

The Effect of Water on the Adsorbed NO_x species over BaO/Al₂O₃ NO_x Storage Materials: A Combined FTIR and In Situ Time-Resolved XRD study

János Szanyi^{1*}, Ja Hun Kwak¹, Do Heui Kim¹, Jomathan Hanson², and Charles H.F. Peden¹

¹Institute for Interfacial Catalysis, Pacific Northwest National Laboratory
Richland, WA 99352, USA

²Department of Chemistry, Brookhaven National Laboratory
Upton, NY 11973, USA

Introduction

In a combined spectroscopic study we identified the nature of NO_x species formed on the BaO active storage material during NO₂ adsorption [1]. Two fundamentally different nitrate species were identified; surface nitrates on the monolayer of BaO covering the Al₂O₃ support surface, and bulk-like Ba(NO₃)₂ that forms in the reaction of NO₂ and BaO in excess of that needed for the monolayer coverage. We have also shown how the morphology of the Ba-containing phase was changing in the catalyst activation/NO₂ uptake/NO_x release cycle [2]. Water, a major component of the Diesel exhaust gas mixture, has been shown to significantly affect the NO_x storage process by strongly interacting with the alumina support, and thus eliminating its NO_x uptake [3]. In this study we investigated the effect of water on the NO_x species present on a BaO/Al₂O₃ NO_x storage system (FTIR, TPD), and also the effect of water on the morphology of this material after NO_x uptake (TR-XRD).

Materials and Methods

All the experiments described in this work were conducted on 8- and 20wt%-BaO/Al₂O₃ NO_x storage materials prepared by the incipient wetness method. The FTIR/TPD studies were carried out in a batch reactor. Transmission FTIR measurements were done with a Magna 740 spectrometer operated at 4 cm⁻¹ resolution, and each spectrum recorded was the average of 128 scans. A UTI C100 mass spectrometer was used to obtain the TPD results. The TR-XRD experiments were carried out at the National Synchrotron Light Source at Brookhaven National Laboratory on beam line X7B. The powder samples were mounted into a sapphire tube and the sample activation and adsorption/desorption experiments were conducted under flow conditions.

Results and Discussion

An 8wt%-BaO/Al₂O₃ NO_x storage material was prepared by aqueous incipient wetness method using a Ba(NO₃)₂ solution and a 200 m²/g γ-Al₂O₃. The active BaO phase was formed by the thermal decomposition of Ba(NO₃)₂. The thus-formed BaO/Al₂O₃ sample was exposed to NO₂ at 300K and subsequently to H₂O in an IR cell. A series of IR spectra (collected in transmission mode on a Nicolet Magna 750 spectrometer at 4 cm⁻¹ resolution) recorded as a function of time while the sample was exposed to 2 Torr of H₂O are displayed in Fig. 1. The NO₂-saturated sample shows IR absorption features characteristic of surface and bulk-like nitrates of Ba, as well as weak features assigned to surface nitrates of the alumina support. The most prominent IR bands in the spectrum of the dry NO₂-saturated sample are the ones of surface nitrates (1300 and 1575 cm⁻¹), while bands representing bulk-like nitrates (1320 and 1430 cm⁻¹) exhibit much lower intensities. There are significant changes in the IR spectra following the introduction of 2 Torr of water onto this NO₂-saturated sample; the intensities of IR features representing surface nitrates decrease gradually with the time of water exposure, while bands assigned to bulk-like nitrates increase. There is also a new IR feature developing at ~1220 cm⁻¹ arising, most probably, from HONO formed by the reaction of surface nitrates and H₂O. Following 30 min water exposure the surface nitrate features lose most of their

intensities, while the intensities of the bulk-like nitrates and HONO are the highest. A similar experiment was also carried out in a flow-through cell, and the changes in the Ba(NO₃)₂ phases were followed by TR-XRD (at the NSLS at Brookhaven National Laboratory). In these experiments the freshly prepared 8wt%-BaO/Al₂O₃ sample was first exposed to an NO₂/He stream at 300K until no changes in the Ba(NO₃)₂ diffraction peaks were observed. Then the gas stream was switched to H₂O/He and the changes in the XRD patterns were followed as a function of H₂O exposure time at 300K. A series of XRD patterns obtained in this experiment is displayed in Fig. 2. Prior to H₂O exposure, Ba(NO₃)₂ is present on the alumina support as nano-particles with average particle size (estimated from the full width at half maximum of the (111) Ba(NO₃)₂ diffraction feature) of 5nm. Upon H₂O introduction onto the NO₂-saturated sample the XRD pattern changes dramatically; the Ba(NO₃)₂ diffraction peaks become intense a very sharp, indicating the formation of large Ba(NO₃)₂ particles (>30nm). The results of both the FTIR and TR-XRD experiments indicate that upon exposure of an NO₂-saturated BaO/Al₂O₃ sample to H₂O vapour, significant morphological changes take place in the catalyst as large Ba(NO₃)₂ crystals form. FTIR results (not shown) also show that this process is reversible; as water is removed in a temperature programmed experiment, the surface nitrate features reappear and the intensities of the bulk-like features dramatically decrease. The amount of NO_x adsorbed onto the active BaO phase does not seem to change by the exposure of the system to water vapour.

Significance

The exposure of NO₂-saturated BaO/Al₂O₃ samples to H₂O vapour results in the reversible transformation of surface nitrates to bulk-like nitrates, and the conversion of small Ba(NO₃)₂ particles into large crystals, which has relevance to NSR technology.

Figure 1. FTIR spectra recorded after the exposure of an NO₂-saturated 8wt%-BaO/Al₂O₃ sample (a) to H₂O for the indicated times at 300K.

Figure 2. A series of TR-XRD patterns obtained after a NO₂-saturated 8wt%-BaO/Al₂O₃ sample was exposed to H₂O vapour at 300K.

References

1. J.Szanyi, J.H. Kwak, D.H. Kim, S.H. Burton, C.H.F. Peden, J.Phys.Chem. B, 2005 109 27.
2. J. Szanyi, J.H. Kwak, J.C. Hanson, C.M. Wang, T. Szailer, and C.H.F. Peden, J.Phys.Chem. B, 2005 109 7339.
3. W.S. Epling, G.C. Campbell, J.E. Parks, Catalysis Letters, 2003 90(1-2) 45.



