Deactivation mechanisms of NO_x storage materials arising from thermal aging and sulfur poisoning

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LNT Durability Challenges: Aging & Poisoning

Key Questions

- Which thermal deactivation mechanism is more related to the loss of performance, Pt sintering or $BaAl_2O_4$ formation?
- How the sulfation/desulfation affects the catalytic activity of LNTs?
- How can thermal and sulfur deactivation effects be de-coupled?

Approach

1. Two samples (from JM)

   Simple model "Pt-BaO/Al_2O_3" catalyst

   Enhanced model "Pt-BaO/**CeO_2**-Al_2O_3" material
2. Activity measurements using a reaction protocol designed to separate sulfur and thermal effects
3. Characterization of Catalysts: XRD, TEM, XPS

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Project Scope

1. **Thermal aging: Which thermal deactivation mechanism is related to performance loss, Pt sintering or $BaAl_2O_4$ phase formation?**
   - Correlation of thermal aging with activity
   - *In situ* XRD, TEM, activity measurement

2. Sulfur effect

3. De-coupling of thermal aging and sulfur effects

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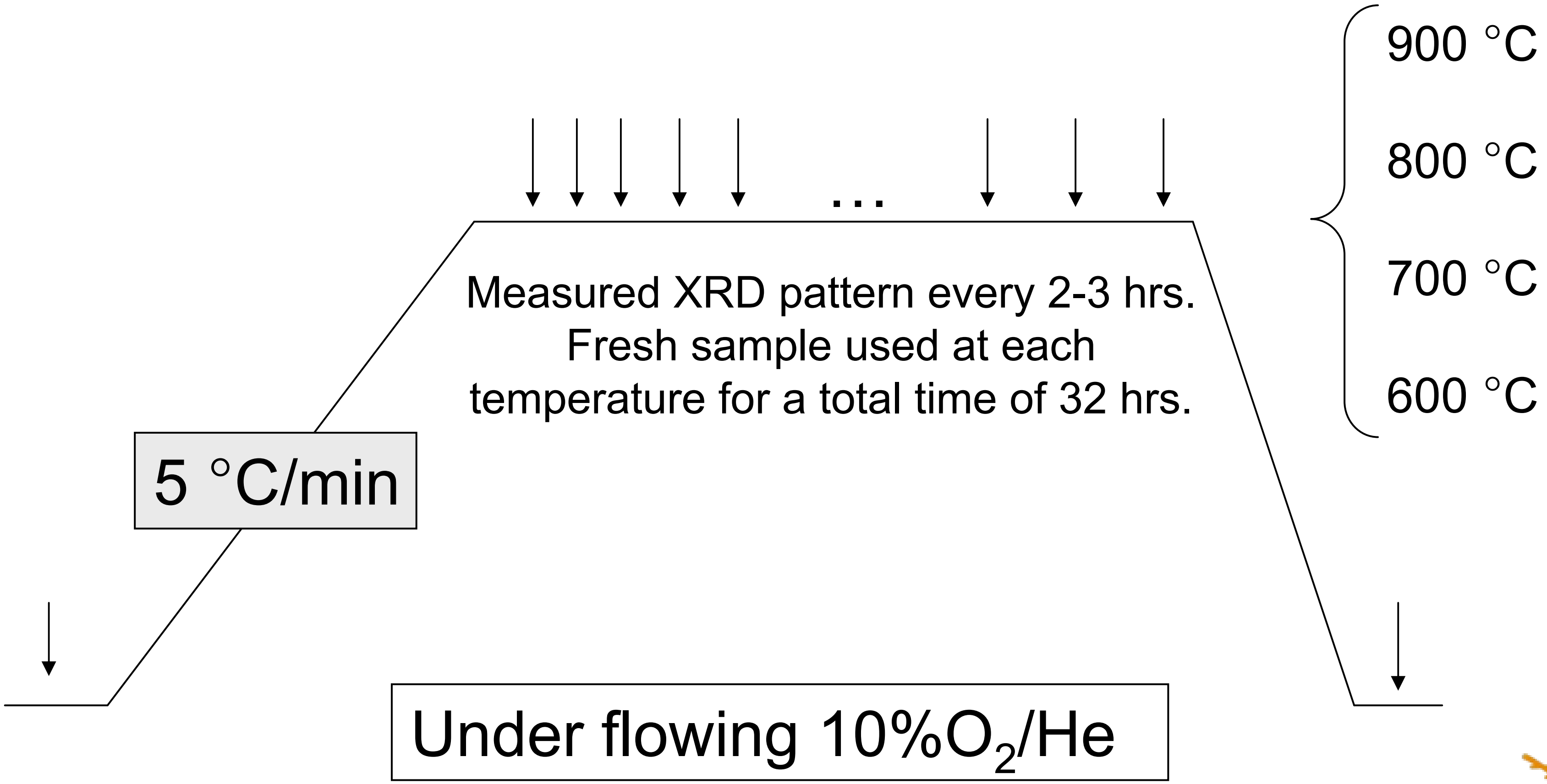
High temperature in situ XRD

- For model Pt-BaO/AL_2O_3 and Pt-BaO/**CeO_2**-AL_2O_3 samples after calcination at 500 °C for 3 hrs



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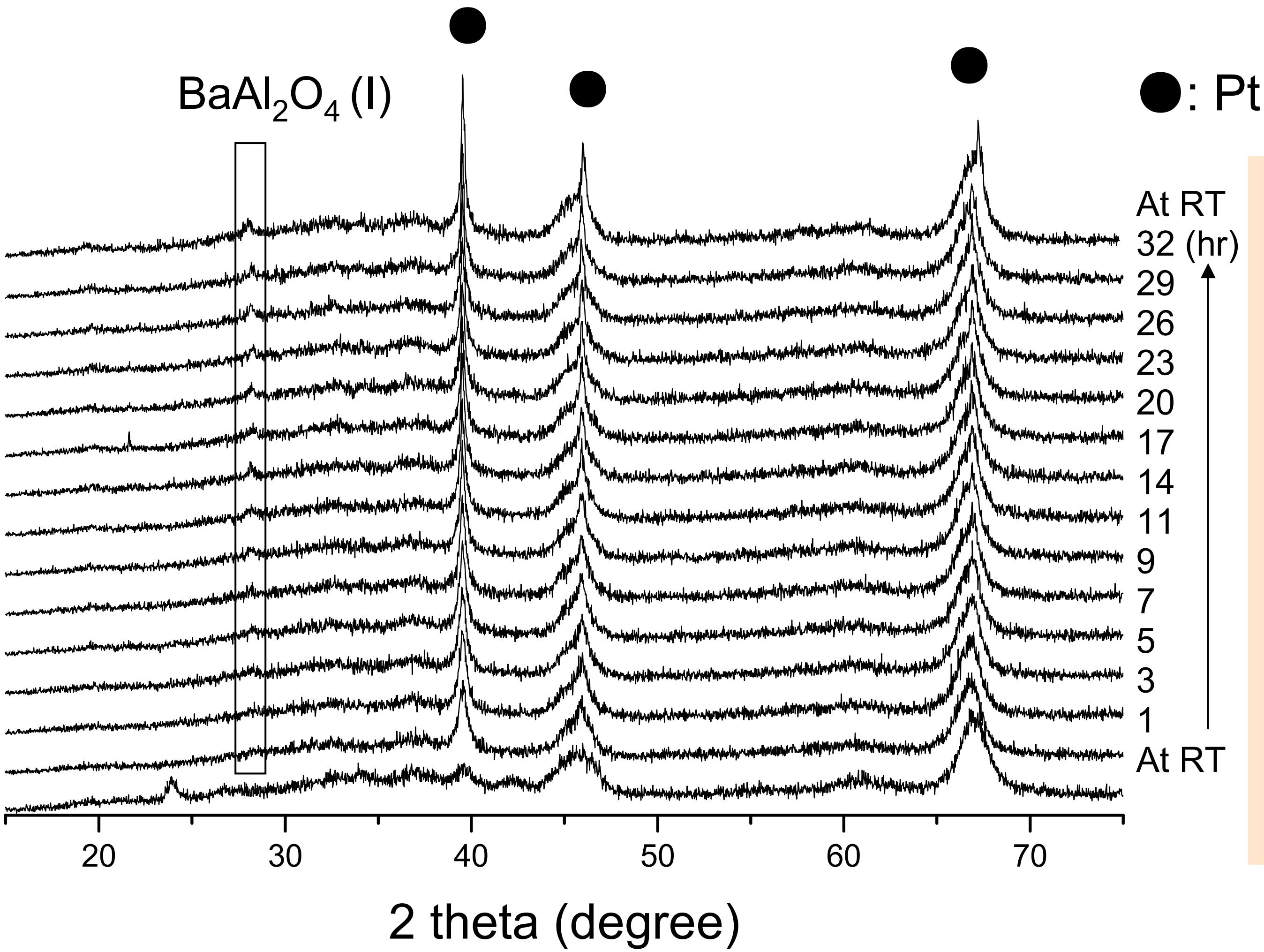
In-situ XRD: 'Simple Model' LNT at 900 °C



