Model NO\textsubscript{x} storage systems: Storage capacity and thermal aging of BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100)

Emrah Ozensoy, Charles H.F. Peden, János Szanyi*

Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, MSIN KS-93, Richland, WA 99352, USA

Received 6 March 2006; revised 26 June 2006; accepted 28 June 2006
Available online 22 August 2006

Abstract

The NO\textsubscript{x} storage properties of a BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) model system, with a BaO coverage of \(\sim\) 2 monolayer equivalent (MLE), was studied. X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) techniques were used to investigate NO\textsubscript{2} adsorption and reaction on the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface. These results were compared with those of the \(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) support material, a thermally aged BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) model system, and a realistic BaO (20 wt%)/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} high-surface area counterpart. At \(T > 300\) K, adsorbed NO\textsubscript{2} is converted to nitrates on all of the surfaces studied. Nitrates residing on the alumina sites of the model catalyst surfaces are relatively weakly bound and typically desorb within 300–600 K, leading to NO(g) evolution; while nitrates associated with the baria sites are significantly more stable and desorb within 600–850 K, resulting in NO(g) or NO(g) + O\textsubscript{2}(g) evolution. NO\textsubscript{x} uptake by the baria sites of the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) model system was found to be as much as five-fold greater than that of the \(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) support material. Thermal aging of a BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface at 1100 K before NO\textsubscript{x} uptake experiments brings about a significant (>70%) reduction in the NO\textsubscript{x} storage capacity of the model catalyst surface.

© 2006 Published by Elsevier Inc.

Keywords: NO\textsubscript{x} storage materials; Al\textsubscript{2}O\textsubscript{3}; BaO; Pt; NO; NO\textsubscript{2}; Nitrate; Nitrite; XPS; TPD

1. Introduction

Due to their outstanding catalytic performance for NO\textsubscript{x} reduction under highly oxidizing conditions resulting from diesel engine operation, BaO and transition metal-based NO\textsubscript{x} storage/reduction (NSR) catalysts [1–4] have recently become, along with an ammonia selective catalytic reduction (SCR) approach [5], a viable technology solution for controlling NO\textsubscript{x} emissions from diesel engine powered vehicles. Diesel engines are typically operated at high air to fuel ratios (A/F = 25/1 [wt/wt]) providing up to a 35% improvement in fuel efficiency with respect to that of gasoline engines in which lower A/F ratios (14.5) are used [5]. It should be noted that conventional (Pd or Pt–Rh)/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3}-based three-way catalysts (TWC) commonly used in automotive catalysts for NO\textsubscript{x} reduction purposes fail under highly oxidizing (lean) conditions, that is, A/F > 18 [1].

The first commercial NSR catalyst was developed in 1994 by Toyota Motor Company [1], where a Pt/BaO/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3}-based formulation was used. In this catalyst formulation, the Pt component provides NO oxidation and NO\textsubscript{x} reduction (redox) capabilities, whereas the primary role of BaO sites is NO\textsubscript{x} storage in the form of Ba(NO\textsubscript{3})\textsubscript{2}. The \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} support material enables dispersion of the active sites over a large surface area and may facilitate the reactant transport between the active sites on the catalyst via surface diffusion. NSR catalysts are typically operated in two alternating cycles. In the so-called storage cycle, the exhaust gas composition is abundant in O\textsubscript{2} (i.e., lean conditions). Under these conditions, NO(g), which is the major NO\textsubscript{x} component in the untreated exhaust gas mixture, is readily oxidized to NO\textsubscript{2} on the Pt sites. Next, NO\textsubscript{2} migrates onto the BaO storage sites via gas-phase adsorption and/or surface diffusion and is eventually stored as Ba(NO\textsubscript{3})\textsubscript{2}. After saturation of the active Ba-containing phase with nitrates, a reduction cycle is started by quickly switching to an exhaust gas-phase composi-
tion that is abundant in hydrocarbons (HC), CO, and H₂ (i.e., rich conditions). During the reduction cycle, the Ba component releases the stored nitrates in the form of NO₂ and NO + O₂, which is subsequently transferred onto the Pt sites to be reduced to N₂, resulting in regeneration of the active BaO storage component [1].

Although numerous studies on high-surface area NSR catalysts have been conducted, as recently discussed in a detailed review by Epling et al. [2], only a limited number of surface science studies [6,7] have been carried out addressing the fundamental chemical and physical phenomena occurring on the NSR catalyst surfaces, which ultimately dictate the reaction mechanisms and catalytic performance of these systems. Therefore, we have recently used a systematic approach to identify some of the key surface science phenomena relevant to the NSR systems by means of well-defined mixed-oxide (baria-alumina)-based model systems. We have used a bottom-up synthetic strategy to prepare a model NO₃ storage material. This is achieved by using an ordered θ-Al₂O₃ ultrathin film grown on a NiAl(100) bimetallic alloy substrate mimicking the high-surface area alumina counterpart. The spectroscopic characterization of the alumina support material [8], as well as its interaction with H₂O [8], NO₂ [9], and H₂O + NO₂ [10] in the absence of the active Ba-containing phase, have been investigated previously. Next, deposition, oxidation, and growth of the Ba phase on the θ-Al₂O₃/NiAl(100) substrate were studied via different preparation protocols [11,12] to obtain a model NO₃ storage system in the form of BaO/θ-Al₂O₃/NiAl(100) [12].

