14th CLEERS Workshop
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NOx storage-reduction catalysts: similarities and differences between Ba and K

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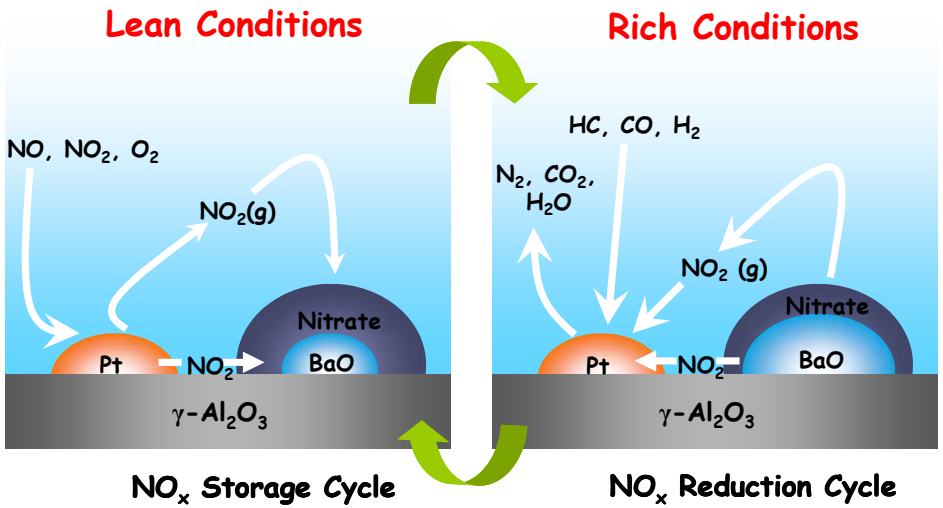
Outline

- Need for higher temperature LNT performance
- NSR catalysts can achieve higher temperature deNOx performance by substitution of the storage and/or support material
- Comparison of performance of Ba- and K-based NSR catalysts
  - Temperature window of optimum operation
  - Dependence on loading
- Similarities and differences in morphology
- Emphasis on understanding potential issues with K-based LNTs

Introduction

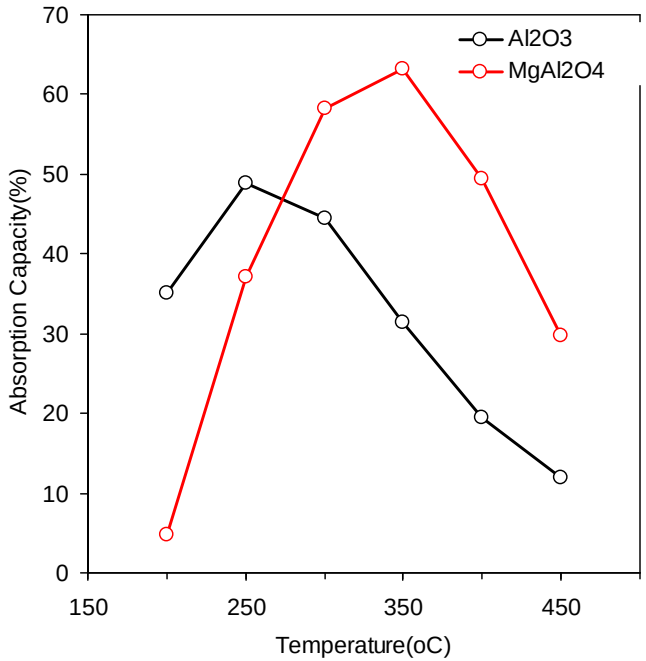
- **Higher temperature NOx reduction performance required for:**
  - **Difficult to meet "not to exceed" regulations during desulfations**
  - **Possible use of LNTs for lean-gasoline and natural gas engine applications**



- PNNL/Cummins/JM CRADA focusing on degradation of possible materials for next-generation high temperature LNTs.
- CLEERS studies are addressing more fundamental issues of these potential new LNT materials related to composition, morphology, and chemical reaction kinetics and mechanisms.
- For these studies, PNNL is preparing potential HT-NSR materials based on literature and prior CLEERS work at PNNL.
- A progress report on initial studies.

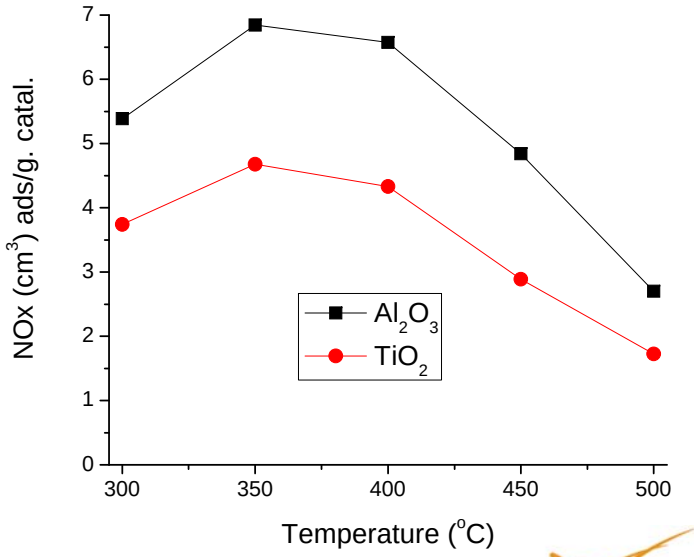
High Temperature LNT Catalyst Materials

- **K-based LNTs known to exhibit higher temperature performance**
- **Recent literature reports suggest titania (TiO_2) may be a better support for K-based LNTs than alumina (Al_2O_3)**
- **Prior CLEERS studies on Ba-based LNTs at PNNL have suggested $MgAl_2O_4$ as a promising support material for high temperature application**



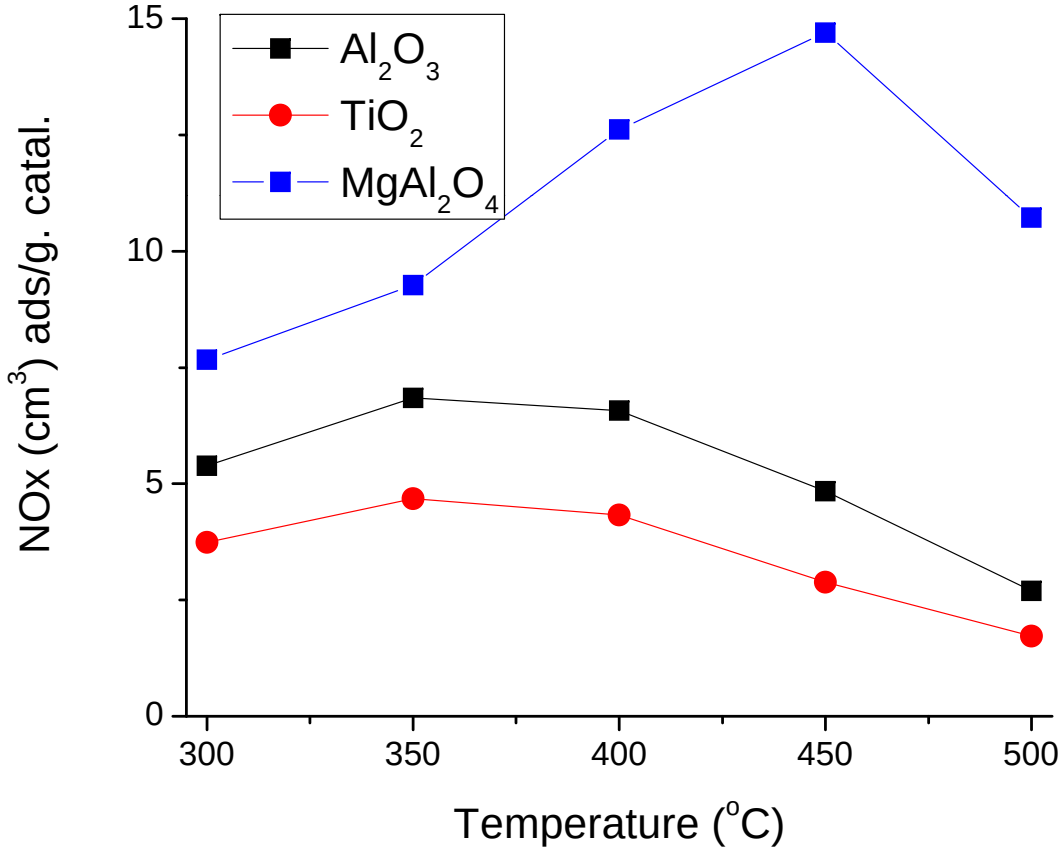
Pt-Ba/Support

Pt-K/Support



K-Based HT-LNT Catalyst Materials

Pt-K/Support



- **Superior activity of $MgAl_2O_4$-supported LNT relative to Al_2O_3- and TiO_2-supported samples over all temperatures.**
- **Moreover, maximum NOx uptake activity at a considerably higher temperature of 450 ºC.**