- Rapid and significant growth of crystalline Pt particle size
- Small amount of crystalline $BaAl_2O_4$ phase appears with small average particle sizes.

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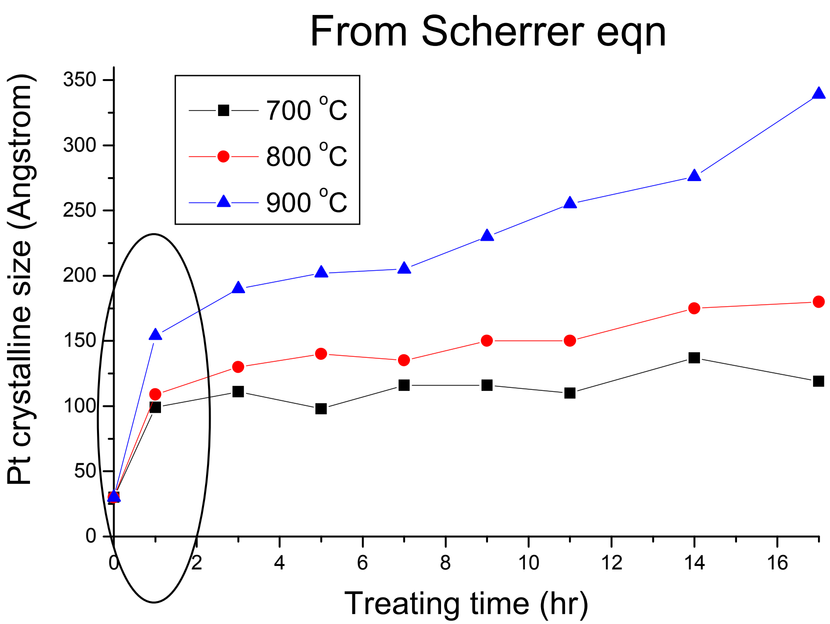
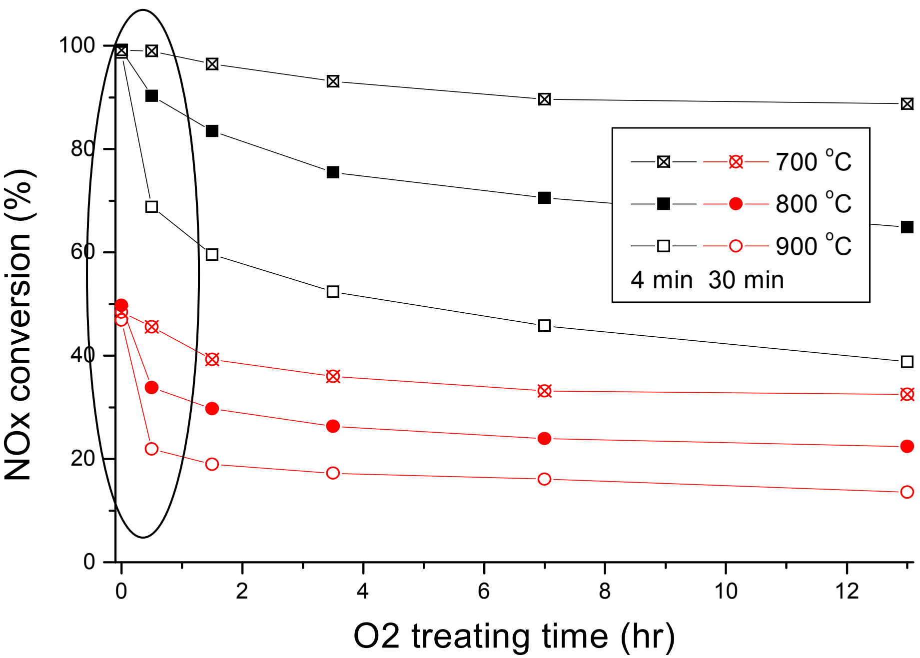
Comparison of Pt Crystallite size vs. Activity

