

## The nature of nitrate species on BaO/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> storage/reduction materials

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### Introduction

Operating internal combustion engines under net oxidizing conditions is desirable to increase fuel efficiency. This mode of engine operation, however, makes traditional three-way catalysts (TWC) ineffective for the reduction of NO<sub>x</sub> in the exhaust gas stream. In the last decade new approaches toward NO<sub>x</sub> reduction in oxygen-rich environments have been sought. The three most promising technologies considered to date are non-thermal plasma assisted NO<sub>x</sub> reduction, urea selective catalytic reduction (SCR), and NO<sub>x</sub> storage/reduction [1]. In NO<sub>x</sub> storage/reduction catalysis an active oxide phase (primarily alkaline or alkaline earth oxides) is used for the uptake of NO<sub>2</sub> formed on the precious metal (PM) component of these catalysts. The thus formed nitrates are released in a subsequent brief rich cycle and converted to N<sub>2</sub> on the PM, similarly to TWC. The fundamentals of NO<sub>x</sub> uptake/release processes have been studied extensively on catalysts based on BaO on an alumina support. Studies using vibrational spectroscopic techniques (IR and Raman) and temperature programmed desorption (TPD) have aimed at understanding the chemical nature of the NO<sub>x</sub> species formed on/in these catalysts [2-3]. The formation of different NO<sub>x</sub> species on the active BaO phase has clearly been shown; however, their assignments were not unambiguous. For example, in TPD studies two distinct NO<sub>x</sub> desorption features were reported; one at lower temperature (release of NO<sub>2</sub>), and another at higher temperature (desorption of NO+O<sub>2</sub>). The origin of these two features, however, has not been explained.

In this presentation, we will report on the nature of nitrate species formed on BaO/Al<sub>2</sub>O<sub>3</sub> (BaAl) NO<sub>x</sub> storage/reduction materials studied by FTIR, TPD, <sup>15</sup>N solid state (SS) NMR, and time resolved X-ray diffraction (TR-XRD) techniques. The two types of nitrates we observe are characterized with FTIR and <sup>15</sup>N SS NMR, and the changes in the morphology of the active BaO phase is followed by TR-XRD.

### Materials and Methods

BaO/Al<sub>2</sub>O<sub>3</sub> catalysts (8 and 20wt% BaO) were prepared on a γ-Al<sub>2</sub>O<sub>3</sub> support by incipient wetness using an aqueous Ba(NO<sub>3</sub>)<sub>2</sub> solution. Prior to NO<sub>2</sub> uptake experiments, the samples were calcined at 773K in flowing air. The FTIR experiments were carried out in transmission mode using a Mattson Research Series spectrometer operated at 4 cm<sup>-1</sup> resolution, and each spectrum was an average of 64 scans. The TPD experiments were conducted in a plug flow quartz reactor. After NO<sub>2</sub> saturation, the sample was heated linearly in a He flow, and the NO<sub>x</sub> released was analyzed by a chemiluminescence NO<sub>x</sub> analyzer. <sup>15</sup>N solid-state NMR spectra were acquired on a Varian/Chemagnetics CMX Infinity 300 MHz instrument, equipped with a Varian/Chemagnetics 7.5 mm HX MAS probe operating at a spectral frequency of 30.40651 MHz. The chemical shifts were referenced to that of <sup>15</sup>NH<sub>4</sub>Cl. The TR-

XRD experiments were carried out at beam line X7B of the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory.

### Results and Discussion

FTIR: After NO<sub>2</sub> adsorption at 300K, absorption features of both bidentate nitrates and ionic (bulk) nitrates are seen. The bidentate/ionic nitrate peak ratio decreases with BaO coverage. The peak intensities of surface nitrates increase in 8wt%-BaAl, while those of the ionic nitrates decrease upon NO<sub>2</sub> uptake at 673K. In 20wt%-BaAl at 673K the bulk nitrate features increase.

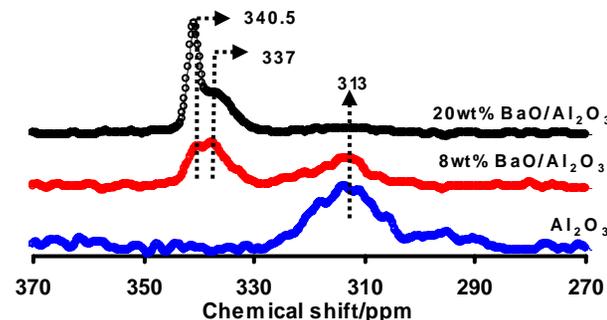
TPD: The NO<sub>2</sub>/NO desorption peak intensity ratio changes with BaO coverage; the lower temperature NO<sub>2</sub> desorption peak intensity is similar for the 8 and 20wt%-BaAl, while the intensity of the high temperature feature is much higher in 20wt%-BaAl. The lower temperature desorption peak scales with the surface area of the catalyst.

<sup>15</sup>N SS NMR (Fig. 1): NMR features of nitrates on Al<sub>2</sub>O<sub>3</sub> (313ppm) (Al<sub>2</sub>O<sub>3</sub> surface) and bulk (340.5ppm) BaO are observed. The intensity of the bulk nitrate surface is much higher in the 20wt%-BaAl than in the 8wt%-BaAl.

TR-XRD: Nano-sized Ba(NO<sub>3</sub>)<sub>2</sub> particles form upon NO<sub>2</sub> uptake at 300K from BaO nano particles. During 573K adsorption the Ba(NO<sub>3</sub>)<sub>2</sub> particle size increases significantly.

### Significance

The results of this study clearly demonstrate the formation of a monolayer BaO film on the alumina surface that adsorbs NO<sub>2</sub> as bidentate nitrate, and responsible for the lower temperature TPD NO<sub>2</sub> feature. The BaO present in the material in excess of a monolayer forms nano-sized BaO, and converts into 3-D Ba(NO<sub>3</sub>)<sub>2</sub> crystals that decompose as NO+O<sub>2</sub> in TPD. The morphology changes are also evident during NO<sub>2</sub> uptake and release.



**Figure 1.** <sup>15</sup>N SS NMR spectra for Al<sub>2</sub>O<sub>3</sub>, 8 and 20wt%-BaO/Al<sub>2</sub>O<sub>3</sub> materials obtained after saturation with NO<sub>2</sub> at 673K.

### References

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