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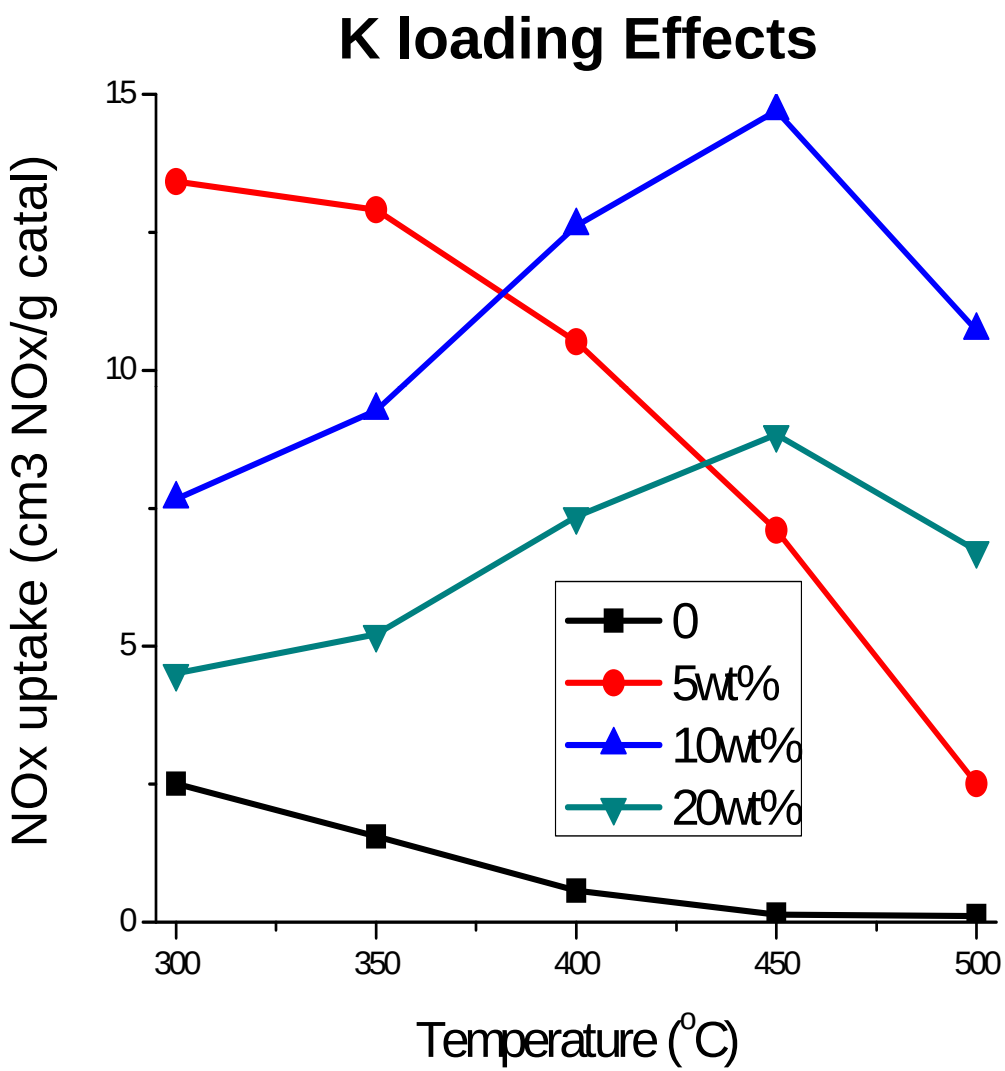
K-loading effects on $MgAl_2O_4$ support materials



- **We're not aware of prior systematic studies of K-loading.**
- **Negligible $MgAl_2O_4$ contribution in NOx uptake at high temperature**
- **Drastic difference between 5 wt% and 10 wt%**
- **Higher loading than 10 wt% does not improve the activity.**

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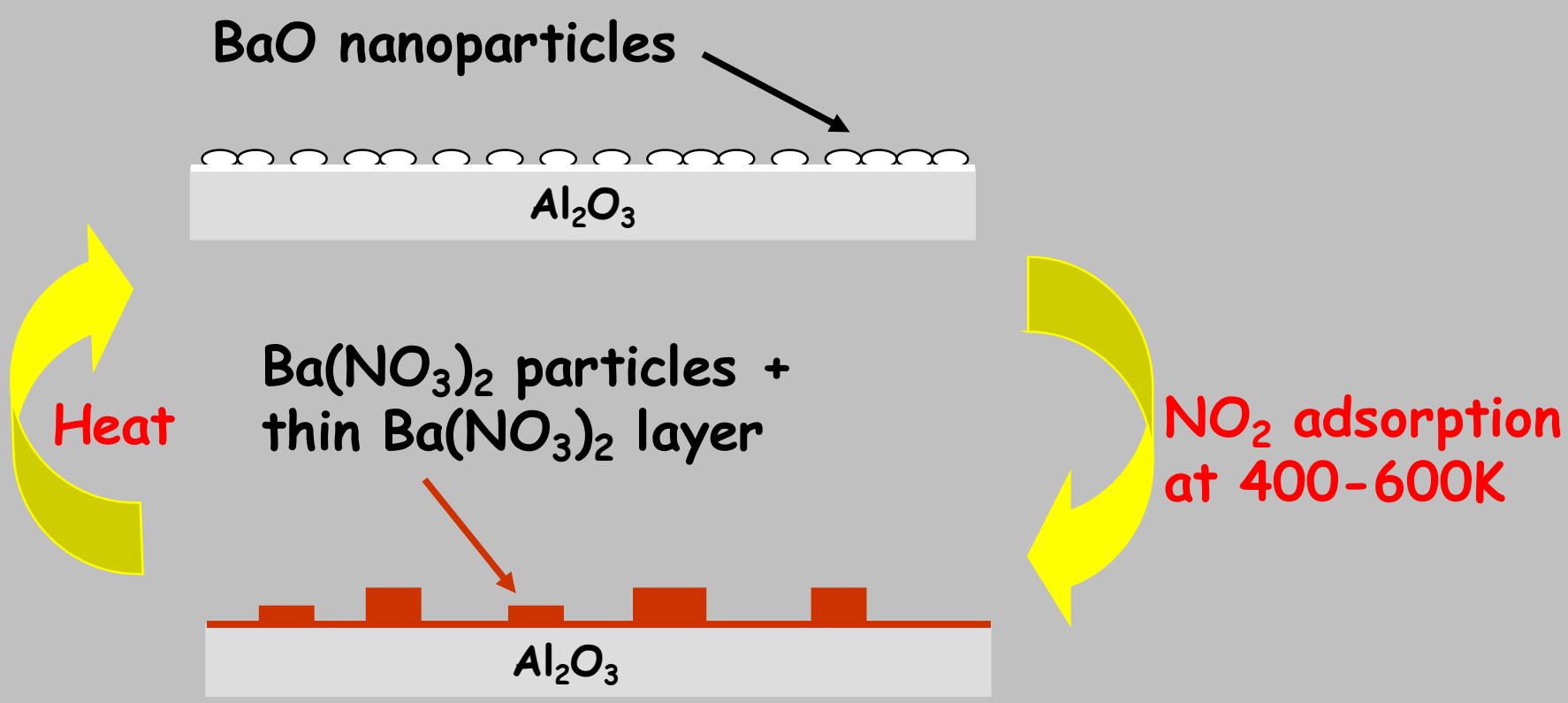
Summary of Ba vs. K Activity Comparisons

- K-based NSRs display enhanced performance high temperatures relative to Ba-based materials (well known)
- Use of $MgAl_2O_4$ support materials provide significant improvements in high temperature performance for both K- and Ba-based NSRs
- K-Pt/$MgAl_2O_4$ displays unusual dependence of performance on K-loading
- Comparison of morphology and morphology changes with Ba-based NSRs
- Understand issues of K-migration that may be a significant road-block to use of K-based NSR materials

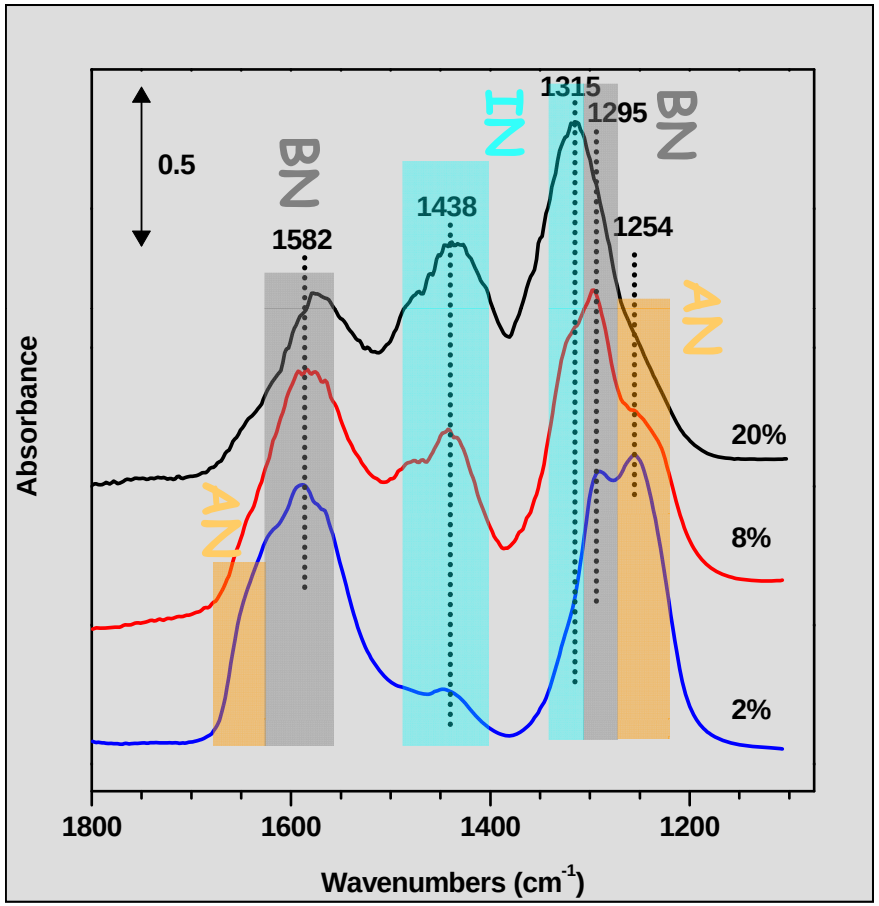
Significant Morphology Changes During Operation of Ba-Based LNTs Were Observed in our Prior CLEERS Studies