As a continuation of this effort, in the current text we focus on the NO₂ storage properties of the BaO/θ-Al₂O₃/NiAl(100) model system on NO₂ adsorption using TPD and XPS techniques. Furthermore, NO₂ uptake of the BaO/θ-Al₂O₃/NiAl(100) mixed metal-oxide surface, as well as the Ba-free θ-Al₂O₃/NiAl(100) substrate and a realistic high-surface area BaO (20 wt%)/γ-Al₂O₃ NO₂ storage material, will be discussed in a comparative fashion. Finally, the thermal aging and deactivation of the NSR systems will be examined. This will be illustrated by NO₂ adsorption and subsequent TPD analysis on a BaO/θ-Al₂O₃/NiAl(100) surface pretreated at high temperatures (1100 K) before NO₂ adsorption, in an attempt to simulate some of the long-term thermal aging effects that can occur under regular operational and regeneration temperatures (573–973 K).

2. Experimental

The experimental setup, sample preparation methods and the data acquisition procedures that are used in the current work have been discussed in detail elsewhere [8–12]. In brief, experiments were performed in an ultra-high vacuum (UHV) surface analysis chamber (Pbase = 2 × 10⁻¹⁰ Torr) equipped with facilities for XPS (PHI-dual anode X-ray source, Omicron EA-125 multichannel electrostatic hemispherical electron energy analyzer), AES (PHI-single pass cylindrical mirror analyzer), a quadruple mass spectrometer (QMS, UTI) for TPD, and a rear-view low energy electron diffraction (LEED) setup (Princeton Research Instruments). θ-Al₂O₃/NiAl(100) surfaces were prepared using the procedure developed by Ibach and co-workers [13,14]. θ-Al₂O₃ ultrathin films grown via this method resulted in ordered alumina films with a thickness of 6 ± 2 Å [8]. A custom-made Ba evaporation source, containing an exothermic Ba ring getter material (SAES Getters Inc.), was used for preparing the BaO/θ-Al₂O₃/NiAl(100) [12]. As described in a previous report [12], this surface was prepared by carrying out Ba deposition and subsequent oxidation in a stepwise fashion. First, a controlled dose of Ba metal was evaporated onto the θ-Al₂O₃/NiAl(100) surface in UHV at 300 K; then O₂(g) (Po₂ = 5 × 10⁻⁷ Torr) was introduced into the chamber at 300 K. Next, the sample temperature was quickly increased to 800 K in the presence of O₂(g), and the sample was annealed at 800 K for 15 min. These dosing and annealing sequences were repeated for each Ba deposition step (total number of deposition/oxidation steps = 8; total time of Ba deposition = 50 min; 1 ML < θBa < 2 ML). It was also pointed out in a previous report [12] that for similar model systems, BaAl₂O₄ formation also can be observed after high-temperature (T > 1000 K) treatments. On the other hand, because the initial sample preparation was done at T ≤ 800 K here, the surface was dominated by BaO species rather than BaAl₂O₄. TPD experiments were performed using a differentially pumped QMS by applying −70 V bias voltage on the spectrometer shield to constrain the ionizing electrons to the interior of the QMS shield, preventing any possible electron beam damage on the sample. All of the TPD data presented in this study were obtained by ramping the temperature of the sample at a constant rate of 2 K/s. A tubular pinhole gas doser, positioned in close proximity to the sample (~2 mm away), was used in the adsorption/desorption (TPD) experiments, which allowed the background pressure in the chamber to stay in the ~10⁻¹⁰ Torr range during the dosing processes, minimizing background desorption artifacts in the TPD data.

Before the introduction of NO₂ gas to the vacuum chamber, the gas-dosing line and pinhole doser were passivated by flushing with NO₂ gas for an extended period. This passivation procedure was monitored with QMS by following the 46-amu signal with respect to the 30-amu signal for a constant flux of NO₂. The saturation of the 46/30-amu ratio indicated the deactivation of the dosing line surfaces. This procedure was found to be helpful in minimizing the decomposition of NO₂ before admittance to the vacuum chamber. XPS data were acquired using an AlKα X-ray source (hv = 1486.6 eV) and 50 eV pass energy. The X-ray source was oriented ~50° with respect to the sample normal.