Pt crystallite size



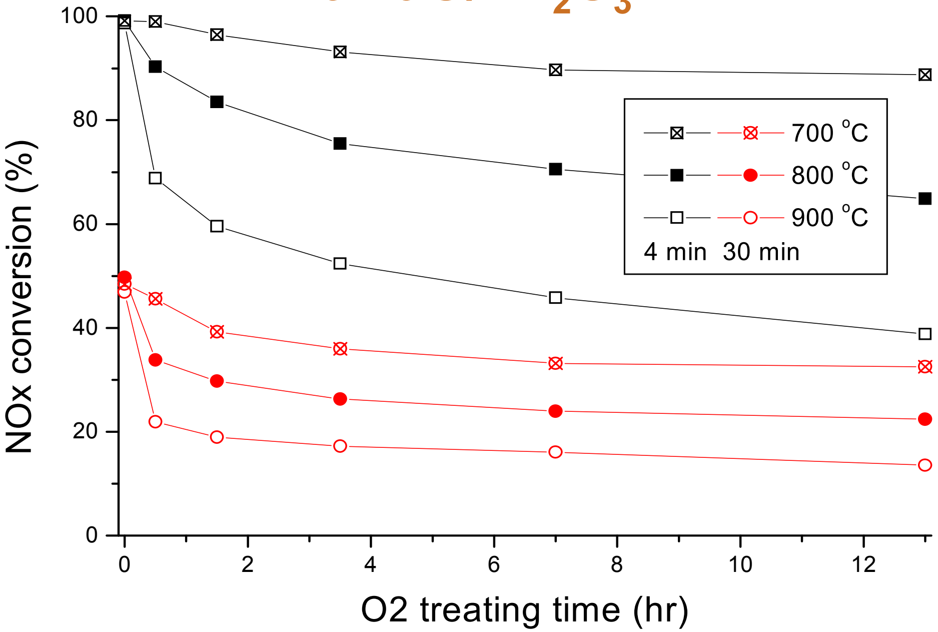
NO_x uptake



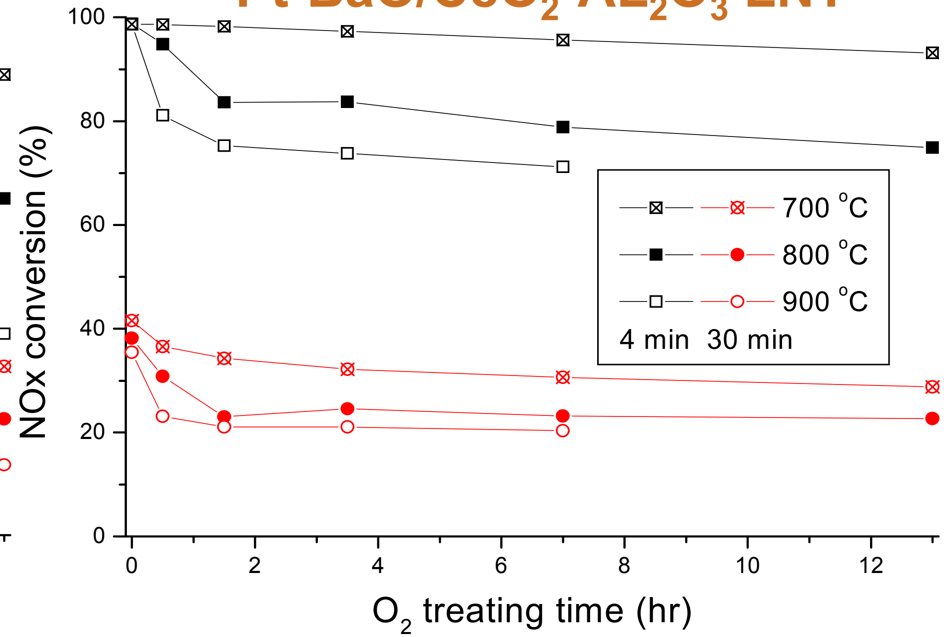
For a 'simple model' Pt-BaO/AL_2O_3 LNT, the decrease in NO_x uptake performance directly correlates with an increase in the Pt crystallite size.

Enhanced Model LNT sample vs. Simple model LNT sample

'Simple Model' Pt-BaO/AL_2O_3 LNT



'Enhanced Model' Pt-BaO/CeO_2-AL_2O_3 LNT



Although the initial activity of the 'Simple Model' LNT is higher, its performance decreases much more drastically with pretreatment temperature and time.

Why does the Pt-BaO/CeO2-AL2O3 "Enhanced Model" LNT show higher activity after thermal aging?

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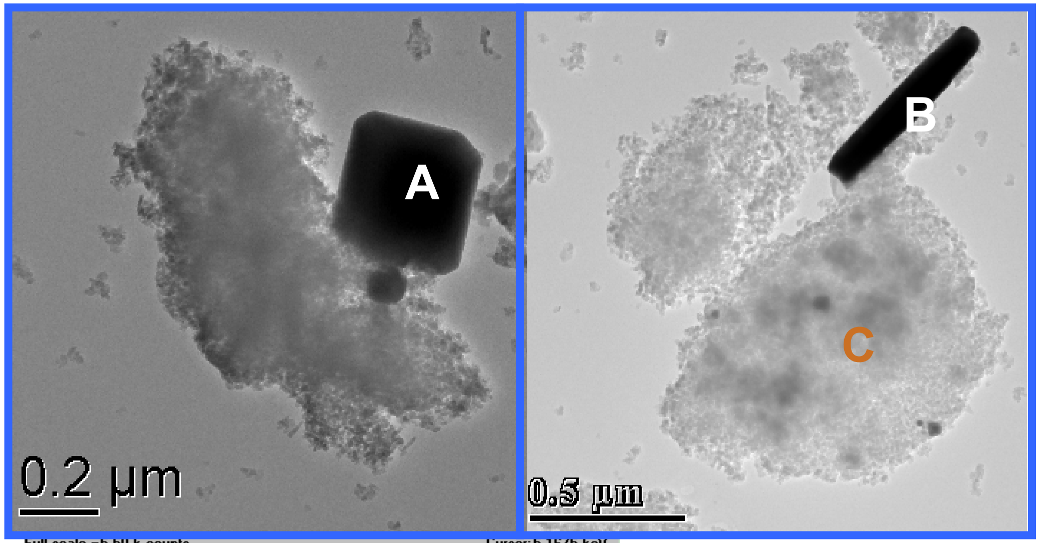
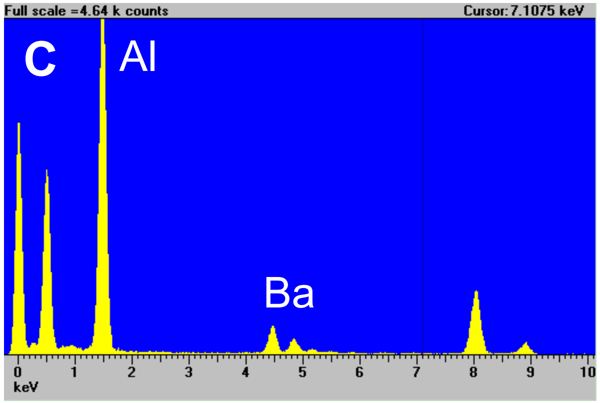
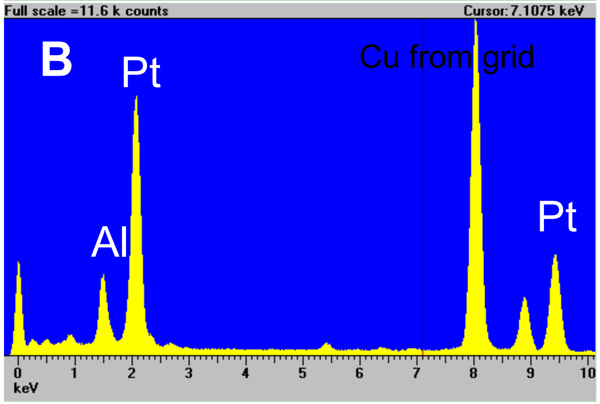
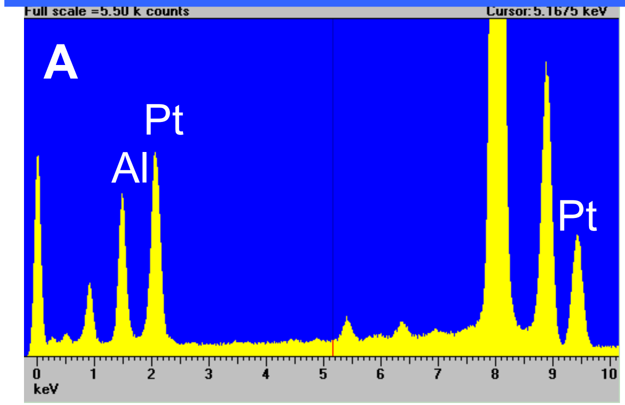
TEM & EDX: ‘Simple Model’ LNT material after 900 °C for 32 hrs

‘Simple Model’
$Pt-BaO/AL_2O_3$ LNT









Very easy to find large (>100 nm) Pt particles!