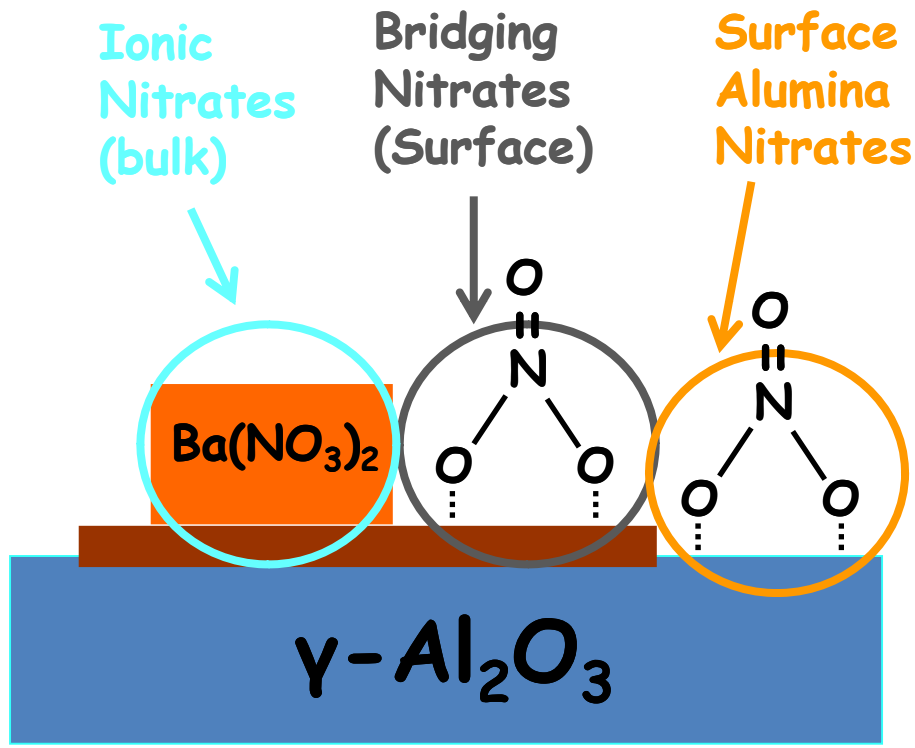


Szanyi, Kwak, Hanson, Wang, Szailer, Peden,
J. Phys. Chem. B 109 (2005) 7339-7344.

Multiple active Ba phases were identified using a variety of techniques including FTIR

FTIR spectra of NO_2 adsorbed on Ba(2, 8 or 10%)/Al_2O_3 samples



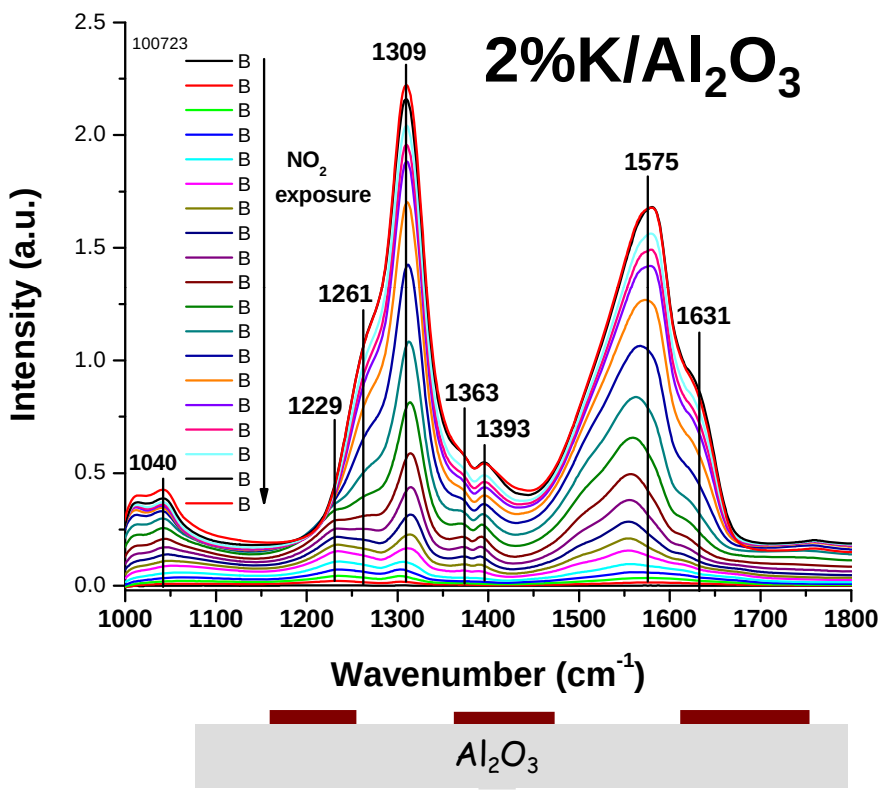


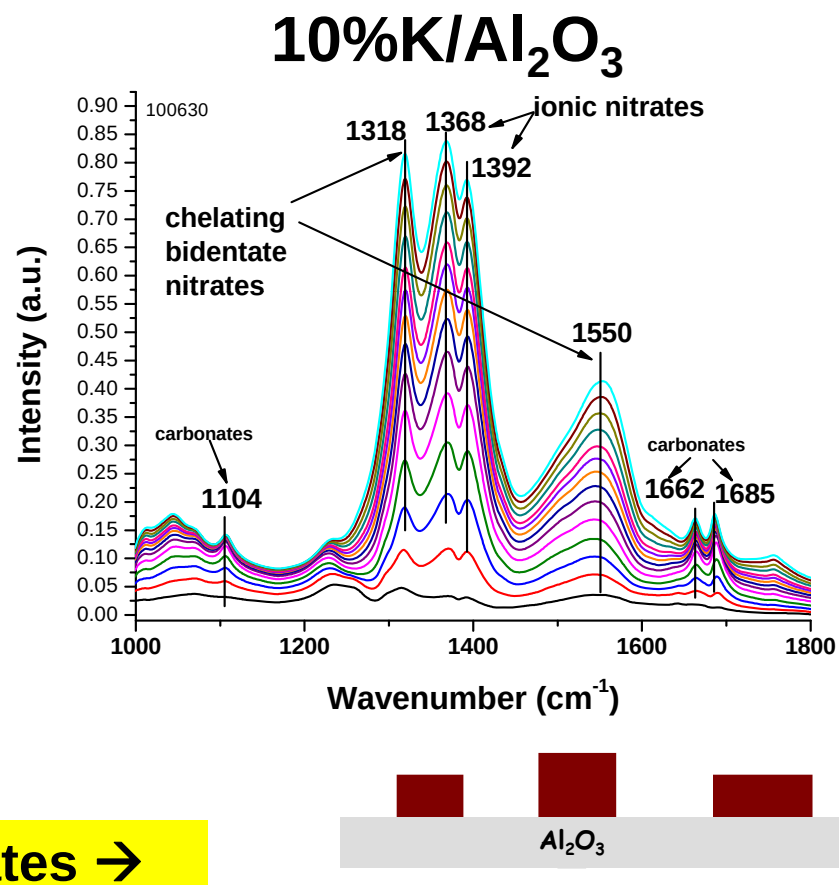
'Signatures' of these structures also evident in ^{15}N NMR and TPD spectra.

Szailer, T.; Kwak, J.H.; Kim, D.H.; Szanyi, J.; Wang, C.M.; Peden, C.H.F., Catal. Today **114** (2005) 86.

Similar to Ba, FTIR Spectral Changes Consistent with Multiple K-oxide Phases

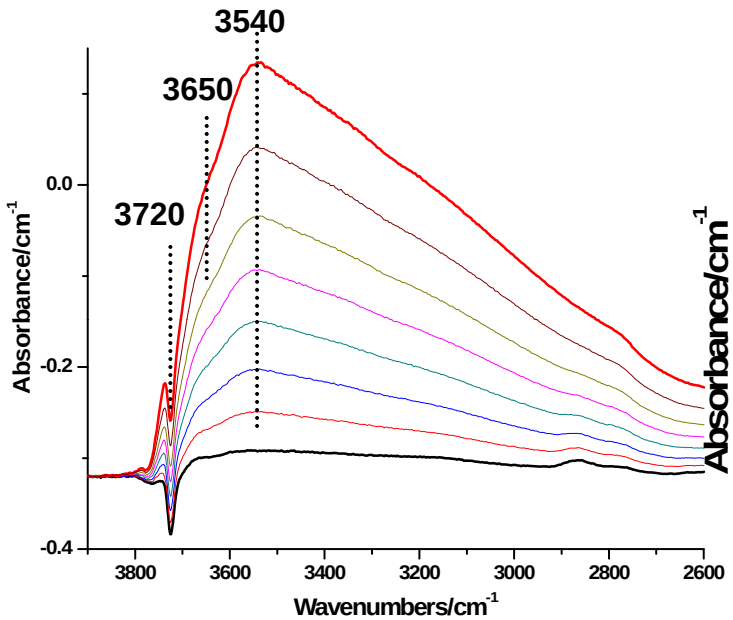
FTIR spectra of NO_2 adsorbed on K(2 or 10)/Al_2O_3 samples