3. Results and discussion

Fig. 1 illustrates the procedures used for the synthesis of the BaO/θ-Al₂O₃/NiAl(100) model system [11,12]. In this procedure, the NiAl(100) surface (Fig. 1a) was cleaned and used as a substrate to grow the θ-Al₂O₃/NiAl(100) ultrathin film (Fig. 1b) [8,13–17]. Next, the BaO layer was prepared via a step-by-step growth protocol as described in Section 2. In this protocol, Ba metal is dosed on a clean θ-Al₂O₃/NiAl(100) surface at 300 K in UHV, resulting in a well-dispersed Ba surface
component that strongly interacts with the oxygen-terminated \( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) surface (Fig. 1c) [11]. Subsequently, the Ba-dosed surface is annealed in O\(_2\) at 800 K for each Ba deposition step, leading to the formation of fully oxidized 3D BaO clusters (Fig. 1d) [12]. The total BaO coverage at the end of the deposition and oxidation series is within 1 monolayer equivalent (MLE) < \( \theta \)\(_{\text{Ba}}\) < 2 MLE [12]. During oxidation and growth of the 3D BaO clusters, film thickening and a loss in the order of the alumina film structure are also observed [12].

Fig. 2 presents XPS results comparing the N\(_1\)s regions of the XPS data corresponding to \( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) and BaO/\( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) surfaces before and after NO\(_2\) uptake. In these experiments, after the XP spectrum of the clean surfaces at room temperature were acquired (spectra a and c in Fig. 2), the samples were transported to the elevated pressure cell and saturated with NO\(_2\)(g) at 300 K (\( P \)\(_{\text{NO}}\)\(_2\) = 1.5 Torr, total NO\(_2\) exposure = 4.5 \times 10^8 L, where L = 1 \times 10^{-6} \text{Torr s}\). After evacuation, the samples were moved back to the main UHV chamber, and XPS data were obtained at 300 K. The XPS data shown in Fig. 2 clearly indicate that saturating \( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) (Fig. 2b) and BaO/\( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) (Fig. 2d) surfaces with NO\(_2\) at 300 K resulted in the formation of nitrate species, as evident from the N\(_1\)s features at 407.7 and 407.1 eV, respectively [9,18]. In contrast, considering the noticeable dissimilarity in the binding energy values of the nitrate species, various differences in the adsorption sites, adsorption strengths, or surface coordinations of these nitrate species were likely over these two materials (consistent with the TPD results discussed below). XPS experiments were also carried out by dosing lower exposures of NO\(_2\) (0–20 L) on the BaO/\( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) surface at 80 K and the thermal evolution of N\(_1\)s species at 80–850 K was monitored (results not shown). The results of these experiments were qualitatively similar to those obtained for the \( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) surface [9], where the surface was dominated by nitrate species at \( T > 180\) K, whereas at \( T < 180\) K, BaO/\( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) surfaces were populated with mostly molecular species, such as NO\(_2\) and N\(_2\)O\(_4\) (NO\(_2\)-dimer), with a minor contribution from nitrite species. The results of this XPS experiment indicated that from physisorbed NO\(_2\)/N\(_2\)O\(_4\) nitrites formed first on both the \( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) and BaO/\( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) surfaces. As the sample temperature was increased, the nitrites were gradually converted into nitrates; at elevated temperatures, the only ionic NO\(_3\) species observed were nitrates. These results are consistent with the previously proposed formation mechanism of the ionic NO\(_3\) species—that is, on exposure of BaO/alumina systems to NO\(_2\), first nitrites form, and then these nitrites are converted to nitrates. In situ vibrational spectroscopic studies are currently underway to further examine the NO\(_3\) species on this model system at both cryogenic and elevated temperatures. The most significant implication of the XPS results given in Fig. 2 is that, in accordance with previous reports on high-surface area BaO/\( \gamma \)-Al\(_2\)O\(_3\) and \( \gamma \)-Al\(_2\)O\(_3\) catalysts [2,19,20], nitrate species are formed on NO\(_2\) adsorption on \( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) and BaO/\( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) surfaces at room temperature. In addition, comparing the intensities of the nitrate signals in the XPS data shown in Fig. 2 emphasizes the significantly higher NO\(_3\) uptake by the BaO/\( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) model storage system with respect to that of the \( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) support. Fig. 3 presents TPD results for the NO\(_2\)/\( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) adsorption system for various adsorbate coverages. A comprehensive discussion of these results and the complimentary XPS data can be found elsewhere [9]. TPD (Fig. 3) and XPS [9] experiments reveal that NO\(_2\) [21] adsorbs predominantly in a molecular fashion on the \( \theta \)-Al\(_2\)O\(_3\)/NiAl(100) surface at low temperatures by first occupying surface cationic sites in the monolayer, resulting in a perturbed first-order desorption behavior with a temperature desorption maximum at 144 K for \( \theta \)\(_{\text{NO}}\)\(_2\) = 1 monolayer (ML). After completion of the ML, formation of physisorbed NO\(_2\) multilayers is evident, which leads
Composition and desorption of these ionic NO species in the high-temperature region of the TPD curves. At 80 K (Fig. 4), the low-temperature region of the TPD spectra given in Figs. 3 and 4 qualitatively resembles that in Fig. 3, where for lower NO2 exposures, a single desorption feature grew in intensity with a perturbed first-order desorption behavior. The intensity of this feature eventually saturated with increasing NO2 coverage, resulting in a desorption maximum at 154 K. After the saturation of the 154 K feature, an additional desorption feature developed with intensity monotonically increasing with increasing NO2 coverage, without saturation. This second desorption feature showed a zero-order behavior, with a desorption maximum at 134 K for the highest NO2 coverage given in Fig. 4 [22]. Based on the discussion given above and the consistency between the TPD line shapes and the relative intensities of the 30 and 46-amu signals, as well as the N1s signal in the XPS measurements obtained under similar experimental conditions (not shown), we attribute the NO2 desorption from the BaO/θ-Al2O3/NiAl(100) surface at T < 250 K predominantly to molecular NO2 species, namely an NO2 monolayer desorbing at 154 K and physisorbed NO2/N2O4 multilayers with desorption maxima around 134 K.

