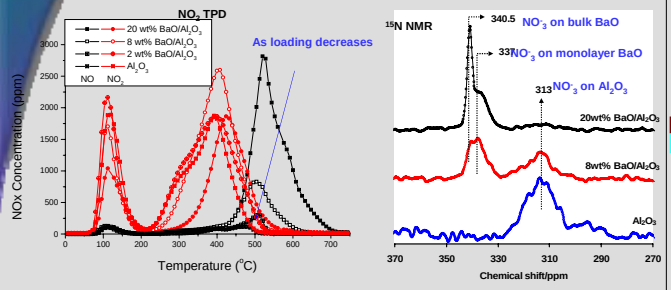
Morphology and Composition cycle of BaO/Al_2O_3 NSR Catalysts during NO_2 Uptake and Release: A multi spectroscopy and microscopy study

Do Heui Kim, Ja Hun Kwak, Charles H.F. Peden, Tamas Szailer, Jon Hanson[1] and János Szanyi
Institute for Interfacial Catalysis
Pacific Northwest National Laboratory and Brookhaven National Laboratory[1]
RICHLAND, WA USA

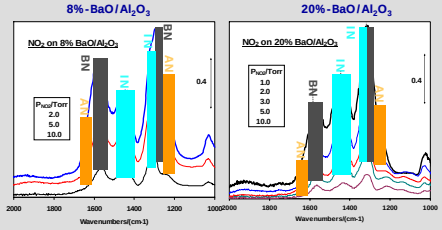
Introduction

- Aimed at developing a practically useful fundamental understanding of NOx adsorber materials, especially focusing on
  1) the NOx adsorption/desorption process over barium oxides,
  2) the behavior of barium morphology with different environment and temperature,
  3) the reactivity of H_2 and CO with stored NOx.
- Studies initiated 1 year ago.

NO_2 adsorption/desorption over BaO/Al_2O_3: three types of nitrates species

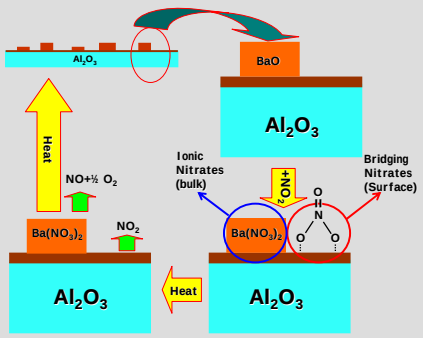


FTIR after adsorbing NO_2 at RT



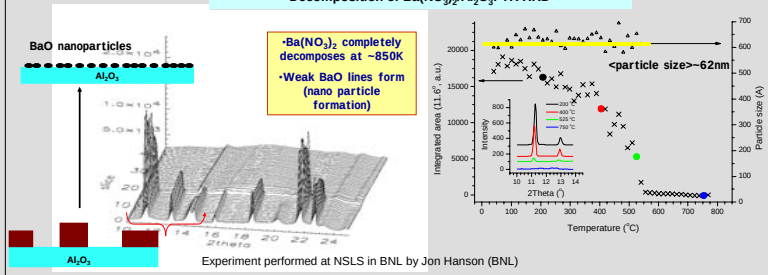
Ionic (IN) (bulk) and bridging (BN) (surface) nitrates are observed on both BaO/Al_2O_3 catalysts. The ratio of bridging/ionic nitrates varies with BaO loading. (Al_2O_3-bound nitrates (AN) are also present.)

NO_2 Adsorption/Desorption behavior of BaO/Al_2O_3



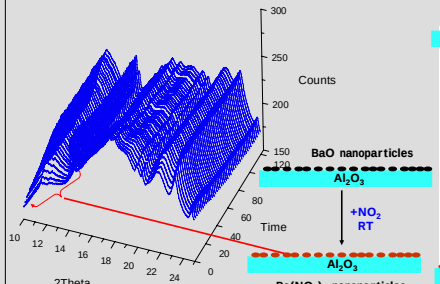
Change of barium morphology with different environment and temperature

Decomposition of $Ba(NO_3)_2/Al_2O_3$: TR-XRD

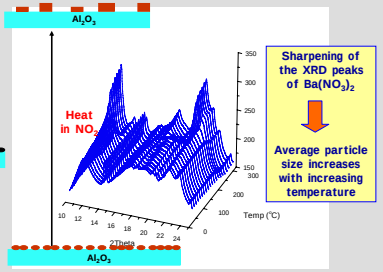


Experiment performed at NSLS in BNL by Jon Hanson (BNL)

