higher...
temperatures by enabling the formation of a greater amount of thermally stable bulk-like nitrates.

4. Conclusions

Al₂O₃/ZrO₂/TiO₂ (AZT) ternary mixed oxides functionalized with Pt and BaO were synthesized in powder and monolithic forms and were utilized in NOx Storage Reduction/Lean NOx Trap (NSR/LNT) catalysis as alternative catalytic materials. Adsorption of NOx and SOx species and their interactions with the catalyst surfaces were systematically investigated via in-situ FTIR technique revealing different NOx coordination geometries governed by the presence and the loading of BaO in the powder catalyst formulation. While BaO-free Pt/AZT stored NOx as surface nitrates, BaO incorporation also led to the formation of bulk-like ionic nitrate species. NOx adsorption results obtained from the current Temperature Programmed Desorption (TPD) data indicated that NOx Storage Capacity (NSC) was enhanced due to BaO incorporation into the powder catalyst and NSC was found to increase in the following order: Pt/AZT < Pt/8BaO/AZT < Pt/20BaO/Al₂O₃ < Pt/20BaO/AZT. Increase in the NSC with increasing BaO loading was found to be at the expense of the formation of bulk-like sulfates after SOx exposures. These bulk-like sulfates were observed to require higher temperatures for complete regeneration with H₂(g). Catalytic activity results obtained via flow reactor tests with monolithic catalysts suggested that Pt/AZT and Pt/8BaO/AZT catalysts with stronger surface acidity also revealed higher resistance against sulfur poisoning and superior SOx regeneration on the NSC capacity at 473 K and 573 K in spite of their relatively lower NSC. Monolithic Pt/20BaO/AZT catalyst revealed superior NSC with respect to the conventional Pt/20BaO/Al₂O₃ benchmark catalyst at 573 K after sulfur regenerations. On the other hand, this trend was reversed at high-temperatures (i.e. 673 K). Interestingly after sulfur poisoning and high temperature regeneration at 973 K with hydrogen, the NSC at especially 573 K increased and was significantly higher for several cases compared to the fresh catalyst. This can be related to the structural changes in the materials after high temperature reduction and this behavior was the strongest for the materials containing both BaO and AZT.

Preliminary results were presented demonstrating the enhancement of the high-temperature NSC of AZT-based materials by exploiting multiple NOx-storage components where BaO functioned as the low/mid-temperature NOx-storage domain and K₂O served as the high-temperature NOx storage domain. Enhancement in the high-temperature NOx-storage in the BaO-K₂O multiple storage domain systems was attributed to the formation of additional thermally stable bulk-like nitrates upon K₂O incorporation.

Acknowledgements

Authors acknowledge the financial support from the Scientific and Technological Research Council of Turkey (TUBITAK) (Project Code: 111M780). EO and ZS also acknowledge the scientific collaboration with TARLA project founded by the Ministry of Development of Turkey under grant no DPT2006K-120470. EO acknowledges Science Academy (Turkey) BAGEP fund. In addition, the authors acknowledge the Swedish Research Council (642-2014-5733).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cattod.2018.01.028.

References