As a quantitative comparison, it should be noted that in Fig. 4, the total integrated NO2 desorption signal at 80–850 K for the highest NO2 exposure used was about five times that of the saturation of the first chemisorbed NO2 layer on this surface.

Besides these noticeable resemblances between the low-temperature molecular NO3 desorption signals given in Figs. 3 and 4, significant dissimilarities also exist that should be addressed. Comparing the integrated TPD intensity for the molecular NO2 species just after saturation of the 144 K desorption feature in Fig. 3 and the 154 K feature in Fig. 4 shows that the integrated TPD intensity of the 154 K feature in Fig. 4 is about a factor of 2.5 greater than the 144 K feature in Fig. 3. This observation suggests that a significantly larger quantity of chemisorbed NO2, which desorbs reversibly in a molecular fashion during the TPD experiments, can be accommodated in the first adsorption layer on the BaO/θ-Al2O3/NiAl(100) surface with respect to that on the Ba-free θ-Al2O3/NiAl(100) surface. Multiple factors can be associated with this observation. First, the total surface area of the BaO/θ-Al2O3/NiAl(100) surface is presumably greater than the Ba-free θ-Al2O3/NiAl(100) surface due to the presence of 3D BaO clusters, as well as to the disordering of the alumina support surface during the BaO growth. Second, the higher affinity of BaO sites toward the NO2 species might allow a more densely packed chemisorbed NO2 layer on the BaO/θ-Al2O3/NiAl(100) surface. This is also in line with the fact that the 154 K feature in Fig. 4 shows a significantly broader FWHM compared with the 144 K feature in Fig. 3, implying a greater variety of adsorption sites for chemisorbed NO2 on the BaO/θ-Al2O3/NiAl(100) system. Due to the large surface coverage of BaO on the alumina thin film, a relatively small portion of the alumina support surface is expected to be exposed to the adsorbate gas. This assumption is also consistent with the relatively lower concentration of the strongly bound ionic NO3 species on the alumina sites of the BaO/θ-Al2O3/NiAl(100) surface, as discussed below.