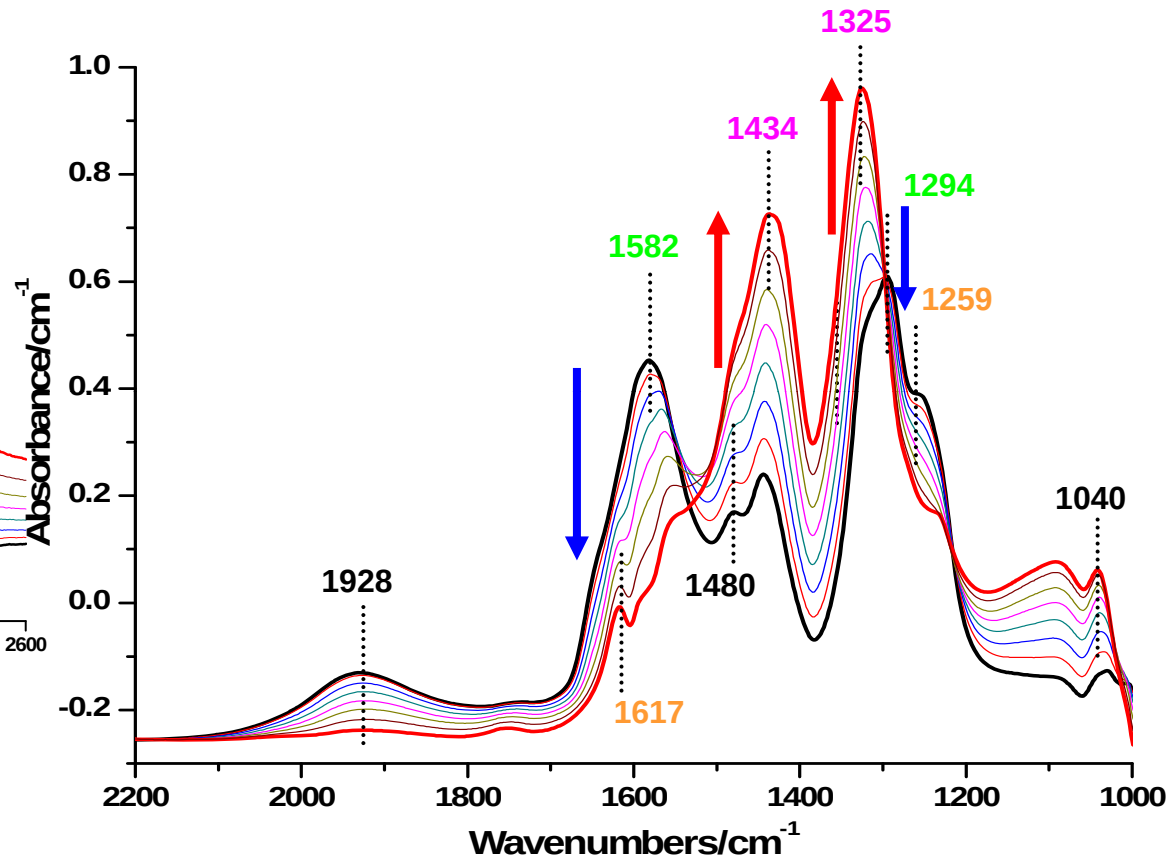




2 wt% K: mostly bidentate nitrates → surface nitrates?
10 wt% K: ionic nitrates and bidentate nitrates → surface and bulk nitrates?

H_2O on NO_2(300K)/8%-BaO/Al_2O_3 at 300K

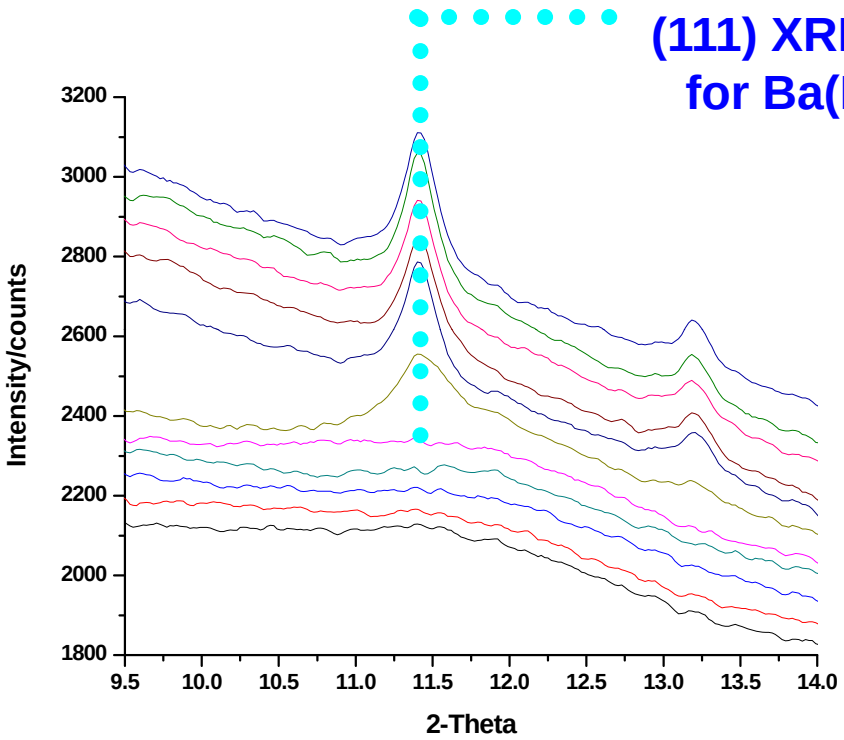




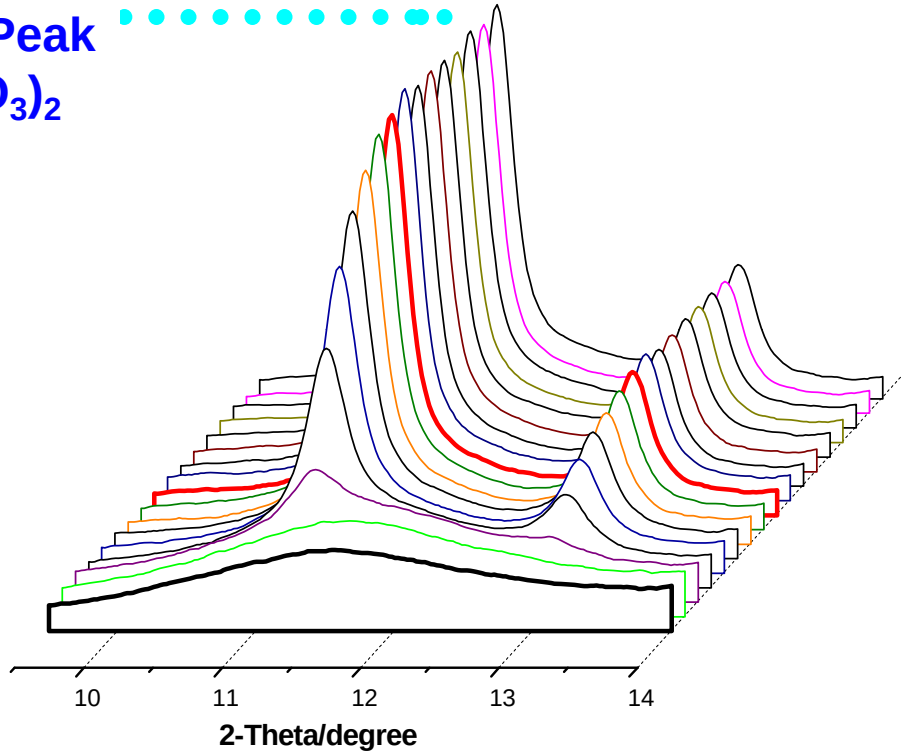
* Disappearance of surface Ba nitrates
* Large increase in bulk Ba nitrate intensities

Szanyi, Kim, Kwak, Hanson, Wang, Peden, Chem. Com., 2007, 984.

Synchrotron TR-XRD confirms $Ba(NO_3)_2$ morphology changes upon H_2O adsorption



8%-BaO/Al_2O_3

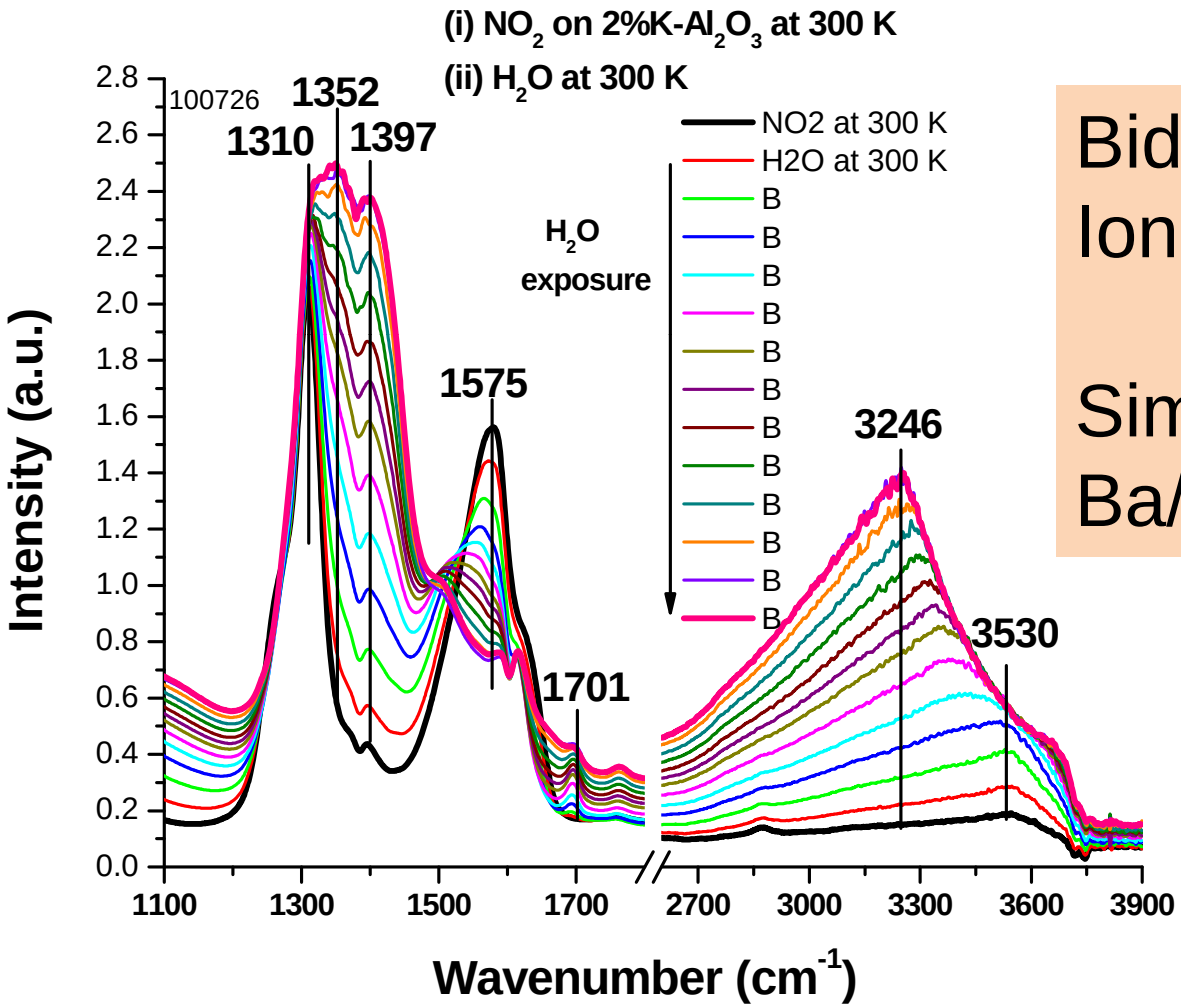


20%-BaO/Al_2O_3

Nano-sized (<5nm) $Ba(NO_3)_2$ $\xrightarrow{+H_2O}$ large (>15nm) $Ba(NO_3)_2$ crystals.

