

NO₂ Adsorption on BaO/Al₂O₃: The Nature of Nitrate Species

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Temperature programmed desorption, infrared spectroscopy, and ¹⁵N solid state NMR spectroscopy were used to characterize the nature of the nitrate species formed on Al₂O₃ and BaO/Al₂O₃ NO_x storage/reduction materials. Two distinctly different nitrate species were found: surface nitrates that are associated with a monolayer BaO on the alumina support, and a bulk-like nitrate that forms on this thin BaO layer. The surface nitrates desorb as NO₂ at lower temperatures than do the bulk-like nitrates, which decompose as NO+O₂ at higher temperatures. The amount of NO_x stored in the monolayer nitrate is proportional to the surface area of the catalyst, while that in the bulk nitrate increases with BaO coverage.

Introduction

The drive to develop more fuel efficient vehicles has resulted in the introduction of “lean-burn” engine technology, in which the engine is operated under net oxidizing conditions. The removal of harmful exhaust gases, in particular the reduction of NO_x from these engines, is a great challenge to the catalysis community. Traditional three-way catalysts are ineffective for the reduction of NO_x under oxidizing conditions, due to the high oxidizing power of the noble metal components of these catalysts. Therefore, new approaches for NO_x reduction have been sought and developed in the past decade. The three most promising technologies are nonthermal plasma-assisted NO_x reduction, urea selective catalytic reduction (SCR), and NO_x storage/reduction (NSR). NO_x storage/reduction catalysis is based on the ability of BaO to reversibly form Ba(NO₃)₂ under lean engine operating conditions, and release the stored NO_x in the hydrocarbon rich catalytic cycle.¹ The storage of NO_x on alumina-supported BaO has been studied extensively in the past several years, using primarily vibrational spectroscopic techniques and temperature-programmed desorption (TPD).^{2–6} During thermal decomposition of the NO_x-saturated BaO/Al₂O₃ catalysts, two distinct desorption features were commonly seen: at lower temperature NO₂ was observed to evolve only, while at higher temperature the desorption of NO was accompanied by the evolution of O₂.^{2,7,8} Despite the significant efforts aimed at understanding the NO_x storage–release processes, the origin of the two NO_x desorption features observed in temperature-programmed studies has not been addressed. In this communication we provide an explanation for the appearance of these two TPD features and the variations of their relative intensities with varying BaO content. The results of this combined FTIR, TPD, and ¹⁵N solid state NMR study reveals the formation of a unique Ba(NO₃)₂ monolayer strongly interacting with the Al₂O₃ support, and upon decomposition releases NO₂ only. BaO, in excess of a monolayer, forms bulk-like Ba(NO₃)₂ in NO₂ adsorption and decomposes by releasing NO+O₂.

Experimental Section

The BaO/Al₂O₃ NSR catalysts were prepared by the incipient wetness method, using an aqueous Ba(NO₃)₂ solution and a 200 m²/g γ-alumina support. After impregnation, the catalysts were dried at 395 K and then calcined at 773 K in flowing air for 2 h. This procedure ensured the decomposition of almost all the Ba(NO₃)₂ phase into BaO. The TPD experiments were carried out in a fixed-bed microcatalytic quartz reactor. Calcined catalyst samples of 100 mg were pretreated at 473 K for 1 h and cooled to room temperature in flowing He prior to NO₂ adsorption experiments. All the NO₂ adsorption experiments were conducted at 300 K using a 0.5% NO₂/He (99.999% purity, Matheson) gas mixture. After saturation, the catalysts were purged with He for 2 h and then the sample temperature was raised in a temperature programmed fashion at 8 K/min to 1073 K, while the evolved NO_x gases were monitored with a chemiluminescence NO_x analyzer (42C, Thermo Environmental).

The infrared measurements were carried out in transmission mode, using a Mattson Research Series spectrometer operating at 4 cm^{−1} resolution. Prior to each spectral series acquisition, a background spectrum was taken of the clean, adsorbate-free sample. The infrared cell was a 2 3/4 in. six-way stainless steel cube equipped with CaF₂ windows. The cell is connected to a gas handling/pumping station and through both leak and gate valves to a mass spectrometer (UTI 100C). The catalyst sample was pressed onto a fine tungsten mesh, which, in turn, was mounted onto a copper sample holder assembly attached to ceramic feedthroughs of a 2 3/4 in. flange. This set up allowed heating of the samples to ~1000 K and cooling to cryogenic temperatures. The sample temperature was monitored through a chromel/alumel thermocouple spot-welded to the top center of the tungsten mesh. In a typical experiment, the sample held at a given temperature was exposed to NO₂ and the changes in the IR spectra were followed as a function of time. After no changes were seen (less than 10 min) the IR cell was evacuated at 300 K and a spectrum was acquired.