NO2 desorption features that appear at T > 250 K in Fig. 4 provide valuable insights regarding the NO2 storage behavior of the BaO/θ-Al2O3/NiAl(100) model system. The inset in Fig. 4 shows a feature at 154 K and physisorbed NO2/N2O4 multilayers with desorption maxima around 134 K.
presents a detailed view of the high-temperature region of the TPD data. An asymmetric desorption signal is apparent at 250–550 K, coinciding with the desorption temperature of the NO\textsubscript{2} species that are desorbing from the \(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface as a result of the decomposition of nitrate species on the alumina sites (Fig. 3). Thus, we attribute the tailing desorption signal in the inset of Fig. 4 at 250–550 K to the desorption of nitrate species residing on the alumina sites of the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) model system. For the highest NO\textsubscript{2} exposure given in Fig. 4, the coverage of these alumina-bound nitrate species reaches about 35% of the molecular NO\textsubscript{2} species that are desorbing at 154 K in Fig. 4 [i.e., the saturation of the first NO\textsubscript{2} chemisorption layer on BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100)]. The lack of any \(\mathrm{O}_2\) desorption signal (Fig. 5) at 250–550 K also supports this assignment, because our previous TPD study [9] reported that nitrate desorption from the \(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface results in only NO(g) evolution, where remaining oxygen atoms either decorate surface defects or diffuse into subsurface region of the \(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) system. Apparently, diffusion of oxygen into subsurface creates complications in comparing the model system with a realistic counterpart that lacks such a bimetallic substrate. On the other hand, as we will discuss it in the latter part of this paper, the types of NO\textsubscript{2} species stored by the model system have a significant resemblance to the real NO\textsubscript{2} storage material. Therefore, despite the additional surface phenomena that can occur on the model system, there is a very good correlation between these two cases, which provides valuable detailed information regarding the NO\textsubscript{2} storage process in real NSR systems. The thermal window between 550 and 850 K in Fig. 4 also includes an NO desorption signal originating from the decomposition of nitrate species from the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface. The inset of Fig. 4 clearly shows that a new desorption feature, due to strongly bound nitrate species, starts to appear with desorption maxima that are shifting to higher temperatures (704–794 K) with increasing NO\textsubscript{2} exposures. Comparing Figs. 3 and 4 readily reveals that such a desorption feature is not associated with the nitrate species adsorbed on the alumina sites, because the TPD data presented in Fig. 3 lacks a similar strong desorption signal at \(T \geq 600\) K. Thus, we attribute the desorption features between 550 and 850 K to strongly bound nitrate species on the BaO domains of the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface. The TPD spectrum corresponding to the lowest NO\textsubscript{2} exposure used in the series of experiments given in the inset of Fig. 4 suggests that at low NO\textsubscript{2} surface coverage, chemisorbed NO\textsubscript{2} species are almost completely converted to strongly bound nitrates (either on the BaO or Al\textsubscript{2}O\textsubscript{3} domains) and diffuse onto the BaO domains, presumably forming Ba(NO\textsubscript{3})\textsubscript{2}, during the TPD experiment. Lack of a NO\textsubscript{2} desorption signal between 250 and 500 K for the lowest NO\textsubscript{2} exposure used in Fig. 4 also indicates that, due to the availability of a large number of strongly binding (and also thermodynamically favorable) BaO sites, nitrates formed on the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface do not populate alumina domains, but rather diffuse onto the BaO domains during the temperature ramp. However, with increasing NO\textsubscript{2} exposure, BaO domains start to be more densely populated with nitrate species, and the nitrate diffusion on the BaO domains and/or Ba(NO\textsubscript{3})\textsubscript{2} formation becomes kinetically hindered during the rapid temperature ramp of the TPD experiment. Therefore, some of the nitrate species start to populate less strongly binding adsorption sites on the alumina surface (250–550 K). Furthermore, due to the increasing nitrate concentration on the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface, at higher NO\textsubscript{2} exposures, not all of the adsorbed NO\textsubscript{2} species can be converted into nitrates, and some of the adsorbed NO\textsubscript{2} molecules begin to desorb reversibly in a molecular fashion at \(T < 250\) K. Therefore, it can be argued that during the TPD experiments for very low NO\textsubscript{2} exposures, formation and surface diffusion of nitrate species are not kinetically limited, and the nature of the NO\textsubscript{2} species on the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) model system is dictated predominantly by thermodynamics. The opposite is true for higher NO\textsubscript{2} exposures; where, due to blocking of the active catalyst sites by chemisorbed NO\textsubscript{2} or nitrate species, not all of the adsorbed NO\textsubscript{2} molecules can be converted into the thermodynamically stable nitrate species, and a large portion of the adsorbed NO\textsubscript{2} molecules desorb reversibly in a molecular fashion before being converted into nitrates during the rapid temperature ramp in TPD. It also should be mentioned that the relatively lower concentration of nitrates on the alumina sites of the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) system (i.e., 250–550 K signal in Fig. 4) is consistent with the high BaO surface coverage, preventing direct exposure of most of the alumina surface sites to the gas-phase adsorbate.

The comparison between Figs. 3 and 4 clearly illustrates the drastic improvement in the NO\textsubscript{2} storage capacity of the model catalyst system due to the presence of a BaO-containing catalyst component. The integrated TPD intensity (between 550 and 850 K) corresponding to the strongly bound nitrate species on the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface, for the highest NO\textsubscript{2} exposure used in Fig. 4, is about 5 times greater than the nitrate desorption signal from the \(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface (between 250 and 650 K) given in Fig. 3. This is in very good agreement with previous studies on high-surface area catalysts in which the BaO (20 wt\%/γ-Al\textsubscript{2}O\textsubscript{3}) system was reported to have an order of magnitude higher NO\textsubscript{2} storage capacity with respect to the γ-Al\textsubscript{2}O\textsubscript{3} support material [2]. From a thermodynamic standpoint, the stability of the stored nitrate species are significantly increased as a result of the presence of baria sites in the model catalyst composition. It is also apparent in Fig. 4 that, due to the kinetically limited nitrate formation on the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) surface at high NO\textsubscript{2} exposures, the integrated TPD intensity of the NO\textsubscript{2} desorption feature within 704–794 K saturates with increasing NO\textsubscript{2} exposures and eventually settles at a value about 75% of the saturation coverage of the first chemisorbed NO\textsubscript{2} layer (154 K in Fig. 4) on this surface. However, as we show below, the saturation of the nitrate desorption signal at 704–794 K in the inset of Fig. 4 does not imply that the maximum nitrate uptake by the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) model catalyst is reached.