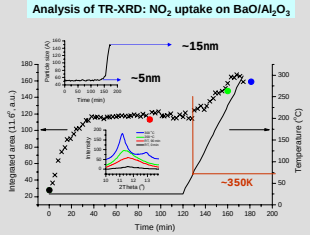
NO_2 uptake at 300K on 20%-BaO/Al_2O_3



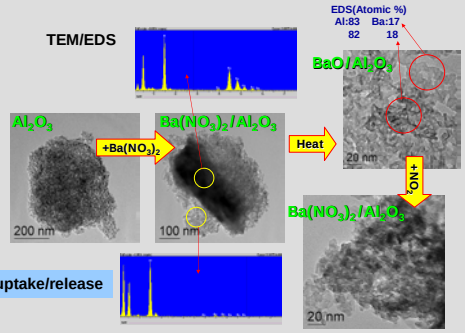
NO_2 uptake at 300→ 573K on BaO/Al_2O_3: TR-XRD



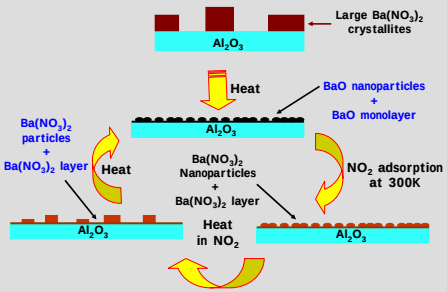
Analysis of TR-XRD: NO_2 uptake on BaO/Al_2O_3



TEM/EDS

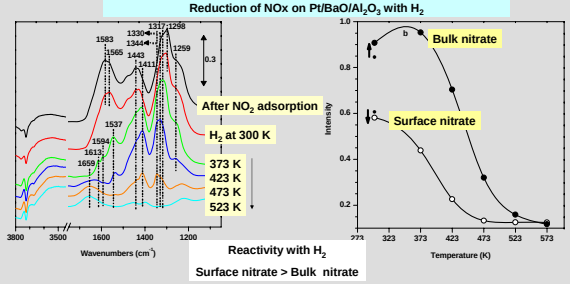


The morphology cycle of BaO/Al_2O_3 in NO_2 uptake/release



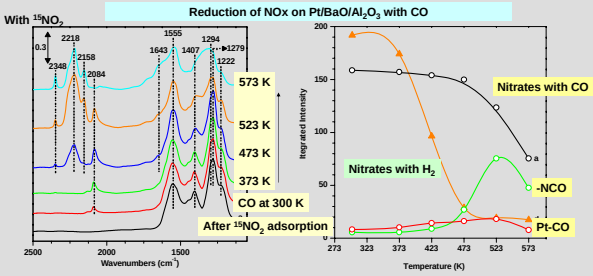
Reduction behavior of stored NOx on $Pt/BaO/Al_2O_3$ with H_2 and CO

Reduction of NOx on $Pt/BaO/Al_2O_3$ with H_2



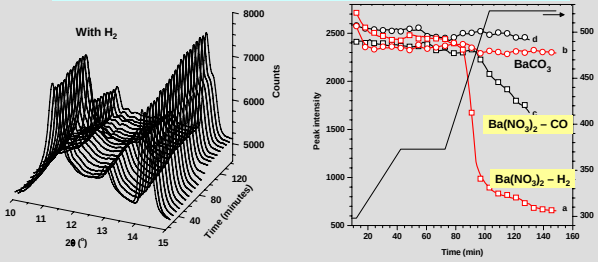
Reactivity with H_2
Surface nitrate > Bulk nitrate

Reduction of NOx on $Pt/BaO/Al_2O_3$ with CO



Slower reduction of nitrates than H_2
Formation of –NCO species on Ba, Pt and Al

TR-XRD spectra collected during the reduction of NOx species with H_2/CO on $Pt/BaO/Al_2O_3$



Reactivity of bulk $Ba(NO_3)_2$
H_2 > CO

Conclusions

1. FTIR and NMR spectroscopies show the feature of three types of nitrates (on Al_2O_3, monolayer type and bulk type) over NO_2 adsorbed BaO/Al_2O_3. The species have different desorption behavior.
2. Barium phase is cycling with respect to the gas environment and temperature. After NO_2 adsorption, larger $Ba(NO_3)_2$ crystalline is formed upon heat treatment at 300 °C, and decomposed to form nano crystalline BaO.
3. H_2 is a much more effective in reducing nitrates than CO. Especially, the surface nitrates are reduced faster at lower temperature than bulk nitrates with hydrogen. During the reduction of CO, isocyanates (-NCO) are observed and stable up to 573 K.

Acknowledgement

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