¹⁵N solid-state NMR spectra were acquired on a Varian/Chemagnetics CMX Infinity 300 MHz instrument, equipped

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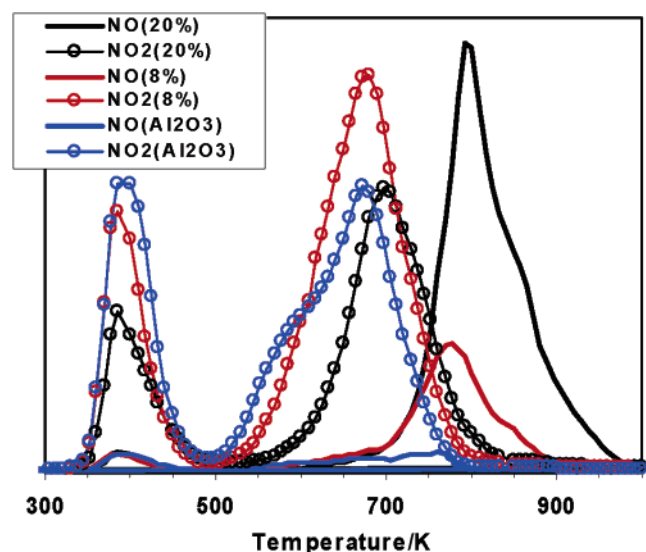


Figure 1. TPD spectra from Al_2O_3 and 8 wt % and 20 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ after NO_2 saturation at 300 K.

with a Varian/Chemagnetics 7.5 mm HX MAS probe operating at a spectral frequency of 30.40651 MHz. In the in-situ NMR cell, 0.5 g of catalyst sample was pretreated under vacuum ($<1 \times 10^{-7}$ Torr) at 773 K for 2 h. NO_2 saturation of the samples was conducted at 673 K. The NO_2 -saturated samples were transferred into the gastight rotor (7.5 mm o.d.) for solid state ^{15}N NMR measurements. All ^{15}N NMR spectra were externally referenced to ^{15}N -ammonium chloride at 0 ppm. All spectra were obtained spinning at 5 kHz and using a 10 s recycle delay.

Results and Discussion

TPD spectra acquired after NO_2 adsorption at 300 K for Al_2O_3 and 8 wt % and 20 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ catalysts are shown in Figure 1 ([NO] and [total NO_x] were measured by chemiluminescence; $[\text{NO}_2] = [\text{total } \text{NO}_x] - [\text{NO}]$). The TPD spectrum from the NO_2 -saturated Al_2O_3 support shows only a broad NO_2 desorption feature between 523 and 873 K. The feature below 500 K seen for every sample studied here is due to the desorption of weakly held NO_2 on the oxide surfaces. The inverse dependence of the intensity of this desorption feature on BaO coverage is related to the decrease in surface area with BaO content. In the TPD spectrum of the NO_2 -saturated 8 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ sample, two desorption traces are observed: an NO_2 feature with peak desorption rate at ~ 673 K and an NO peak with maximum desorption rate at ~ 775 K. The desorption of NO was always accompanied by the evolution of O_2 , which was verified by periodic analysis of the evolved gases using mass spectrometry. Our experimental setup, however, did not allow the quantification of the NO/ O_2 ratio during TPD experiments.

The shape and the broadness of the NO_2 desorption feature indicate that part of this trace is originating in desorption from the Al_2O_3 support. Increasing the BaO coverage to 20 wt % results in a large increase in the intensity of the NO desorption trace. The NO_2 desorption trace shifts to higher temperature (~ 695 K), and the maximum NO desorption rate is seen at ~ 795 K. Note the dramatic decrease in the ratio of the amount of evolved NO_2/NO with increasing BaO coverage. While only NO_2 is desorbing from the pure Al_2O_3 support, the larger fraction of NO_x desorbing from the 20 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ is NO. The observed desorption patterns cannot simply be explained by the superposition of the TPD traces from the nitrated Al_2O_3 support