How about the effect of H_2O on K nitrate morphology?

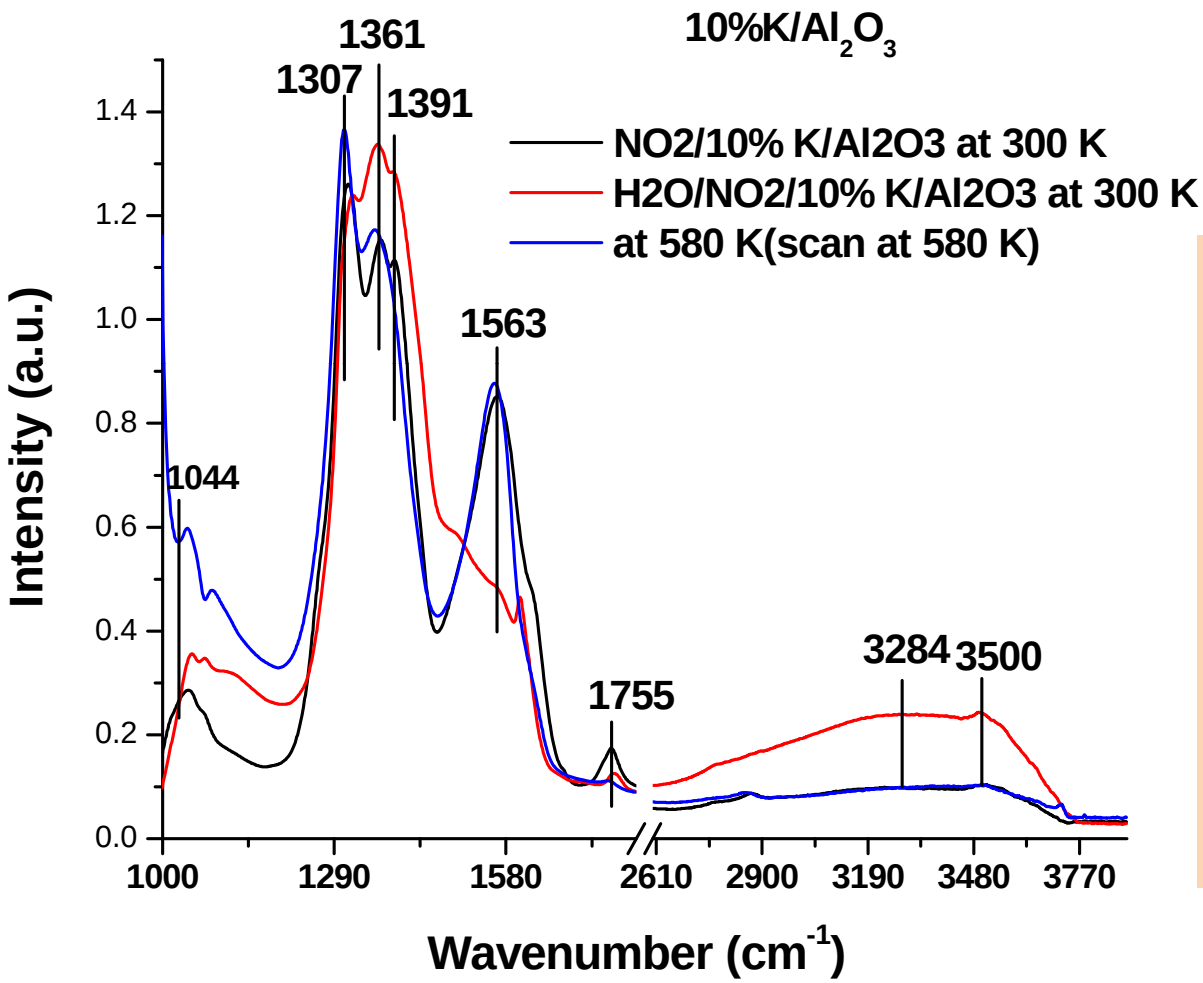
H_2O effect on NO_2 adsorbed $K(2)/Al_2O_3$



Bidentate nitrate → Ionic nitrate

Similar behavior as Ba/Al_2O_3

H_2O effect on NO_2 adsorbed $K(2)/Al_2O_3$



Bidentate nitrate → Ionic nitrate

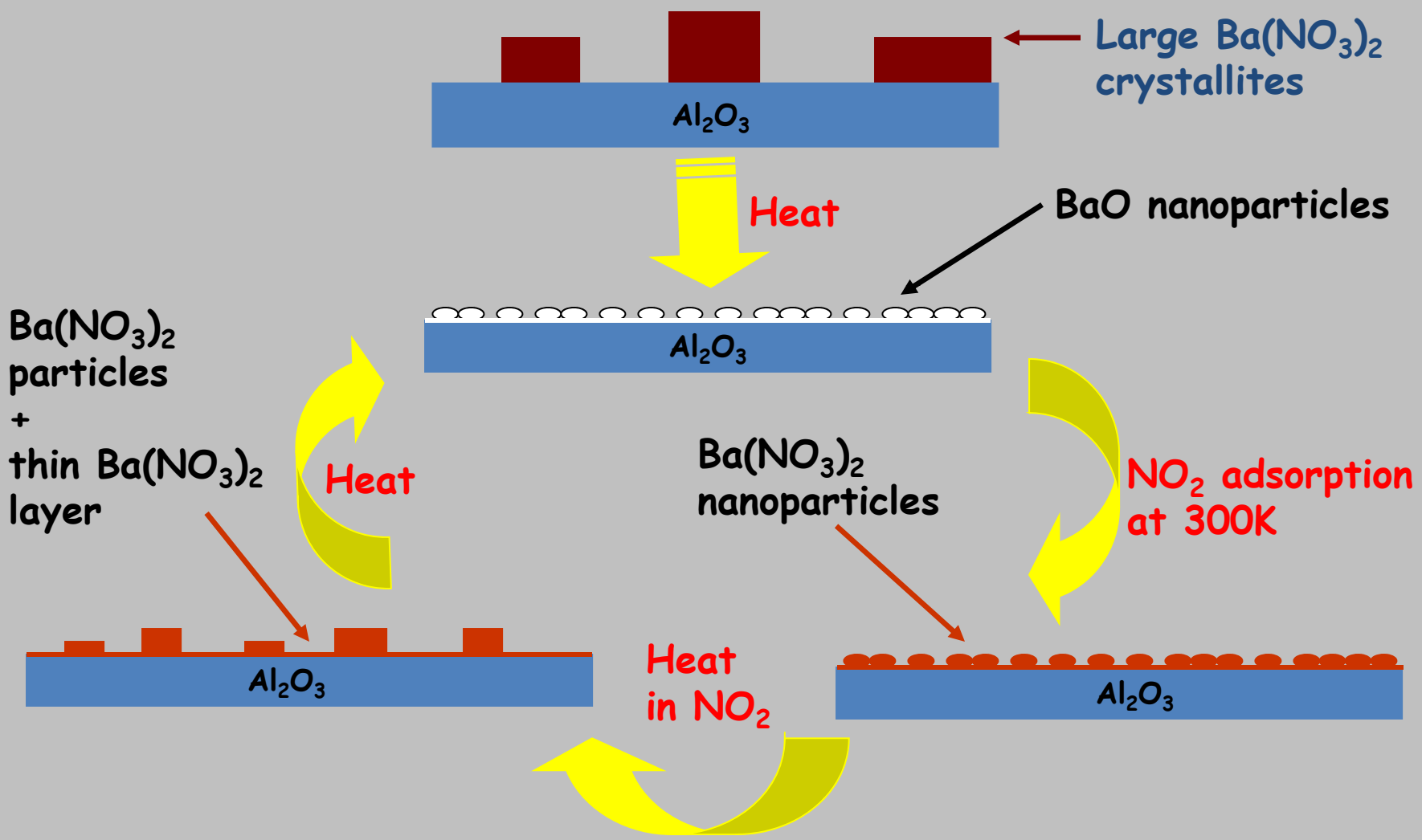
Reversible depending on the presence or absence of H_2O

Summary of nitrate morphologies: Ba vs. K

- **Loading effects:** Both Ba and K form two types of nitrates species (bulk type and highly dispersed), depending on loading.
- **H_2O effects:** H_2O induces reversible changes in morphology between highly dispersed and bulk-type nitrates for both Ba and K.