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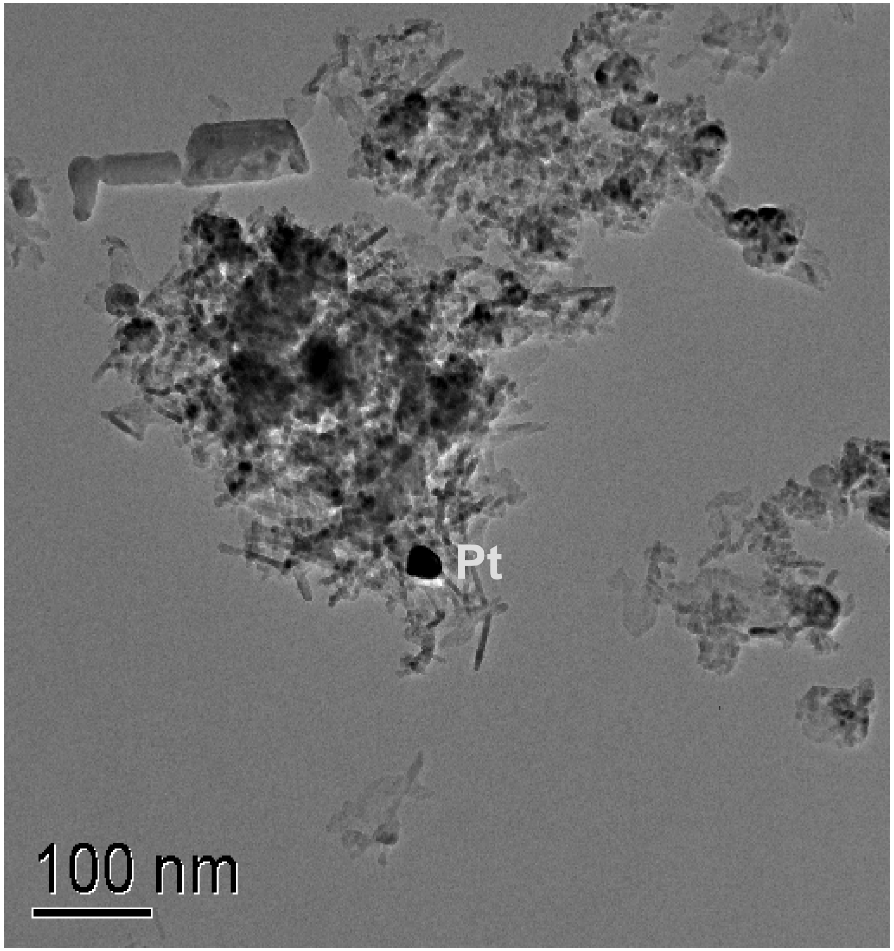
TEM: 'Enhanced Model' Sample after *in-situ* XRD at 900 °C



- Very difficult to find large (>30 nm) Pt particles!
- Also hard to find the small Pt particles in the support, implying the role of ceria to prevent the Pt sintering

'Enhanced Model'
Pt-BaO/CeO_2-AL_2O_3 LNT

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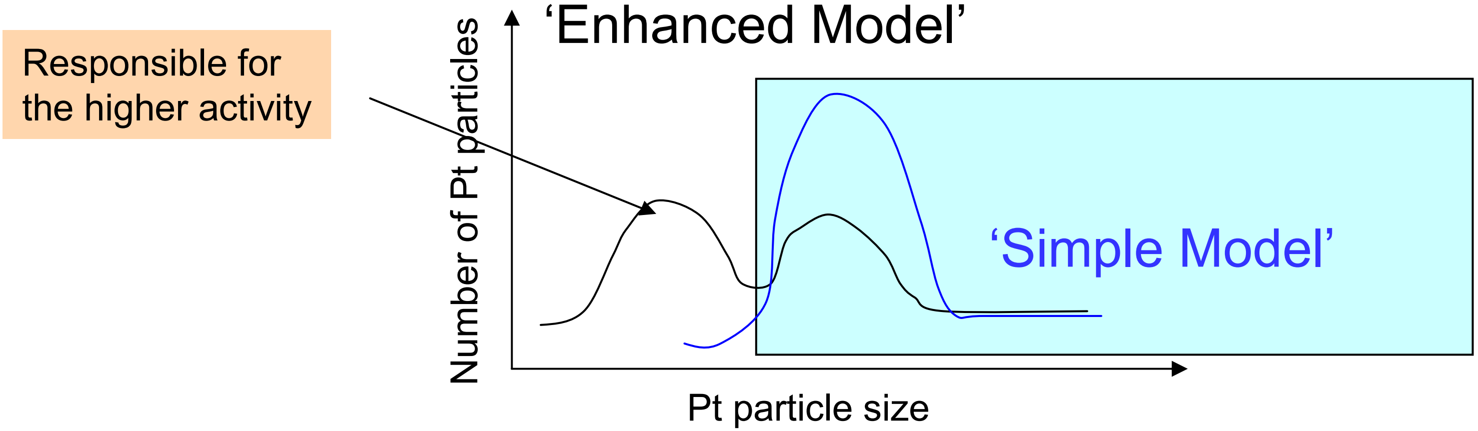
Summary: 'Simple Model' and 'Enhanced Model' LNTs after *thermal aging*

'Simple Model': Most of the Pt sintered to form very large particles (> 50 nm). Well correlated with the decrease in NO_x uptake performance.

'Enhanced Model': A small amount of Pt sintered to form larger particles (> 30 nm). We assume that the rest of Pt maintains a small size ('invisible' to XRD).