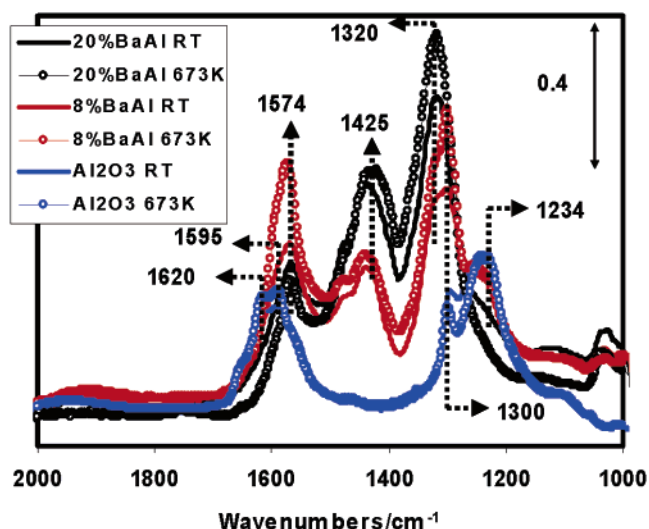


Figure 2. IR spectra from Al_2O_3 and 8 wt % and 20 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ after NO_2 adsorption at 300 K (solid lines), and 673 K (open circles). (IR spectra were acquired after 10 min exposure to NO_2 at each temperature.)

and $\text{Ba}(\text{NO}_3)_2$ formed in NO_2 adsorption. As we will show in the discussion of the IR and NMR results, there is no $\text{Ba}(\text{NO}_3)_2$ -free Al_2O_3 surface present after NO_2 adsorption in the 20 wt % sample. Thus, all the NO_x desorbed from this sample (and most of that from the 8 wt % sample) is associated with the BaO storage material. However, the NO_2 desorption feature cannot originate from bulk $\text{Ba}(\text{NO}_3)_2$ since that decomposes only above 900 K into NO and O_2 only. We propose that the NO_2 desorption trace from $\text{BaO}/\text{Al}_2\text{O}_3$ samples originate from adsorbed nitrates on a monolayer of BaO on Al_2O_3 , while the NO is evolving from the decomposition of crystalline $\text{Ba}(\text{NO}_3)_2$ particles. This assignment is further supported by the fact that the amount of NO_2 evolved in the TPD experiment is directly proportional to the surface area of the catalyst. Therefore, the amount of NO_2 desorbed is measuring the amount of BaO present on the Al_2O_3 surface in monolayer coverage.

A series of FTIR spectra obtained from Al_2O_3 , 8 wt % and 20 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ after NO_2 exposure at 300 K is displayed in Figure 2. IR spectra recorded after heating the samples at 673 K in an NO_2 atmosphere for 10 min are also shown in the figure. The IR features observed are in accord with those reported previously²⁻⁶ for $\text{BaO}/\text{Al}_2\text{O}_3$. On the Al_2O_3 support, two types of nitrates are formed in NO_2 adsorption: bridging [$1234, 1250 \text{ cm}^{-1}$ and $1595, 1620 \text{ cm}^{-1}$] and chelating bidentate [1300 cm^{-1} and 1570 cm^{-1}] nitrates. On the 8 wt % BaO sample, IR features representing both bidentate (1300 and 1575 cm^{-1}) and ionic (1300 and $1420\text{--}1480 \text{ cm}^{-1}$) nitrates are detected. Note that on the 8 wt % BaO sample, nitrates adsorbed onto the Al_2O_3 support can clearly be seen (shoulders at 1250 and 1600 cm^{-1}) as well. Increasing the BaO coverage to 20 wt % results in the nearly complete disappearance of the Al_2O_3 -related nitrate bands, while the intensities of the ionic nitrate features increase significantly. In particular, there are prominent increases in the relative intensities of the ionic nitrates relative to those of the bidentate nitrates. Heating the alumina support at 673 K for 10 min in NO_2 atmosphere does not change the IR spectrum of the nitrate species. In the 8 wt % BaO sample the high temperature heating in NO_2 atmosphere results in a very large increase in the intensities of the bidentate nitrates (bands at 1300 and 1574 cm^{-1}), while the doublet feature of ionic nitrates in the $1420\text{--}1480 \text{ cm}^{-1}$ range seem to lose some intensity. For the 20 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ sample, the intensities

