Pt-free, Perovskite-based Lean NO_x Trap Catalysts

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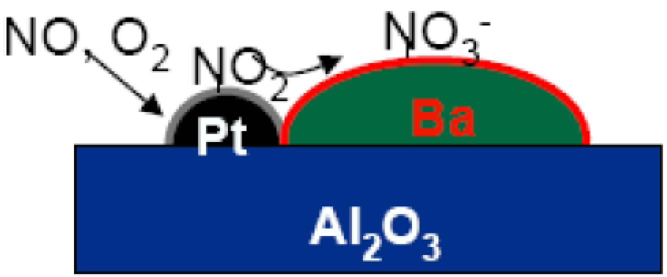
Overview

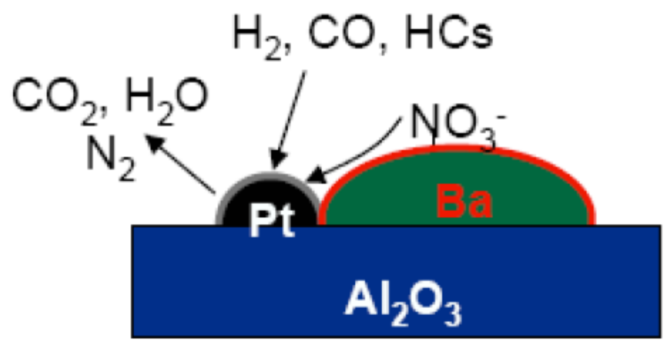
- ❑ LNT Chemistry
- ❑ NO Oxidation on Perovskite Catalysts
- ❑ PGM-free LNT Catalysts
- ❑ Pt-free LNT Catalysts

Lean NO_x Trap (LNT) Chemistry

Lean



Rich



Critical step

$NO + O_2 \rightarrow NO_2$ (Pt site)

$NO_2 + BaO \rightarrow Ba(NO_3)_2$ (Ba site)

$NO_x + H_2 \rightarrow N_2 + H_2O$ (Pt site)

$NO_x + CO \rightarrow N_2 + H_2O$ (Pt site)

NO_x stored as nitrate/nitrite

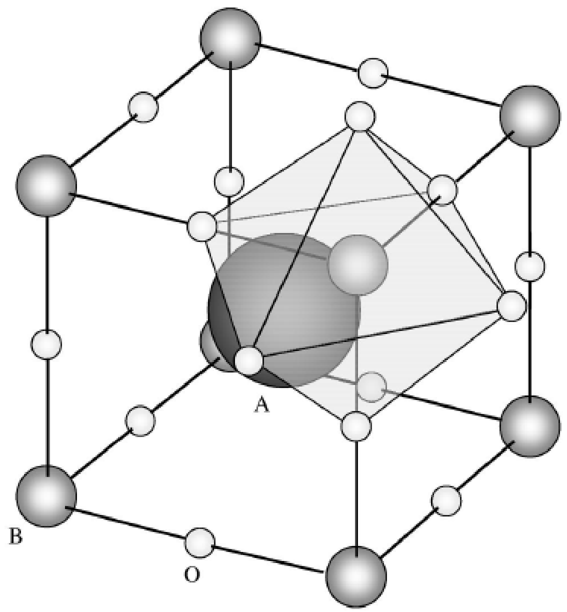
NO_x released & reduced

Storage

Regeneration

Goal: Reduce Pt usage and total PGM cost

Perovskite Oxides Catalysts



Perovskite

General formula: **ABO_3**

A: Rare earth metal (i.e. La)

B: Transition metal (i.e. Co, Mn, and Fe)

