

Water-induced bulk $\text{Ba}(\text{NO}_3)_2$ formation from NO_2 exposed thermally aged $\text{BaO}/\text{Al}_2\text{O}_3$

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Abstract

Phase changes in high temperature treated ($>900^\circ\text{C}$) 8 or 20 wt% BaO supported on $\gamma\text{-Al}_2\text{O}_3$ model lean NO_x trap (LNT) catalysts, induced by NO_2 and/or H_2O adsorption, were investigated with powder X-ray diffraction (XRD), solid state ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, and NO_2 temperature programmed desorption (TPD) experiments. After calcination in dry air at 1000°C , the XRD and solid state ^{27}Al MAS NMR results confirm that stable surface BaO and bulk BaAl_2O_4 phases are formed for 8 and 20 wt% BaO/ Al_2O_3 , respectively. Following NO_2 adsorption over these thermally treated samples, some evidence for nanosized $\text{Ba}(\text{NO}_3)_2$ particles are observed in the XRD results, although this may represent a minority phase. However, when water was added to the thermally aged samples after NO_2 exposure, the formation of bulk crystalline $\text{Ba}(\text{NO}_3)_2$ particles was observed in both samples. Solid state ^{27}Al MAS NMR is shown to be a good technique for identifying the various Al species present in the materials during the processes studied here. NO_2 TPD results demonstrate a significant loss of uptake for the 20 wt% model catalysts upon thermal treatment. However, the described phase transformations upon subsequent water treatment gave rise to the partial recovery of NO_x uptake, demonstrating that such a water treatment of thermally aged catalysts can provide a potential method to regenerate LNT materials.

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1. Introduction

Increasing concern about the availability and cost of fuels, as well as high rates of CO_2 emissions provides strong incentives for more general application of lean burn and diesel engines with superior fuel efficiency. However, the removal of nitrogen oxides (NO_x) from these engines remains a challenge since conventional three-way catalysts are not applicable in their highly oxidizing exhaust. Lean NO_x traps (LNTs), also known as NO_x adsorber or NO_x storage-reduction catalysts, were introduced by Toyota in the mid-1990s and are considered one of the most promising technologies for removing NO_x [1,2]. The concept of the LNT relies on the switching of the engine operating conditions between lean (excess of O_2) and rich

cycles (excess of reductants) [3]. During the lean cycle, NO_x is oxidized over Pt and stored as nitrates on/in the storage material. Then, periodically, the engine is operated under rich conditions to provide a stoichiometric to rich exhaust that includes reductant (hydrocarbon, CO, and/or H_2) for reaction with the stored NO_x to produce N_2 . LNT catalysts typically consist of 1–2 wt% of precious metal (Pt and Rh) and 10–20 wt% of a storage material (commonly BaO and/or K) dispersed on an Al_2O_3 support.

Although there have been extensive studies of the NO_x storage/reduction mechanisms [4–8], a fundamental question concerning which barium phases are most favorable for storing and releasing NO_x still remains. Significantly, it is widely reported that BaO and Al_2O_3 react at high temperature ($>800^\circ\text{C}$) to form an aluminate phase, BaAl_2O_4 [9–17]. However, there is considerable disagreement about the effectiveness of the BaAl_2O_4 phase for NO_x storage. Some researchers [11,17] conclude that an observed decrease in NO_x storage efficiency can be ascribed to a loss of the optimum barium-containing storage component due to the formation of

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BaAl₂O₄. On the other hand, Hodjati et al. [13,14] observed better NO_x sorption performance for BaAl₂O₄ than for BaO and/or BaCO₃. Thus, they proposed that the formation of a BaAl₂O₄ phase should not directly inhibit NO_x trapping, and attributed these results to the lack of interaction between BaAl₂O₄ and CO₂.

We have previously described the effect of barium loading on BaAl₂O₄ formation for various BaO/Al₂O₃ samples [18]. An 8 wt% BaO/Al₂O₃ sample showed essentially no detectable morphological changes upon high temperature thermal treatment, while BaAl₂O₄ formation occurred readily for a 20 wt% one. These results led us to the conclusion that a surface (monolayer) BaO phase is stable to high temperature thermal treatment, while a more ‘bulk-like’ BaO phase provides the source of Ba for BaAl₂O₄ formation.

Meanwhile, Graham et al. [9] of Ford Motor Company reported an interesting phase transformation from BaAl₂O₄ to BaCO₃ when a thermally treated BaO/Al₂O₃ sample was contacted with water at room temperature. In addition, our group [10] found that other barium phases, such as highly dispersed BaCO₃ and BaO phases, were similarly transformed to a crystalline BaCO₃ phase, somewhat segregated from the alumina support material, upon room-temperature water treatment. This process turned out to be largely dependent on the extent of water exposure.