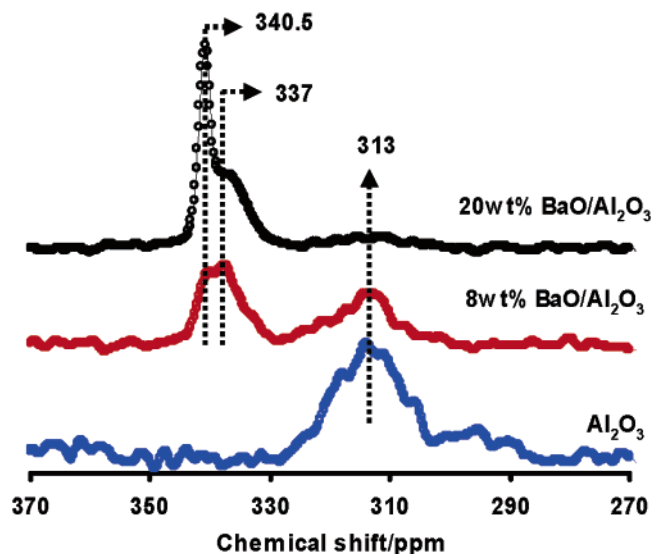


Figure 3. ^{15}N solid state NMR spectra from Al_2O_3 and 8 wt % and 20 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ after NO_2 saturation 673 K.

of the ionic nitrates (1320 and 1420 cm^{-1}) increase as a result of the high-temperature anneal in NO_2 , while that of the bidentate nitrates decrease. The almost complete disappearance of the alumina-related nitrate bands in this sample following the high-temperature anneal in NO_2 is also noteworthy.

The IR spectra presented above reveal that in room-temperature NO_2 adsorption, nitrate species are formed on both the alumina support, and on the BaO particles. It is also evident that some of the Al_2O_3 support surface is free of BaO, even at a relatively high BaO coverage of 20 wt %, and it is more pronounced at lower BaO coverages. The IR spectra clearly show that both bidentate (surface) and ionic (bulk) nitrates are formed in both BaO-containing samples, and that the relative intensity of the ionic nitrate peaks increase with BaO coverage. The IR results after the 673 K heating suggest that there is redistribution of the Ba nitrates on the alumina surface at high temperatures. A monolayer Ba nitrate forms on the surface of the Al_2O_3 support, resulting in increased intensities of the bidentate nitrates, and a concomitant decrease in the intensities of the ionic nitrates in the 8 wt % BaO sample. However, at this low coverage, this well-ordered Ba-nitrate film is not covering completely the entire Al_2O_3 surface, as alumina-related nitrate bands are still visible. The presence of ionic nitrates indicates that at this BaO coverage the nitrate layer is not able to access the entire alumina surface. In the 20 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ sample, the Al_2O_3 surface is almost completely covered with this nitrate monolayer after the 673 K anneal in NO_2 , and large Ba-nitrate particles grow on top of this film. Note the very good correlation between the intensity ratios of the bidentate/ionic nitrates in the IR spectra and those of the NO_2/NO peaks in the TPD spectra (assuming that the extinction coefficients of the two types of nitrate species are not significantly different).

^{15}N solid-state NMR spectra from the Al_2O_3 and 8 wt % and 20 wt % $\text{BaO}/\text{Al}_2\text{O}_3$ catalysts after $^{15}\text{NO}_2$ saturation at 673 K

are displayed in Figure 3. On the Al_2O_3 support, a very broad NMR feature is seen at 313 ppm chemical shift (relative to the $^{15}\text{NH}_4\text{Cl}$). Two new peaks appear at 337 and 340.5 ppm chemical shifts on both $\text{BaO}/\text{Al}_2\text{O}_3$ samples, although with very different relative intensities, and can be assigned to nitrate species.^{9,10}

The NMR peak at 337 ppm chemical shift can be assigned to the nitrate monolayer covering the Al_2O_3 support, while the 340.5 ppm peak represents crystalline $\text{Ba}(\text{NO}_3)_2$ particles. The changes in the ratio of the 337 ppm/340.5 ppm peak intensities in the NMR spectra are in line with the increases of the ionic nitrate peaks in the IR spectra as the BaO coverage increased from 8 to 20 wt %. It is also consistent with the TPD peak ratios of NO_2/NO .

Conclusions

This study clearly shows the formation of a unique $\text{Ba}(\text{NO}_3)_2$ monolayer on the alumina support with distinct properties. The results also suggest a way to control the NO_2/NO ratio evolving from $\text{BaO}/\text{Al}_2\text{O}_3$ systems following NO_x adsorption by varying the BaO coverage. On the other hand, this study raises serious questions about the proposed decomposition mechanism of NO_x -saturated $\text{BaO}/\text{Al}_2\text{O}_3$ materials. One might reasonably postulate that the first NO_3^- in $\text{Ba}(\text{NO}_3)_2$ decomposes by releasing an NO_2 and the second by releasing $\text{NO} + 1/2\text{O}_2$. In this case, the NO_2/NO ratio should always be unity, regardless of the BaO coverage. However, since the NO_2/NO ratio varies widely with BaO coverage, this mechanism cannot be correct. Our structural model is able to account for the variations in the NO_2/NO ratios with changing BaO coverages.

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