This is illustrated in a series of TPD experiments presented in Fig. 5. To use the full NO\textsubscript{2} storage potential of the BaO/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}/NiAl(100) model system, a given exposure of NO\textsubscript{2} (corresponding to the maximum exposure used for the TPD series in Fig. 4) was dosed on the catalyst surface at 80 K, and the
sample was subsequently annealed at 475 K in UHV for 5 min to convert chemisorbed NO₂ species into nitrates. These low-temperature NO₂ dosing and subsequent annealing steps were repeated various times before the TPD data in Fig. 5 were acquired. The spectra labeled c, f, i were obtained after a single NO₂ adsorption at 80 K (without further annealing or additional NO₂ dosing) while spectra b, e, h and a, d, g were obtained after three and six NO₂ dosing (80 K) and annealing (475 K) sequences, respectively. (a–c) 30-amu signal, (d–f) 32-amu signal, (g–i) 46-amu signal.

Based on the foregoing observations, it is apparent that the nitrate decomposition on the baria domains of the BaO/Al₂O₃/NiAl(100) model system can follow different pathways. The O₂ and NO desorption signals at 768 and 798 K suggest that the nitrate species that decomposed at high temperatures (798 K) desorbed via the following pathway:

\[
\text{Ba(NO}_3\text{)}_2 \rightarrow 2\text{NO(g)} + \frac{3}{2}\text{O}_2(\text{g}) + \text{BaO}.
\]

(1)

It should be noted that the concentration of these nitrate species does not saturate readily with multiple NO₂ loadings, in contrast to other baria-related nitrate species that desorb at lower temperatures (620 K), with concentration quickly reaching a constant level after the third NO₂ loading/annealing sequence. The desorption mechanism for the low-temperature (620 K) baria-related nitrate species seems to follow a different pathway, because neither O₂ nor NO₂ desorption was observed at \(T < 700\, \text{K}\). One possible decomposition mechanism for these nitrate species could be

\[
\text{Ba(NO}_3\text{)}_2 \rightarrow \text{BaO} + 2\text{NO}_2(\text{ads}) + \text{O(ads)},
\]

(2)

\[
\text{NO}_2(\text{ads}) \rightarrow \text{NO(g)} + \text{O(ads)},
\]

(3)

\[
\text{O(ads)} \rightarrow \text{O(subsurface)},
\]

(4)

where the nitrate species could dissociate to produce atomic oxygen and a metastable NO₂ (molecular NO₂ and/or a nitrite) species, which further decompose to yield NO(g) and adsorbed atomic oxygen. Subsequently, adsorbed oxygen atoms can diffuse into the subsurface region and oxidize the Al⁰ sites of the NiAl(100) bimetallic substrate (resulting in thickening of the alumina film [9]) or decorate the surface defects of the alumina or BaO domains.

Comparing the NO₂ uptake results for the BaO/Al₂O₃/NiAl(100) model system with a realistic high-surface area catalyst reveals very important similarities between these two systems. Fig. 6 presents such a comparison, where the 30-amu
signal was monitored in TPD after NO2 adsorption on a BaO (20 wt%)/γ-Al2O3 high-surface area material (Fig. 6a) [19] and the BaO/θ-Al2O3/NiAl(100) model system studied here (Fig. 6b). The most important aspect of Fig. 6 is the qualitative agreement between these two systems regarding the thermal window of NO2 release (i.e., 500 K < T < 800 K). Therefore, the BaO/θ-Al2O3/NiAl(100) model system seems to be a promising platform for studying molecular-level phenomena that occur on the complex industrial counterpart. The broad desorption feature in Fig. 6a at T < 500 K was attributed to weakly bound molecular NO2 species on the BaO (20 wt%)/γ-Al2O3 high-surface area system [19], whereas the asymmetric desorption feature at T > 550 K was assigned to the nitrate species associated with the baria domains. As described in detail in a previous report [19], the NO desorption signal in Fig. 6a can be deconvoluted into two components (low and high temperature ones). The feature with a desorption maximum at 660 K was assigned to the nitrate decomposition originating from surface nitrates on the baria domains of BaO (20 wt%)/γ-Al2O3, which decompose to yield NO2(g) and O2(g) as follows:

$$\text{Ba(NO}_3\text{)}_2 \rightarrow \text{BaO} + 2\text{NO}_2\text{(g)} + \text{O}_2\text{(g)},$$  

(5)

$$\text{O(ads)} + \text{O(ads)} \rightarrow \text{O}_2\text{(g)}.$$  

(6)