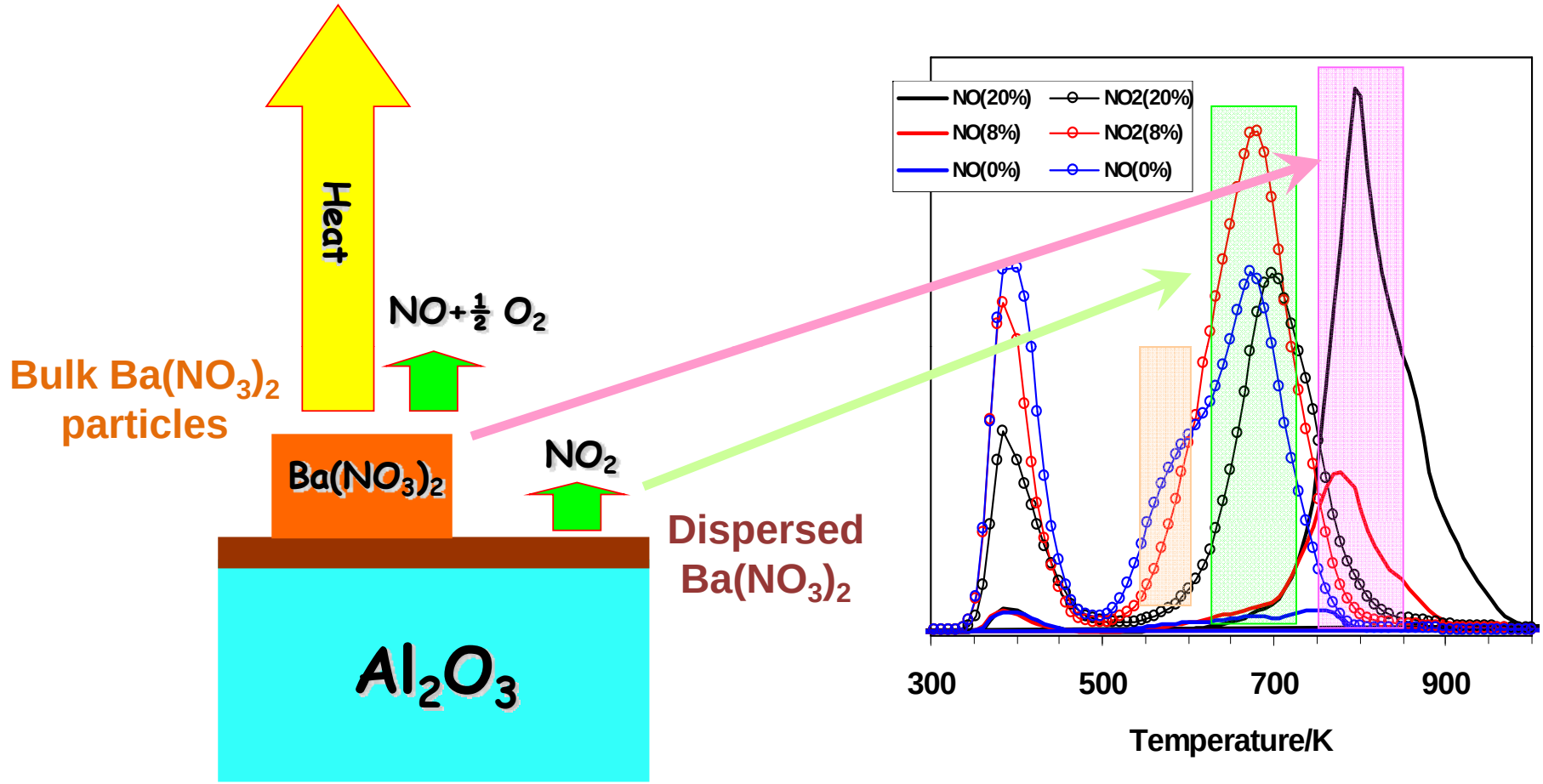
- Morphology changes during nitrate formation and decomposition – work in progress…

Summary of TP-XRD and TEM/EDX studies: Both 'Monolayer' and 'Bulk' $Ba(NO_3)_2$ morphologies present



Szanyi, Kwak, Hanson, Wang, Szailer, Peden, J. Phys. Chem. B **109** (2005) 7339-7344.

Nitrate decomposition: Ba nitrates

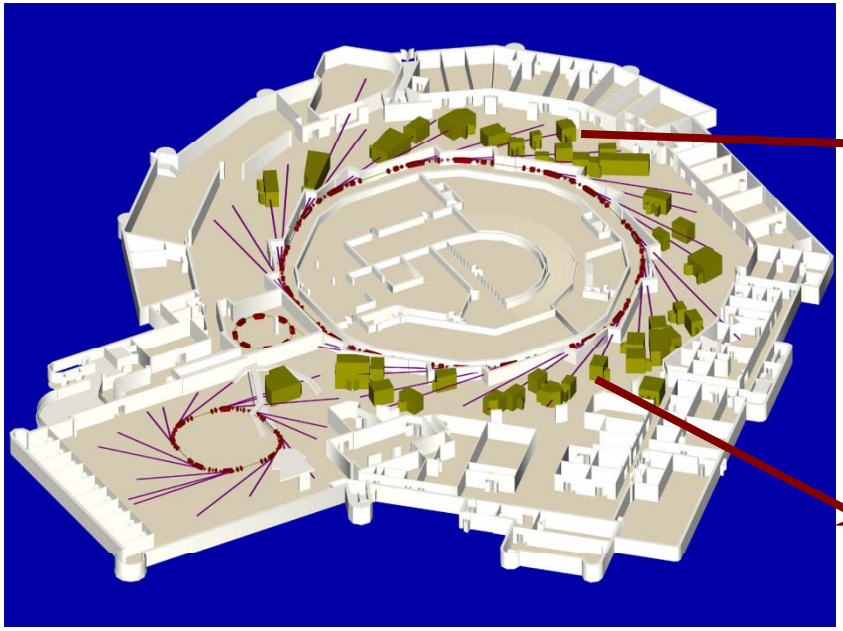


"Surface" nitrates decompose at lower temperatures than "bulk" nitrates

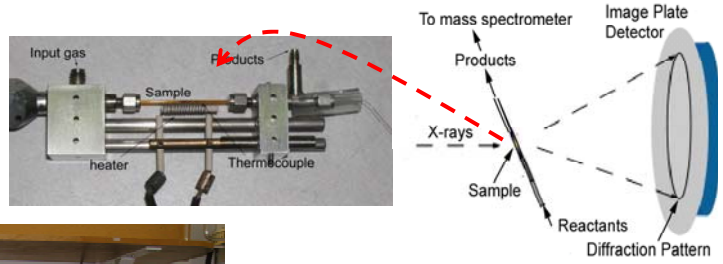
In situ Synchrotron EXAFS/XANES and XRD

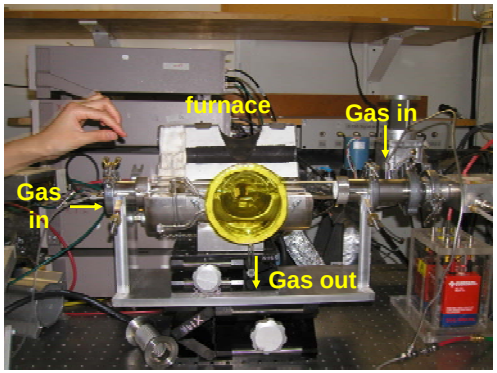
State-of-the-art *in-situ* synchrotron experiments performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Specific techniques used include:

- X-ray absorption near-edge structure (XANES);
- Extended x-ray absorption fine structure (EXAFS); &
- **Time-resolved x-ray diffraction (TR-XRD)**