- **Pt sintering is the most important factor in determining performance stability during the thermal treatment.**
- **However, CeO_2 seems to play an essential role in inhibiting the Pt sintering!**

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Project Scope

1. Thermal aging

2. **Sulfur effect: How does sulfation/desulfation affect the NO_x uptake of the two LNT samples?**
   - Correlation of sulfation with activity

3. De-coupling of thermal aging and sulfur effects

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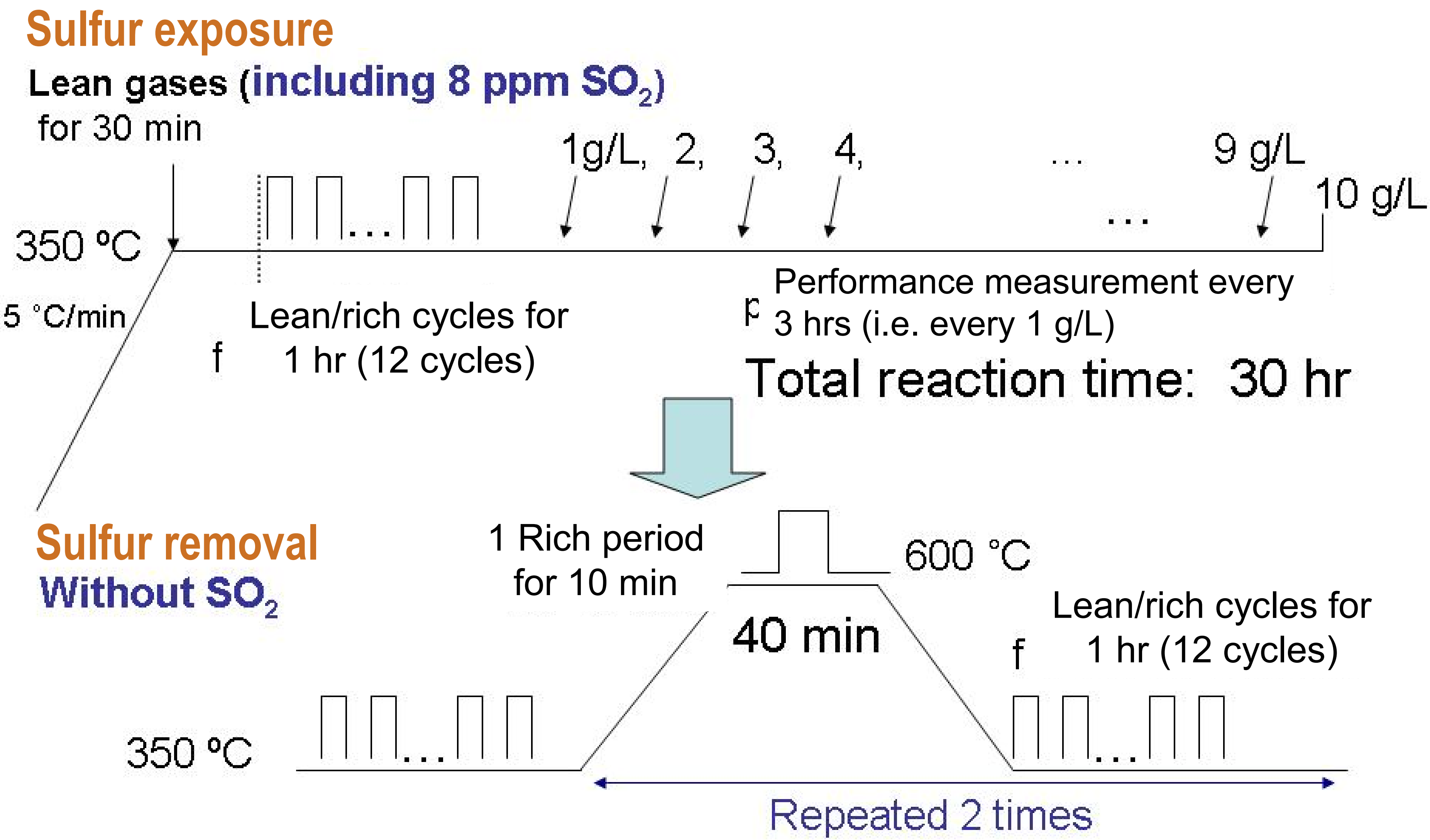
Reaction protocol



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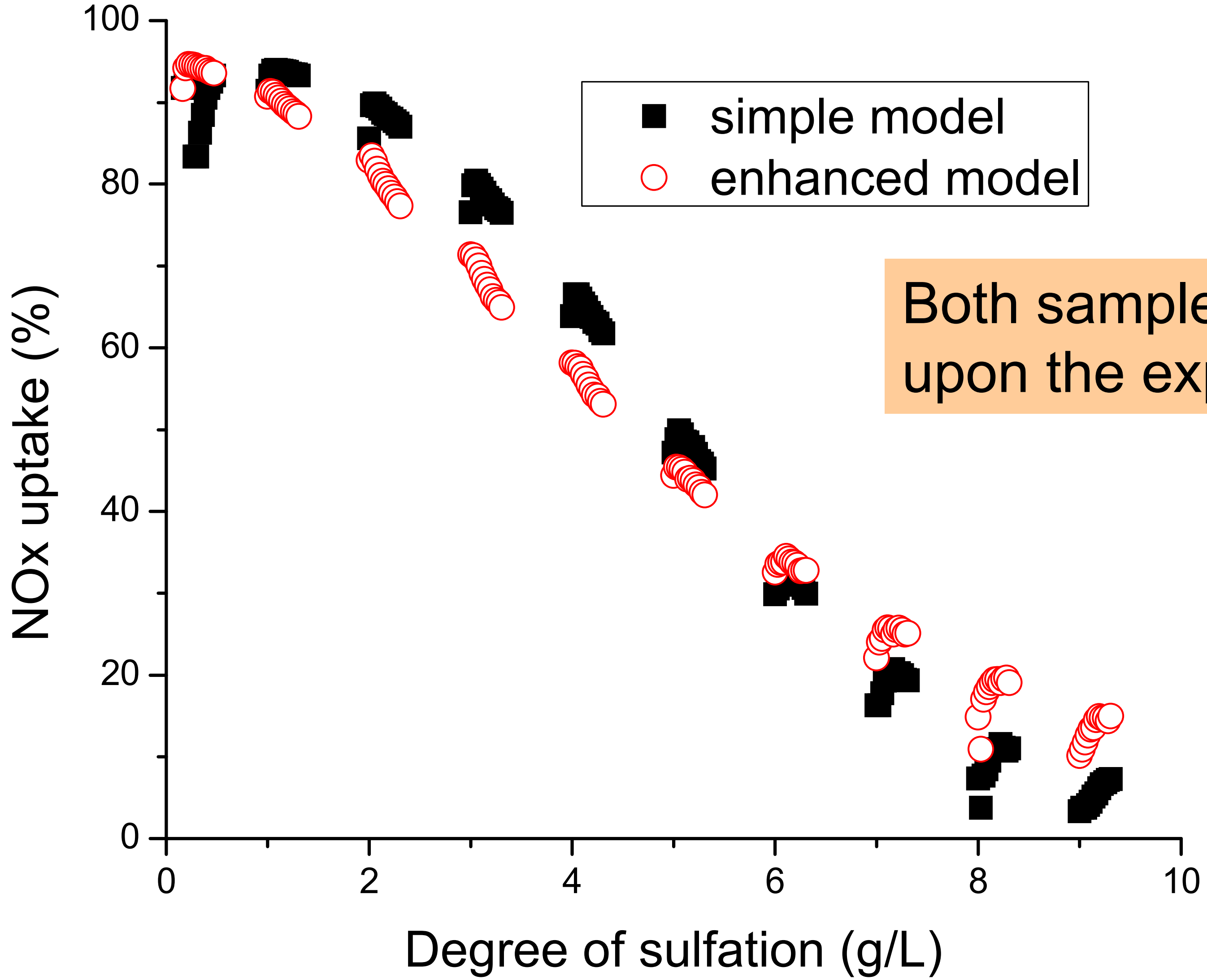
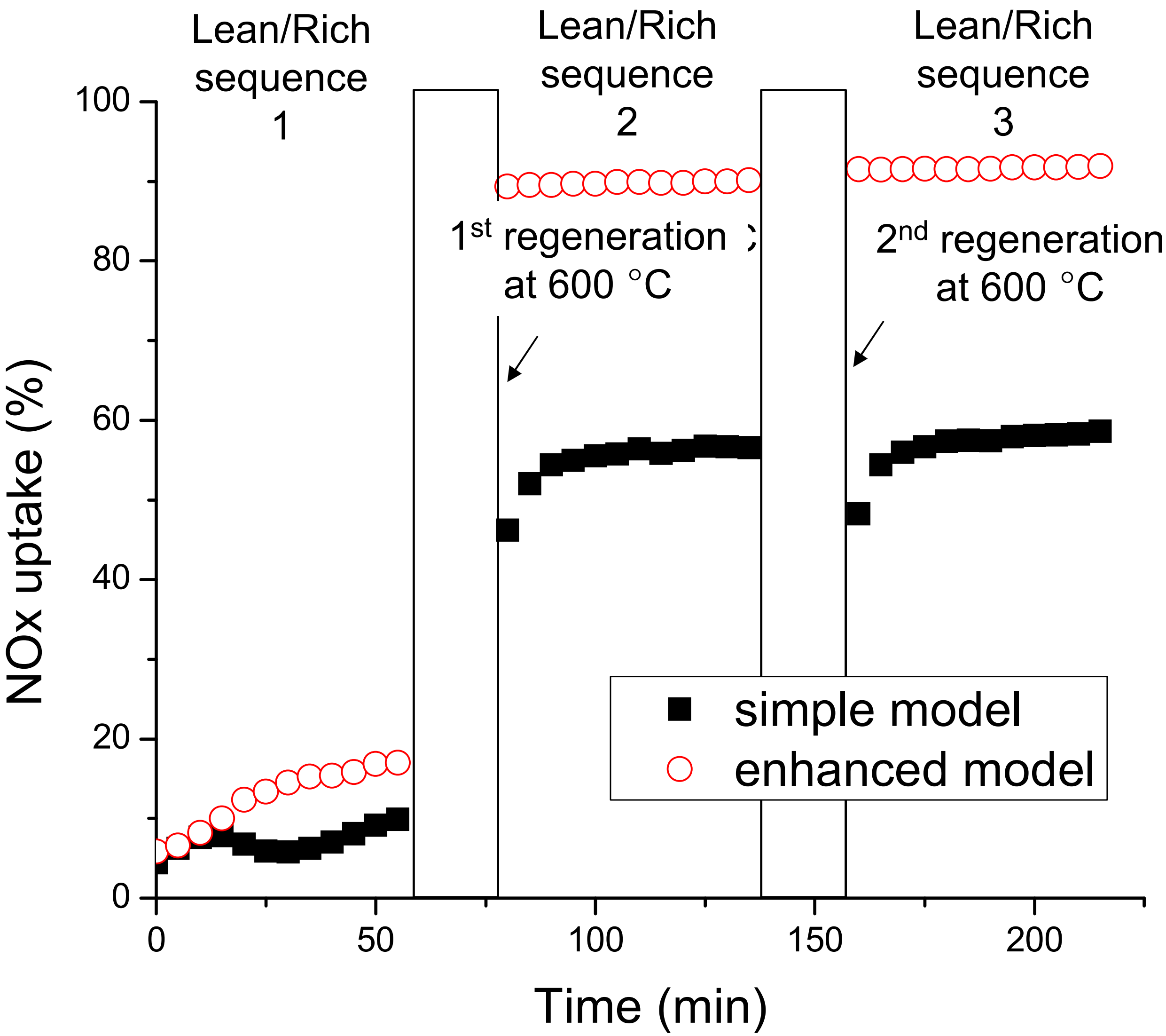
Effect of sulfur exposure on the NO_x uptake