The other component (high temperature feature in Fig. 6) obtained after the deconvolution of the total 30-amu signal (black curve) was suggested to be [19] due to the decomposition of bulk nitrates, or Ba(NO3)2, formed in the subsurface region of the BaO domains. These species were found to desorb as in reaction (1) by yielding NO2(g) and O2(g). This previously proposed model [19] regarding the presence of surface and bulk nitrates on the BaO (20 wt%)/γ-Al2O3 high-surface area material is in good agreement with our current results on the BaO/θ-Al2O3/NiAl(100) model system, where at least two different types of baria-related nitrate decomposition signals were detected in TPD (Figs. 5 and 6) with desorption maxima in good correlation with that of the high-surface area counterpart. Furthermore, the decomposition products appearing at T > 768 K are in the form of NO(g) + O2(g), in line with the decomposition products of bulk nitrates of the BaO (20 wt%)/γ-Al2O3 high-surface area material. Similarly, the 620 K desorption feature for the model system given in Figs. 5 and 6, whose total intensity readily saturates after a certain NO2 exposure, is consistent with a surface nitrate assignment. It can be argued that although decomposition of surface nitrates can produce NO2 on both model and high-surface area systems, the fate of the produced NO2 species differs in these two cases—molecular decomposition as in reaction (5) and decomposition as in reactions (2) and (3). Furthermore, a previous study [12] found that peroxide species can also exist on the BaO/θ-Al2O3/NiAl(100) model system in the presence of an oxidizing agent such as O2. Thus, there might be alternative sources of oxygen desorption in addition to that shown in reaction (6), which may include decomposition of BaO2 species into BaO by releasing oxygen.

The influence of thermal aging on the NO2 uptake of a model NSR catalyst was studied by preparing a BaO/θ-Al2O3/NiAl(100) surface as described in Section 2 and then annealing at 1100 K in UHV for 15 min. Our previous results [12] on the thermal behavior of the BaO/θ-Al2O3/NiAl(100) surface in UHV suggest that the baria component of the model system is not stable above ~1000 K. The primary effect of a high-temperature (T > 1000 K) treatment is the decomposition of BaO domains to yield metallic Ba, which desorbs from the surface, leading to a loss of surface barium coverage. In addition to these processes, some other thermally induced surface phenomena, such as interdiffusion of BaO and alumina components of the model catalyst surface to yield BaAl2O4-like (barium aluminate) domains, are also possible.

Fig. 7 presents the results of TPD experiments performed by exposing a BaO/θ-Al2O3/NiAl(100) surface preannealed at 1100 K to various NO2 exposures. The highest NO2 exposure used in Fig. 7 was about two times greater than that used in Fig. 4. Comparing the low-temperature region (T < 250 K) of the TPD spectra in Fig. 7 to that in Fig. 4 demonstrates significantly broadened desorption signals corresponding to the molecular NO2 states in Fig. 7, indicating the presence of additional adsorption sites. Besides the physisorbed NO2/N2O4 multilayer desorption feature at ~133 K, two extra features at 156 and 180 K, corresponding to additional NO2 chemisorption states, are visible. At 250–600 K, NO desorption associated with the nitrates on alumina sites of the model system is observed. This is followed by an NO2 desorption signal associated with nitrates on the baria domains, leading to an NO desorption maxima at 730–808 K. Fig. 7 clearly shows that the relative NO2 uptake by the alumina and baria domains of the BaO/θ-Al2O3/NiAl(100) surface preannealed at 1100 K was significantly different than a freshly prepared model system (Fig. 4). The integrated TPD intensity corresponding to nitrates on the baria component of the model catalyst surface for the highest NO2 exposure used in Fig. 7 was only about 30% of the baria-related NO2 signal in Fig. 4. This observation clearly shows that although a significantly higher NO2 exposure was used in Fig. 7, due to the reduced NO2 storage...
capacity of the thermally aged model system, a smaller quantity of NO$_3$ was stored by the baria component. In contrast, comparing the integrated TPD intensities associated with nitrate species on the alumina sites of the model surfaces in Figs. 3 ({$\gamma$}-Al$_2$O$_3$/NiAl(100)), 4 (fresh BaO/$\gamma$-Al$_2$O$_3$/NiAl(100)), and 7 (BaO/$\gamma$-Al$_2$O$_3$/NiAl(100) preannealed at 1100 K) clearly shows that the surface coverage of the nitrates on alumina sites in Fig. 7 was about three times greater than in Fig. 4 and six times greater than in Fig. 3. This observation is consistent with a decrease in the surface coverage of BaO domains after annealing at 1100 K, resulting in uncovering of the alumina sites. Furthermore, an increase in the overall surface area of the model storage system may be responsible for the larger nitrate population associated with the alumina sites in Fig. 7. It is also worth mentioning that in TPD experiments conducted after multiple NO$_2$ loadings and release cycles at $T \leq 850$ K, very similar NO$_3$ desorption profiles were seen. However, the NO$_3$ uptake of the model system per given dose of NO$_2$ seemed to decrease very slowly after multiple cycles, similar to the catalytic aging features on extended operation in real systems. In these model systems, the slow storage capacity decrease may originate from the loss of active BaO storage phase (by either desorption or interdiffusion with the thin alumina film).