In-situ TR-XRD





In-situ S XANES & Pt EXAFS

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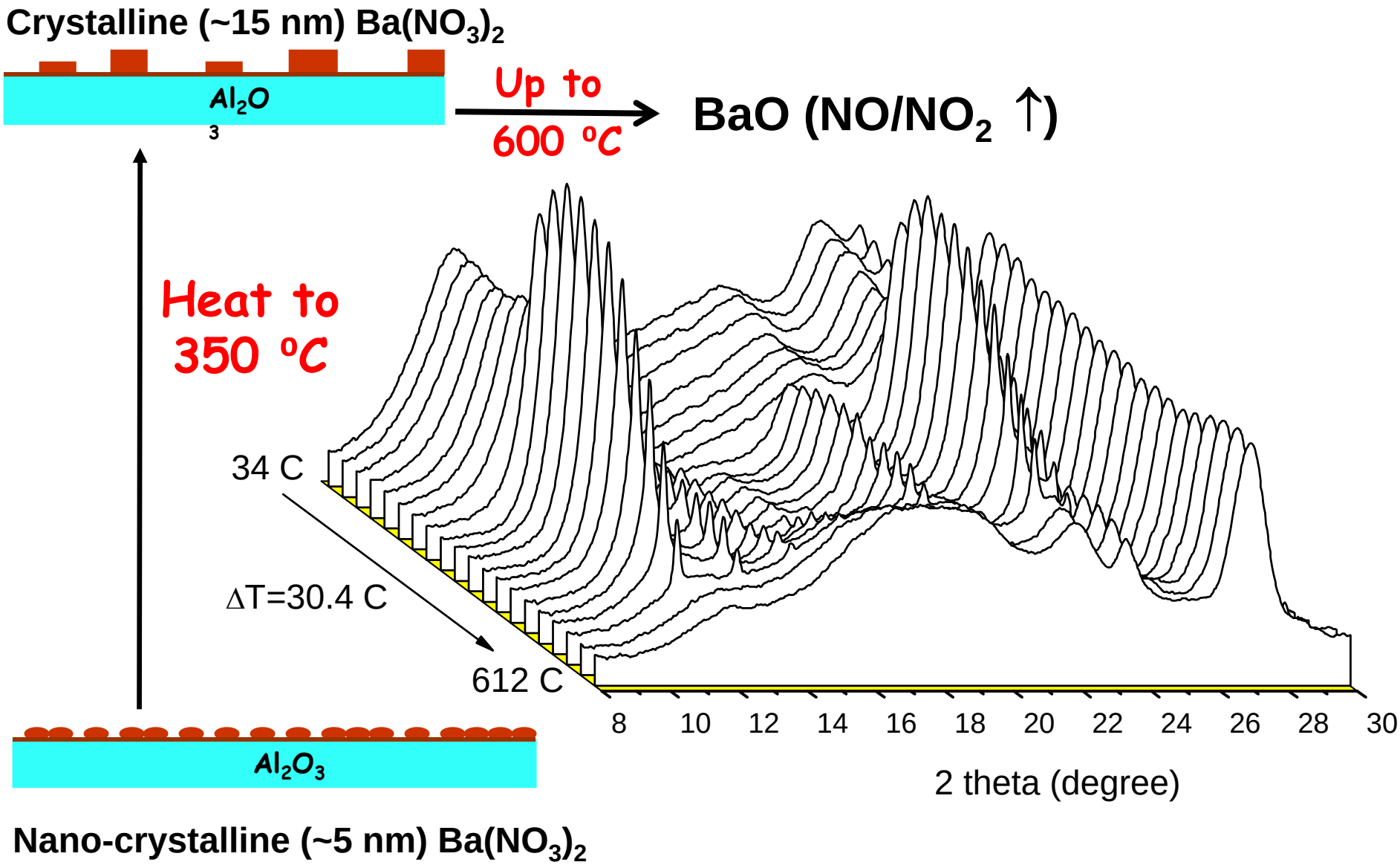
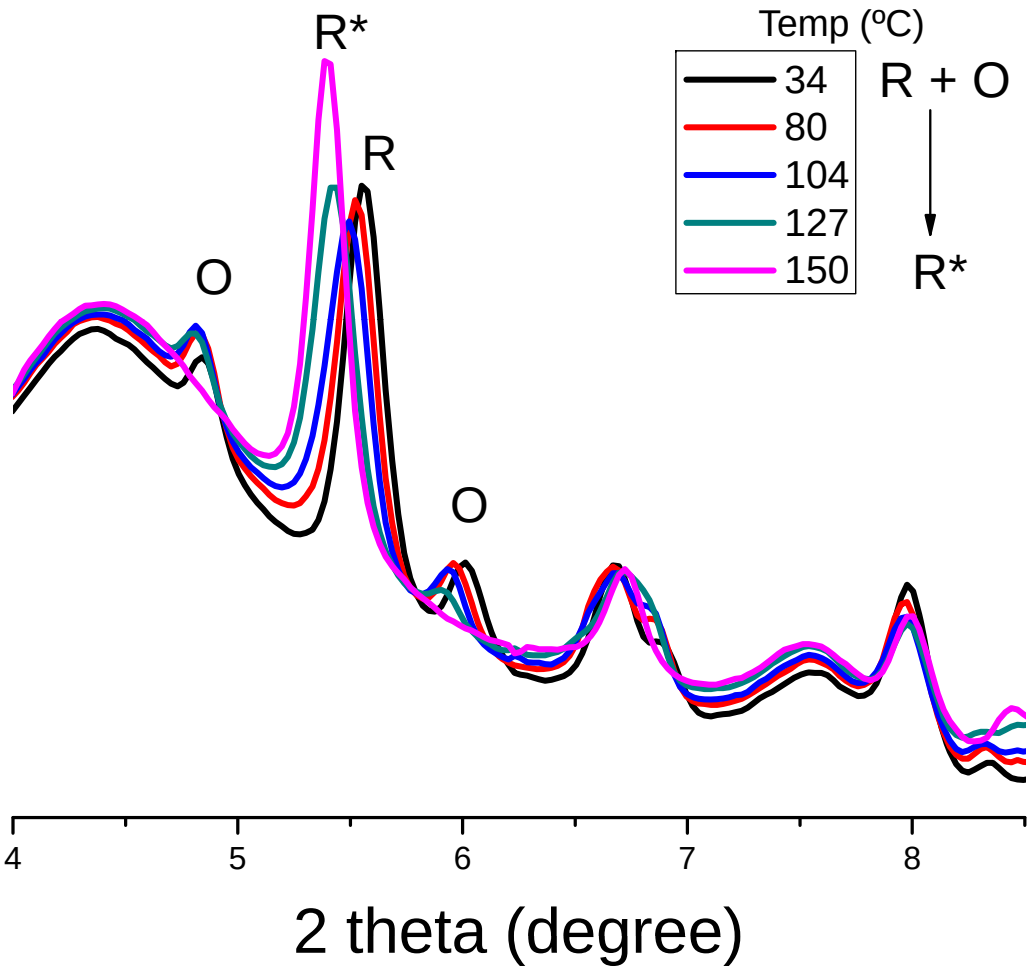
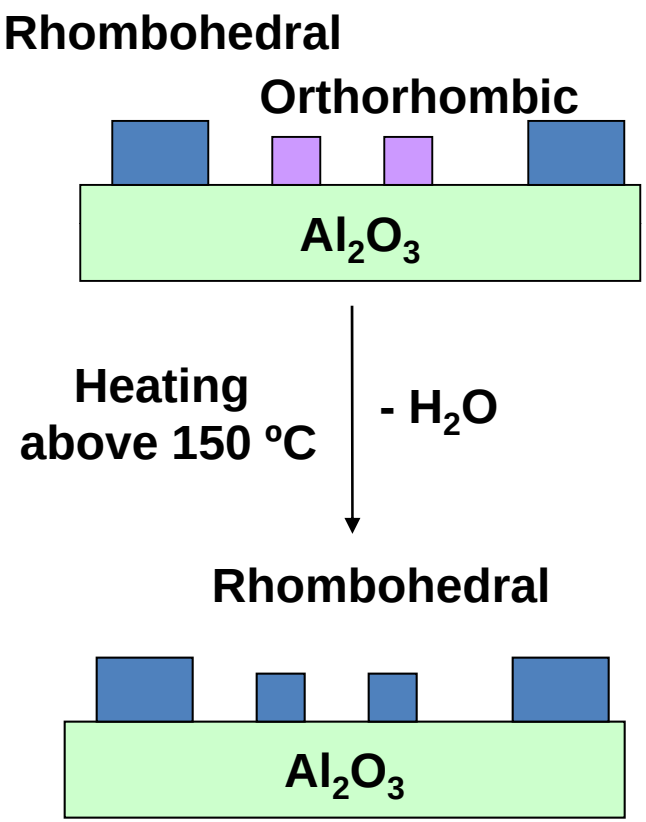
TR-XRD: During NO_2 TPD on $BaO(20\%)/Al_2O_3$



What happens to KNO_3 phase during decomposition? – $KNO_3(20)/Al_2O_3$



$KNO_3(20)/Al_2O_3$, impregnated



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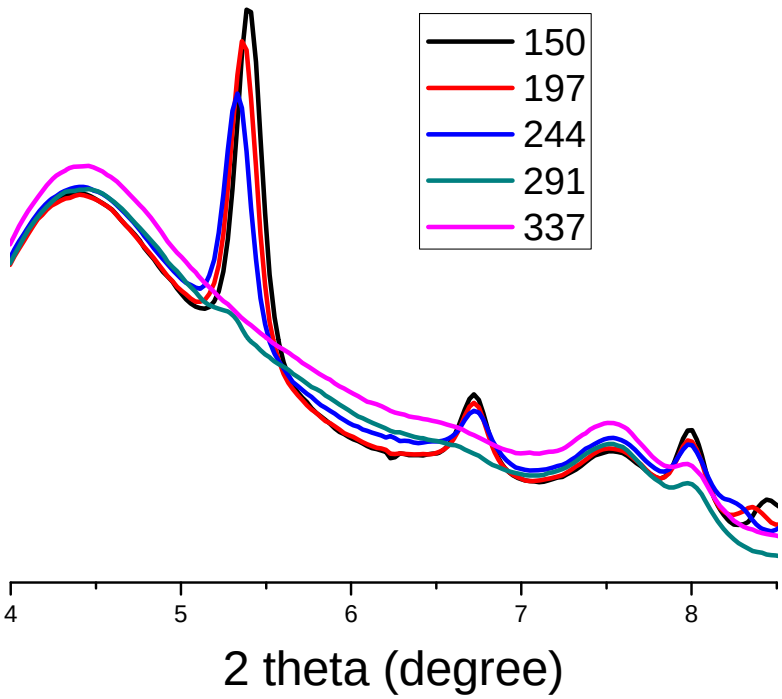
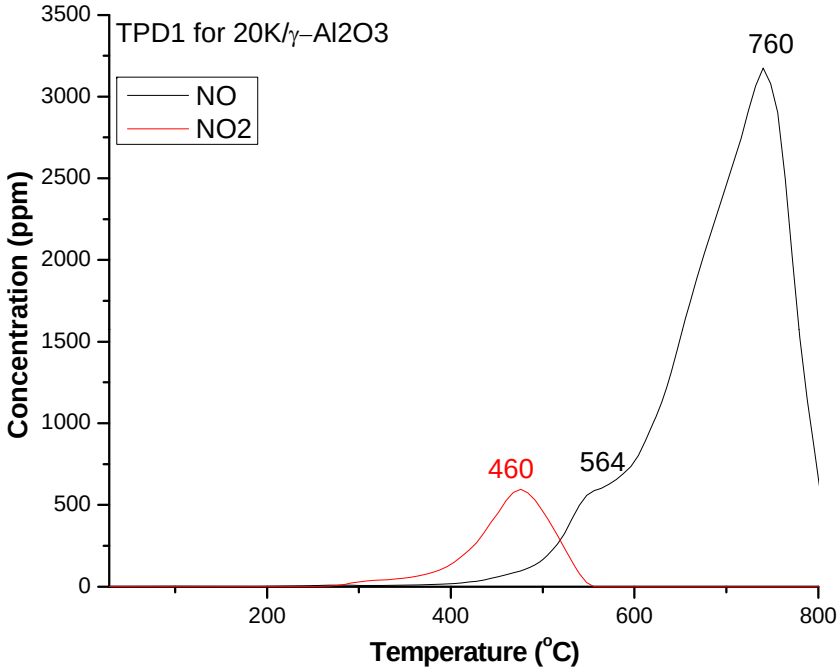
TR-XRD: decomposition of K(20)/Al_2O_3



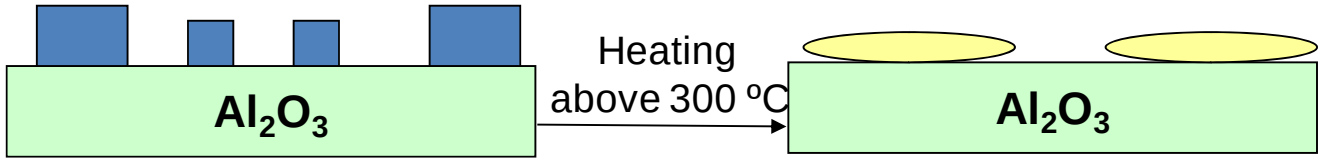
Around 300 ºC, KNO_3 phase (rhombohedral) disappears.