Both samples deactivate upon the exposure of SO_2.

Effect of de-sulfation on NO_x uptake



In spite of the similar NO_x uptake after sulfation, the CeO_2 - containing LNT sample shows superior regeneration ability (due to the promoter).

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Project Scope

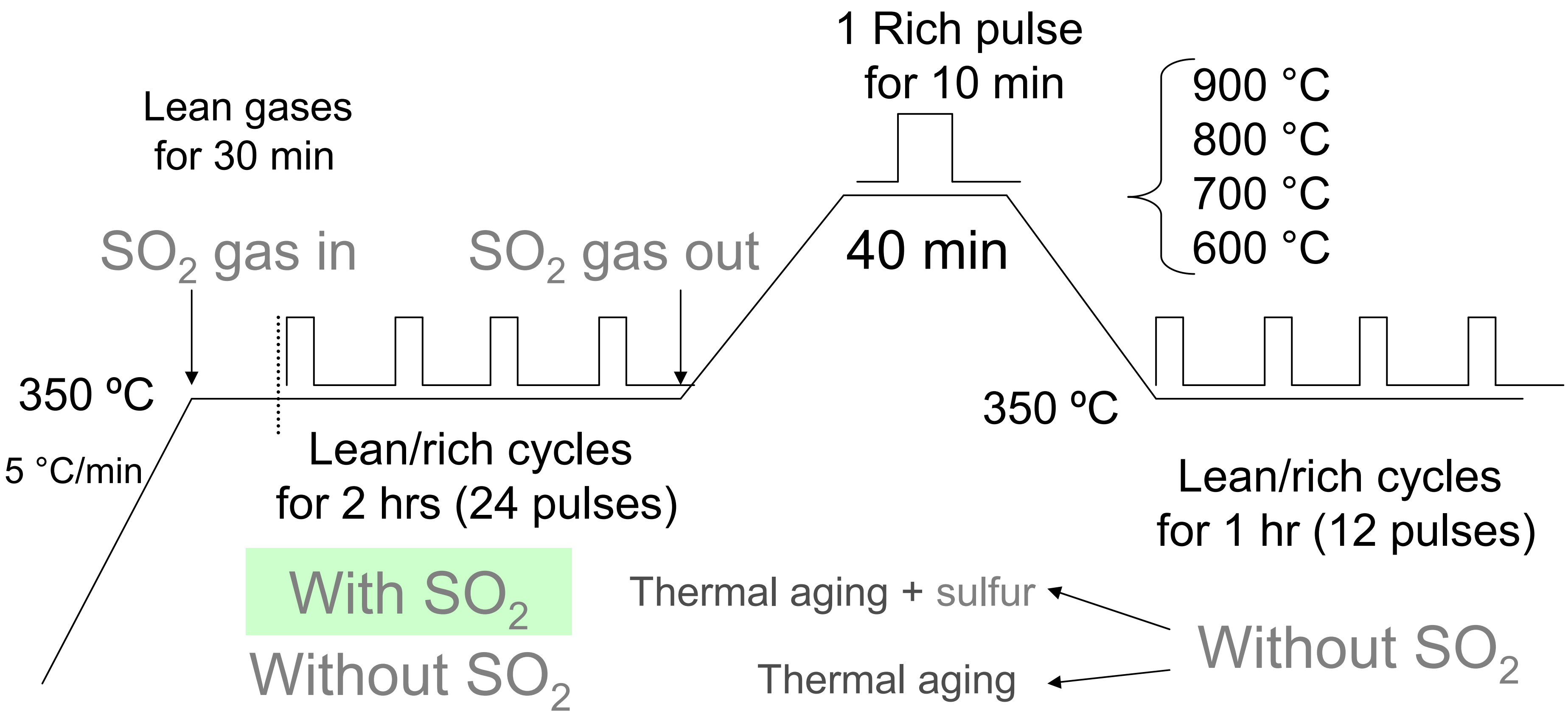
1. Thermal aging

2. Sulfur effect

3. **De-coupling of thermal aging and sulfur effects: How to do it?**
   - Reaction protocol
   - Performance measurements

After de-sulfation at high temperature, does activity drop from thermal aging or incomplete de-sulfation?