4. Summary and conclusions

In this work we have investigated the NO$_3$ uptake of various model NO$_3$ storage materials [i.e., $\gamma$-Al$_2$O$_3$/NiAl(100), BaO/$\gamma$-Al$_2$O$_3$/NiAl(100) and thermally-aged BaO/$\gamma$-Al$_2$O$_3$/NiAl(100) at 1100 K] via NO$_2$ adsorption using XPS and TPD techniques. The primary goal of this contribution was to demonstrate the validity of the proposed model system discussed here in studying the NO$_3$ chemistry on these model NO$_3$ storage materials. In our ongoing efforts, we are concentrating on the details of NO$_3$ uptake and release processes on these model storage systems using a wide array of analytical tools (RAIRS, XPS, ISS, TPD, and scanning probe techniques).

The experimental results of this work can be summarized as follows:

(a) For all of the surfaces listed above, NO$_2$ adsorption at $T < \sim 200$ K led to predominantly molecular NO$_x$ species (NO$_2$ and N$_2$O$_4$) on the catalyst surfaces, whereas by 300 K, these molecular NO$_x$ species either reversibly desorbed or were converted into nitrates.

(b) Nitrate species on the alumina domains of the BaO/$\gamma$-Al$_2$O$_3$/NiAl(100) model catalyst desorbed at 250–600 K, whereas nitrates residing on the baria domains desorbed at $T > 600$ K, indicating the greater adsorption energy and the improved stability of nitrates in the latter case.

(c) BaO/$\gamma$-Al$_2$O$_3$/NiAl(100) model catalysts showed significantly enhanced NO$_2$ adsorption and NO$_x$ storage (nitrate formation) capacity with respect to the $\gamma$-Al$_2$O$_3$/NiAl(100) support material.

(b) At least two different types of nitrate species were found to exist on the baria domains of the BaO/$\gamma$-Al$_2$O$_3$/NiAl(100) model NO$_3$ storage material, which decomposed at 620 and 795 K with dissimilar desorption products [NO(g) vs NO$_2$(g) + O$_2$(g)]. Although the intensity of the nitrate signal at 620 K readily saturated with multiple NO$_2$ loadings before the TPD experiments, the intensity of the 795 K feature continued to grow. These observations are consistent with a previously proposed model in the literature in which NO$_3$ desorption signals at 660 and 780 K were attributed to the presence of surface and bulk nitrates on the baria domains of the BaO (20 wt%)/$\gamma$-Al$_2$O$_3$ high-surface area catalyst.

(e) Thermal aging of BaO/$\gamma$-Al$_2$O$_3$/NiAl(100) at 1100 K resulted in a significant reduction of the NO$_3$ uptake by the baria domains of the model catalyst due to Ba evaporation and a corresponding decrease in surface Ba coverage or Ba interdiffusion into the alumina matrix to form BaAl$_2$O$_4$. In contrast, the weakly bound nitrate population was significantly larger on the alumina-like sites of the thermally aged catalyst than on a fresh BaO/$\gamma$-Al$_2$O$_3$/NiAl(100) model catalyst or $\gamma$-Al$_2$O$_3$/NiAl(100) support material. This can be explained by an increased surface area of the alumina sites due to morphological changes.

Acknowledgments

The authors gratefully acknowledge the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences for the support of this work. The research described in this paper was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the DOE Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is operated for the DOE by Battelle Memorial Institute under contract DE-AC05-76RL01830. The authors thank Dr. Zdenek Dohnálek for helpful discussions.

References


[18] Note that the feature at 397 eV is a background artifact originating from the $\theta$-Al$_2$O$_3$/NiAl(100) substrate.


[21] As discussed in detail in Ref. [9], it is well known that NO$_2$ fragments into lower mass components during its ionization in the QMS, and 30 amu (NO) is dominant. Therefore, the relative intensities of the 46- and 30-amu signals as well as the similarity between the line shapes clearly indicate that the 30-amu desorption features observed for $T < 180$ K in this work are predominantly due to the fragmentation of molecular NO$_2$ in the QMS whereas the 30-amu signal desorbing at $T > 180$ K is attributed to ionic species that thermally decompose to yield gas-phase NO.

[22] For some of the TPD traces given in Fig. 4, intensities of the 134 K features are cut-off, because of the saturation of the QMS multiplier that is operated at a higher sensitivity setting in these TPD measurements.