TPD with NOx analyzer



However, no NOx is desorbed up to 300 °C.

Rhombohedral



Amorphous KNO_3

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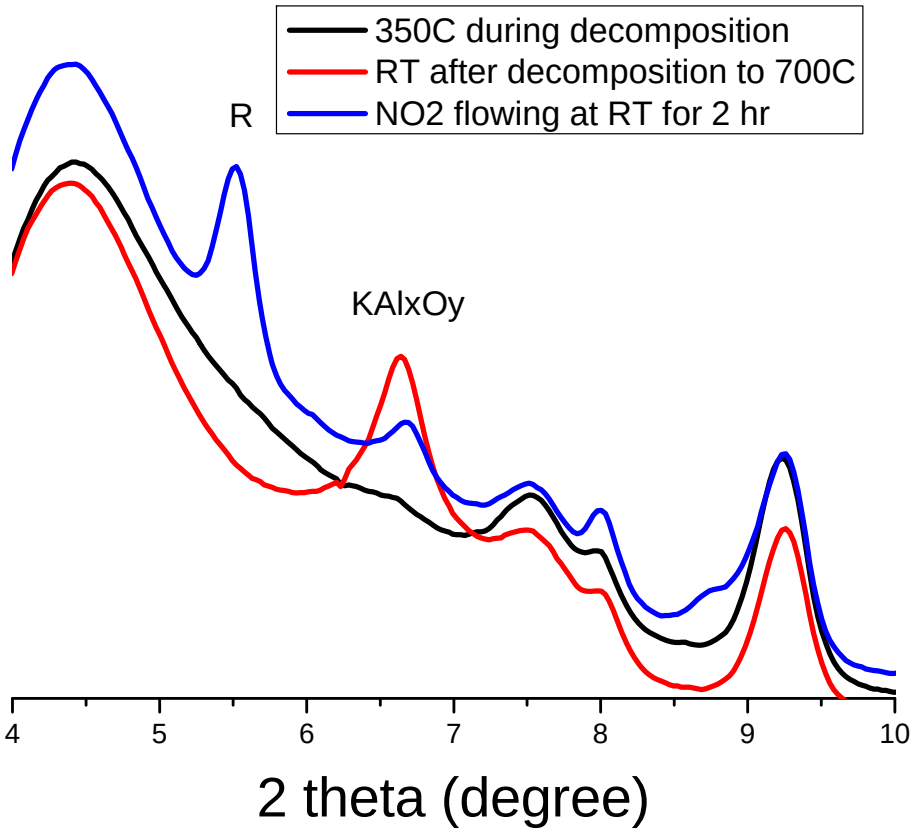
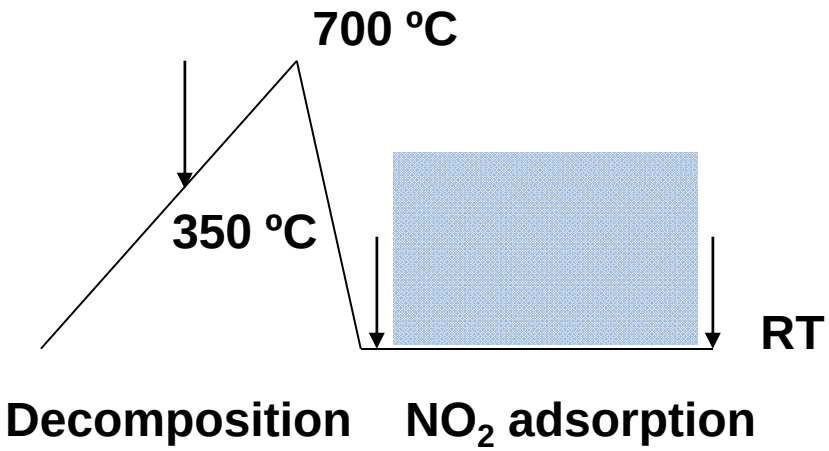
$K(20)/Al_2O_3$: to 700 ºC and NO_2 adsorption



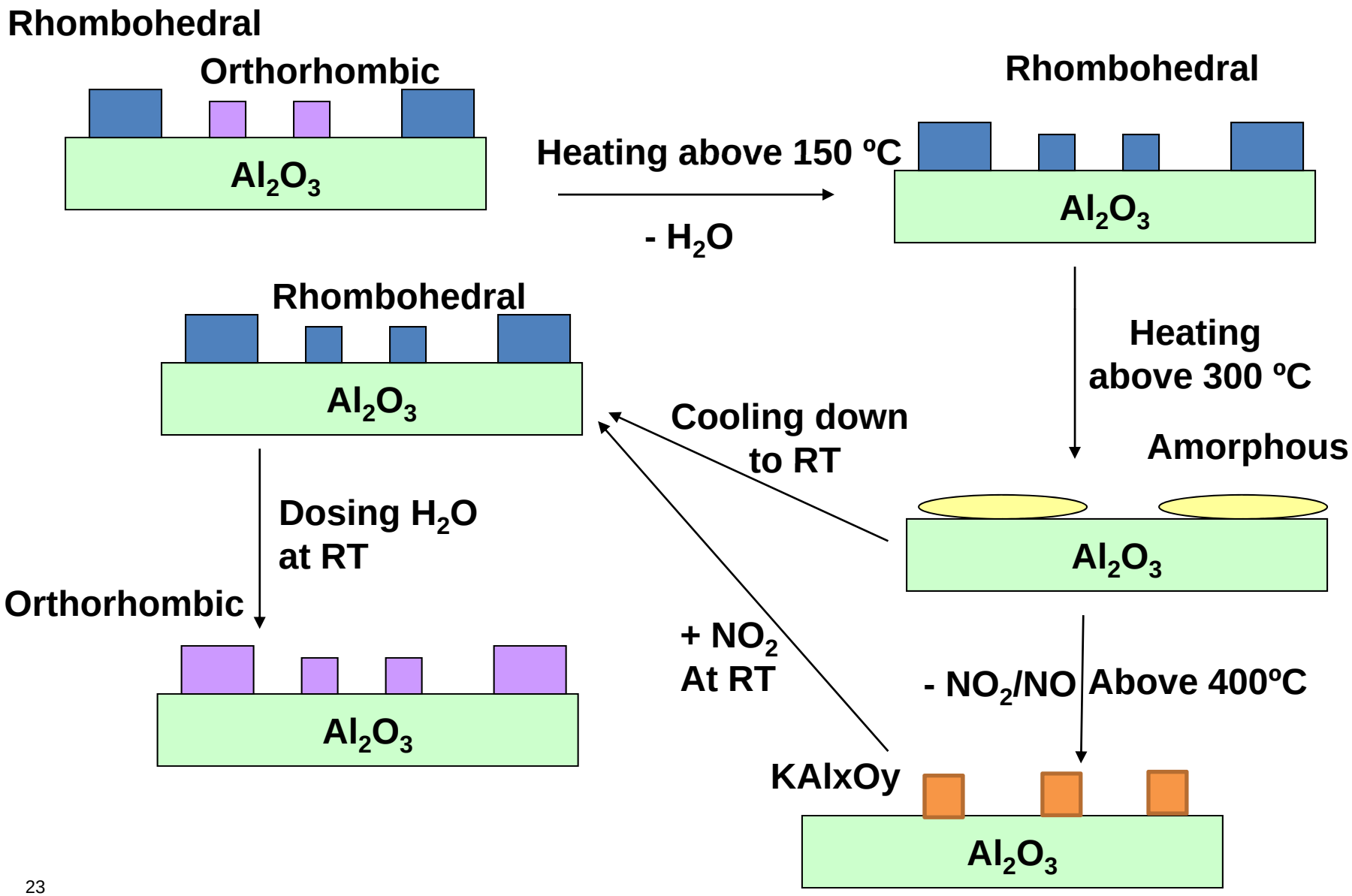


- At 350 ºC, only Al_2O_3
- At 700 ºC, KAl_xO_y phase formed.
- NO_2 transformed KAl_xO_y phase into rhombohedral KNO_3 phase (no orthorhombic phase).

R-KNO_3 → Amorphous KNO_3 → KAlxOy

+NO_2

Current mechanism: KNO_3 morphology changes



Summary and Conclusions

1. Higher temperature performance for current commercial Ba-based NSR catalysts can be obtained by substituting K for Ba and/or the support material, alumina (Al_2O_3), for magnesium aluminate ($MgAl_2O_4$).
2. **Similarities**: Both the Ba- and K-based model NSR catalysts store NO_2 as 2 forms ("surface" and "bulk") of nitrates as a function of loading, and display similar and reversible changes between these two nitrate forms upon contact of H_2O.
3. **Differences**: There are significant differences in the decomposition pathways and morphology changes between these two NSR materials, originating from the different physicochemical properties of $Ba(NO_3)_2$ and KNO_3.

Acknowledgments

U. S. DOE, Office of Energy Efficiency and Renewable Energy/Vehicle Technologies Program

Experiments performed in DOE's Environmental Molecular Sciences Laboratory located at PNNL

National Synchrotron Light Source located at Brookhaven National Laboratory

U.S. Department of Energy
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