Decoupling of de-sulfation and thermal aging



The presence or absence of SO_2 in the reactants made it possible to decouple the de-sulfation and thermal aging processes.

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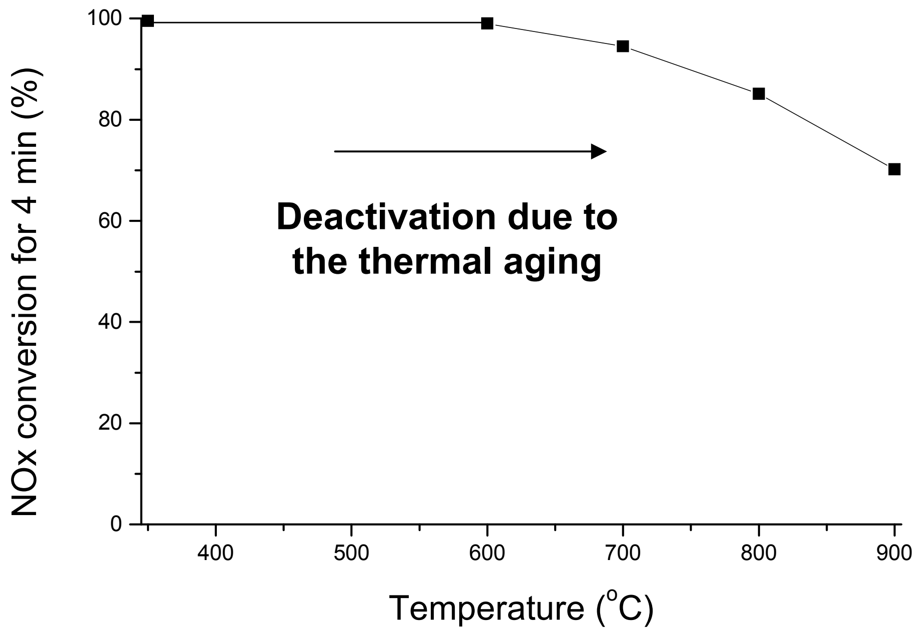
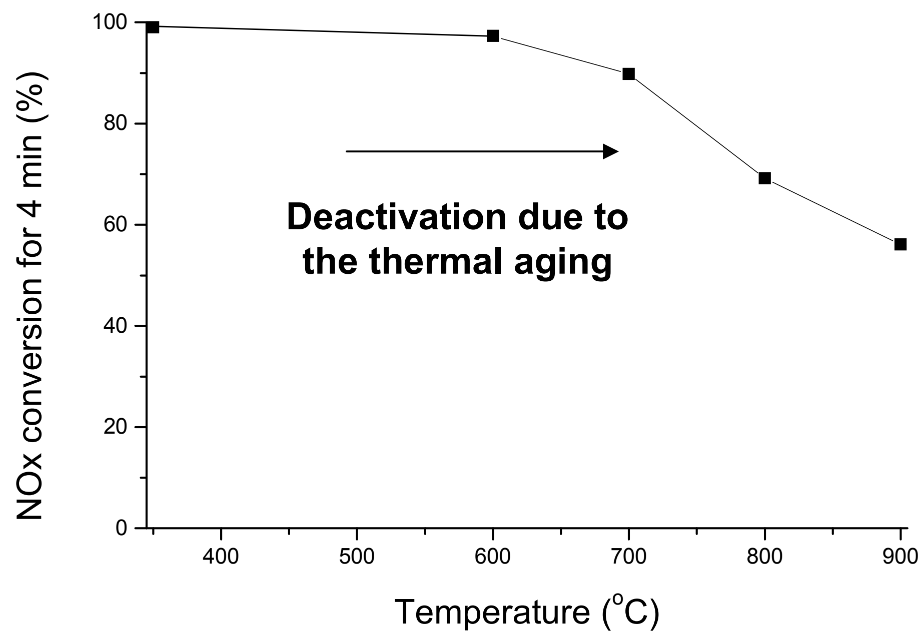
Activity as a function of thermal treatment temperature

'Simple Model'
Pt-BaO/AL_2O_3 LNT



'Enhanced Model'
Pt-BaO/CeO_2-AL_2O_3 LNT



Both materials are thermally deactivated above 700 °C.

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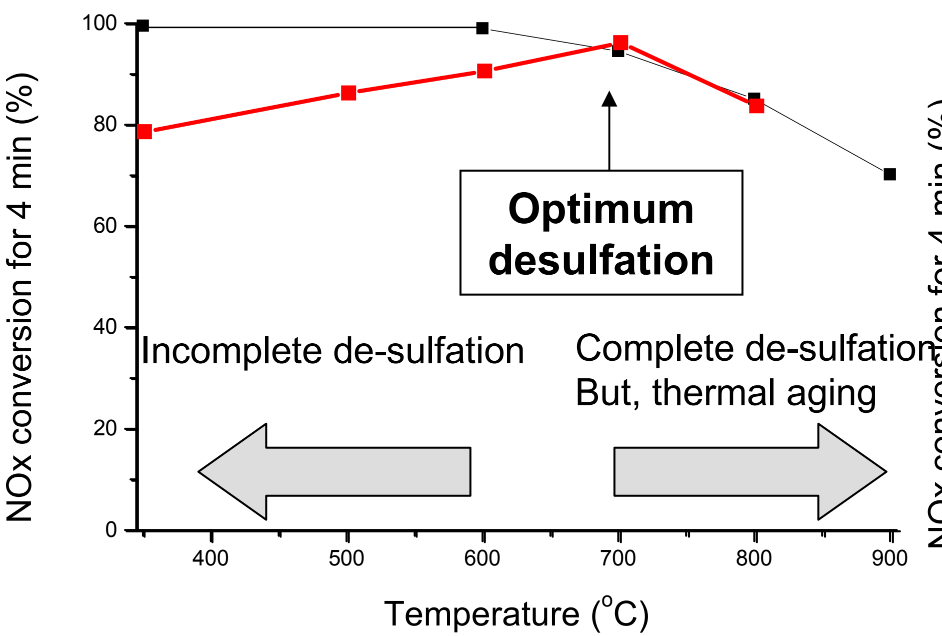
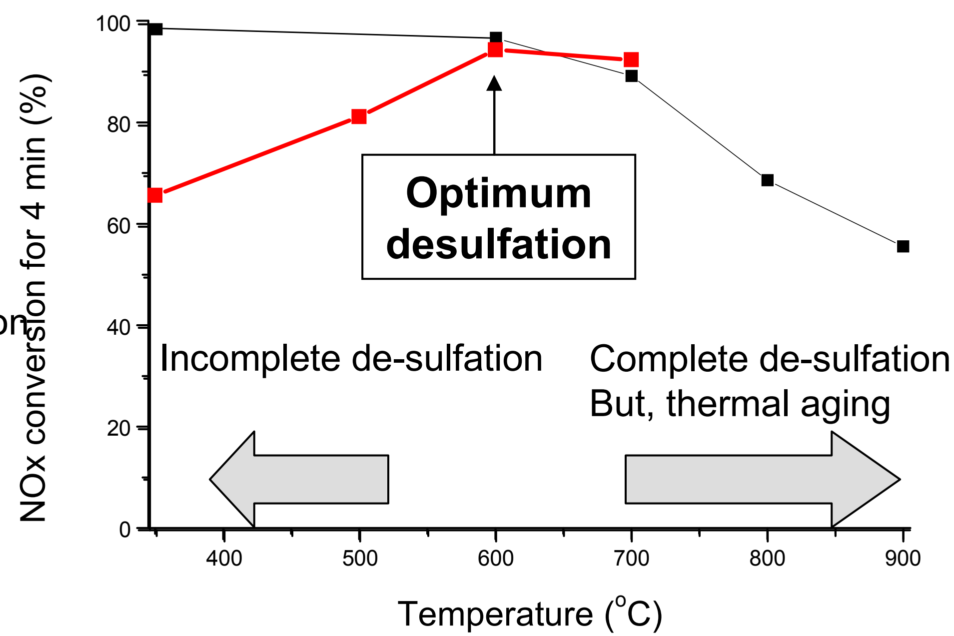
Finding the optimum condition of desulfation