Recently, Gorte and coworkers [19] reported the formation of a bulk Ba(NO₃)₂ phase when NO₂ is adsorbed onto both moderate (~500 °C) and high temperature (≥600 °C) calcined BaO/Al₂O₃ materials, the latter containing BaAl₂O₄ as the primary Ba-containing phase observable in XRD. These authors further claimed that BaO and BaAl₂O₄ appear to be equally effective as NO_x storage materials, both being able to fully utilize the Ba content to form stoichiometric Ba(NO₃)₂ upon NO₂ exposure at room temperature. Although the reaction of BaAl₂O₄ with NO₂ and O₂ to form Ba(NO₃)₂ is exothermic [19], to our knowledge this was the first report that such a dramatic phase change could occur upon room temperature NO₂ adsorption. However, the authors do acknowledge possible uncharacterized effects of H₂O on their results.

With respect to possible effects of water on Ba-containing phases during NO_x uptake and release in LNT catalysts, Baiker and coworkers [20,21] very recently reported interesting phase changes for a high temperature calcined Pt-Ba/alumina material. The XRD observable Ba phase studied initially consisted primarily of BaAl₂O₄. These authors observed little if any changes in the XRD pattern following 4 h of reaction with NO₂ in a water-saturated gas mixture at 400 °C. However, clear evidence for the formation of Ba(NO₃)₂ was present in the XRD pattern after reaction with the same gas mixture at 300 °C. Furthermore, diffraction peaks due to BaAl₂O₄ disappeared after reaction at 30 °C where instead large and sharp peaks for Ba(NO₃)₂ now dominated the XRD pattern [20,21].

Considering the importance of barium phases as active sites for NO_x storage, we investigated these processes in more detail. In this paper, we address the effect of NO₂ adsorption and subsequent water treatment on the phase changes of BaO(x)/Al₂O₃ (x = 8 and 20 wt%) materials by using XRD and solid

state ²⁷Al MAS NMR. Furthermore, we followed the changes in NO_x adsorption capacity of the resulting materials in TPD experiments subsequent to NO₂ exposure at RT. Solid state ²⁷Al MAS NMR proved to be an especially useful technique for observing the changes of the chemical environment around aluminum atoms. The main conclusions based on these results are that bulk nitrate formation is not observed during NO₂ adsorption onto a BaAl₂O₄ phase, contrary to Gorte’s results; however, the treatment of the NO₂ pre-adsorbed, thermally aged sample with liquid water at room temperature facilitates the formation of bulk barium nitrates. This phenomenon is very similar to what has been previously reported [9,10] about the effect of water on Ba-containing phase changes in BaO/Al₂O₃ materials. We also find that BaAl₂O₄ phase formation resulting from high temperature calcination leads to a significant reduction in room temperature NO₂ uptake. Finally, we observed the partial recovery of the NO₂ uptake after the water-induced phase transformations, suggesting that such a water treatment might represent a practically effective method of regenerating certain thermally deactivated LNT samples in real systems.

2. Experimental

The BaO/Al₂O₃ samples were prepared by the incipient wetness method, using an aqueous Ba(NO₃)₂ solution (Aldrich) and a γ-alumina support (200 m²/g, Condea) to yield nominal 8 and 20 wt% BaO-containing samples. After impregnation, the catalysts were dried at 120 °C and then ‘activated’ via calcination at 500 °C in 20% O₂ in N₂ for 2 h. To investigate effects of high temperature treatment on the structure and NO_x adsorption properties of the samples, calcinations at 1000 °C were carried out in a muffle furnace for 10 h. The samples were sealed with parafilm and stored in a dry chamber to minimize carbonate formation.

XRD analysis was carried out on a Philips PW3040/00 X’Pert powder X-ray diffractometer using the Cu Kα1 radiation (λ = 1.5406 Å) in step mode between 15 and 75° 2θ with a step of 0.02°. Data analysis was accomplished using JADE (Materials Data Inc., Livermore, CA) as well as the Powder Diffraction File database (2003 Release, International Center for Diffraction Data, Newtown Square, PA).

Solid state ²⁷Al NMR spectra were acquired on a Varian/Chemagnetic CMX Infinity 300 MHz instrument, equipped with Varian/Chemagnetics 7.5 mm HX MAS probe operating at a spectral frequency of 78.2 MHz. About ~0.3 g of previously pretreated samples were transferred into a gastight rotor (7.5 mm o.d.), and the rotor mounted into the NMR spectrometer. All ²⁷Al MAS NMR spectra were externally referenced to an aqueous solution of Al(NO₃)₃ at 0 ppm. All spectra were obtained at a sample spinning rate of 5 kHz and using 1 s recycle delay.

TPD experiments following NO₂ adsorption were performed in a fixed bed microcatalytic quartz reactor. The detailed procedure is presented in Fig. 1. A gas mixture of 0.5% NO₂/He (99.999% Purity, Matheson) was passed over 100 mg of freshly calcined BaO/Al₂O₃ samples until the NO₂ level returned to its

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