'Simple Model' Pt-BaO/AL_2O_3 LNT



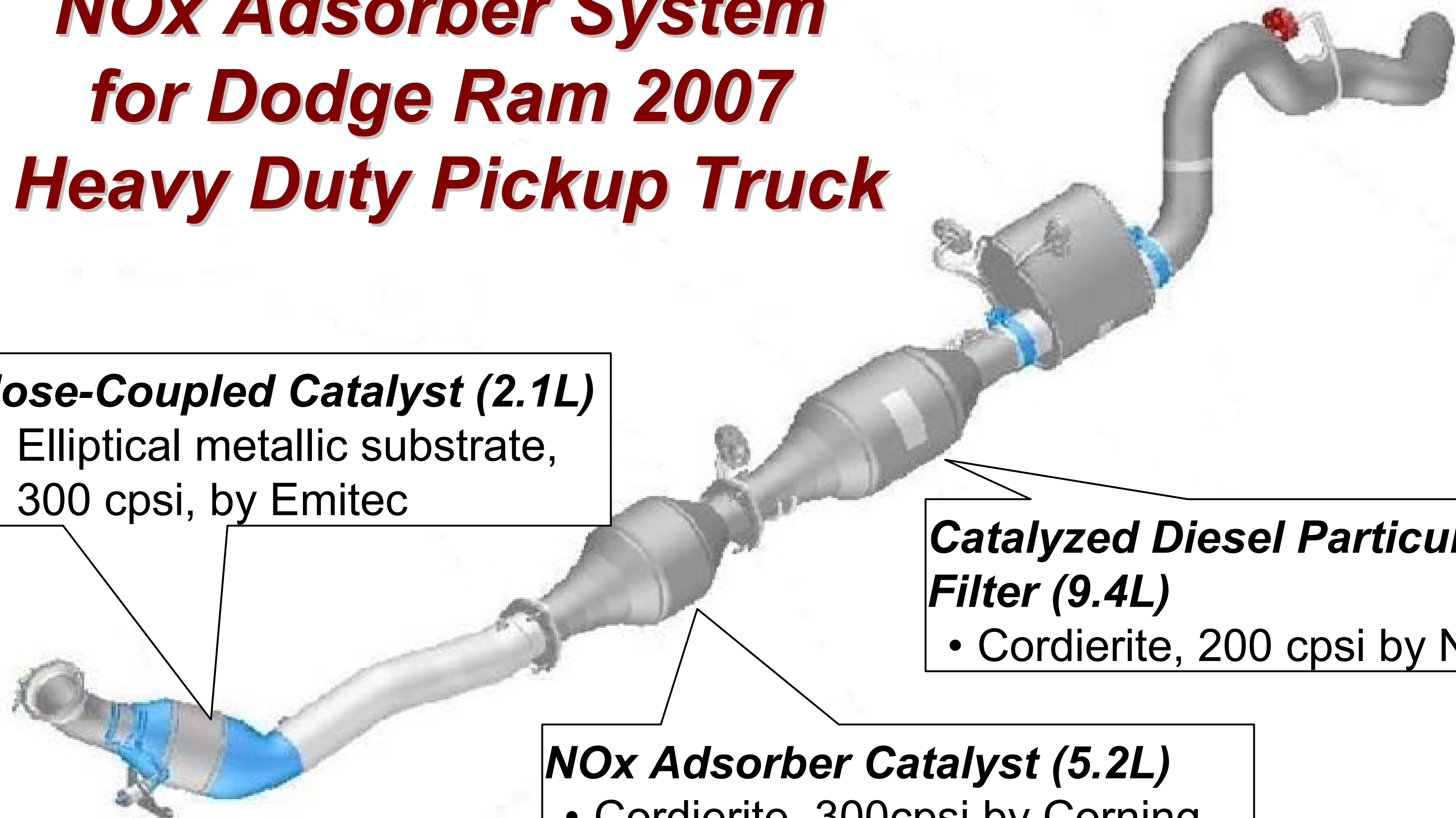
'Enhanced Model' Pt-BaO/CeO_2-AL_2O_3 LNT



It appears that the conversions after de-sulfation follow those of thermally aged samples above 700 °C, where the de-sulfation is almost complete. 'Enhanced Model' LNT shows more complete recovery of performance at 600 °C than the 'Simple Model' one.

LEV II-ULEV Certified System with Cummins 6.7L Engine and A/T System

NOx Adsorber System for Dodge Ram 2007 Heavy Duty Pickup Truck



Close-Coupled Catalyst (2.1L)
- Elliptical metallic substrate, 300 cpsi, by Emitec

Catalyzed Diesel Particulate Filter (9.4L)
- Cordierite, 200 cpsi by NGK

NOx Adsorber Catalyst (5.2L)
- Cordierite, 300cpsi by Corning

Cummins® JM

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Conclusions

1. **Pt sintering is the most critical and irreversible origin arising from the thermal aging,** therefore, the maintenance of the small Pt particles by lowering operating temperature or adding the promoter is the key factor to avoid the thermal deactivation.

2. **The novel LNT material must have ability to de-sulfate at lower temperature where Pt sintering does not occur.** Enhanced model LNT with promoter has better ability to de-sulfate than the simple one at lower temperature, thus recovering the activity more easily.

3. **Suggested reaction procotol allows us to decouple the thermal aging and sulfur effects,** leading to find the optimum condition and catalyst with minimizing the thermal aging and maximizing the de-sulfation.

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