Promoters: Sr, Ba, and Ce promote catalytic properties

❑ Benefits

- Low cost & easy synthesis
- Excellent thermal stability

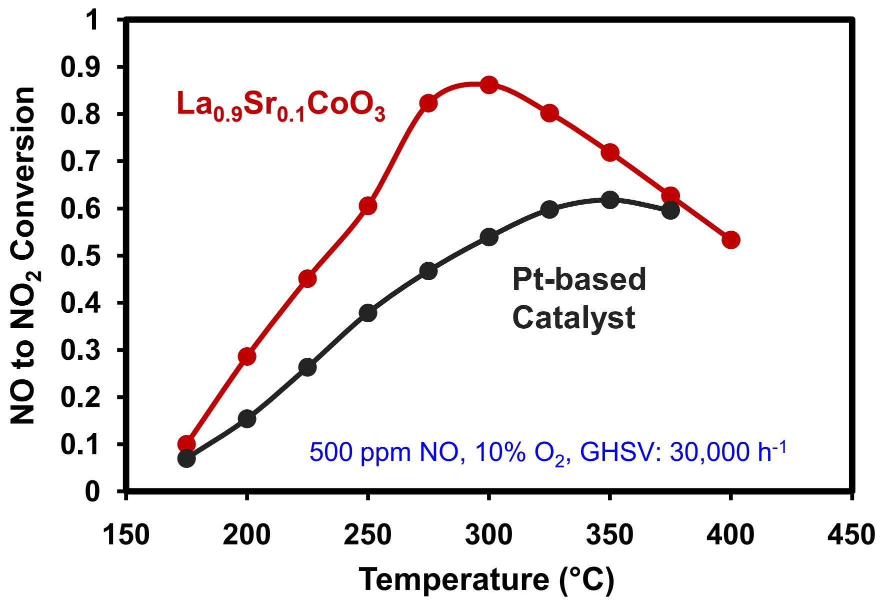
❑ Issues

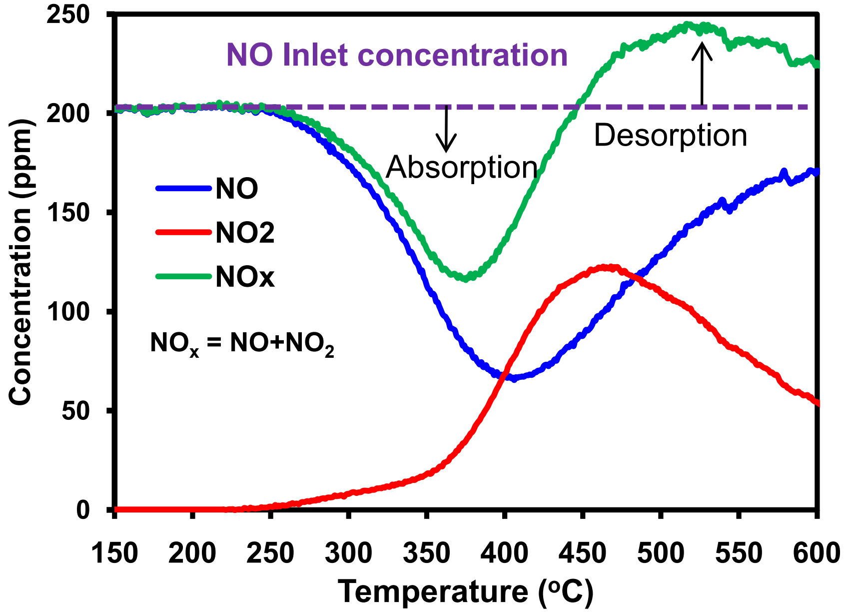
- Low surface area
- Susceptible to sulfur poisoning

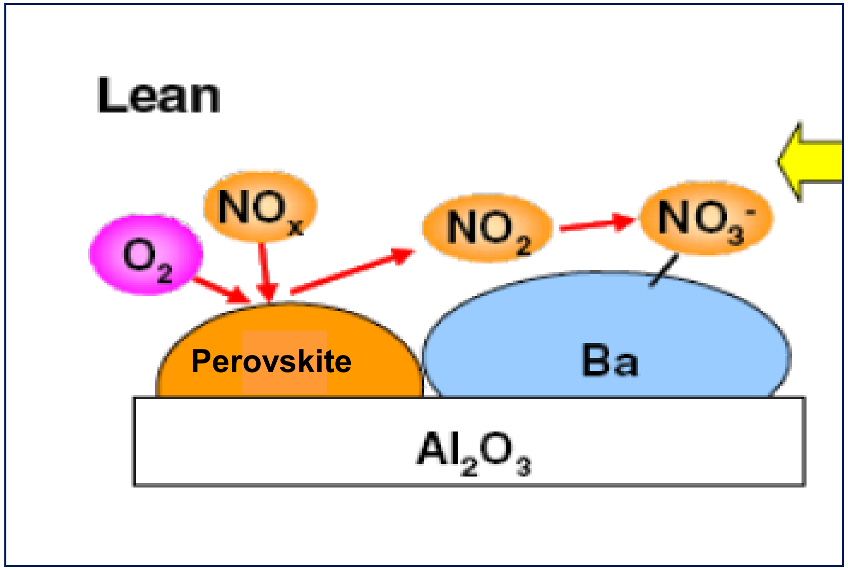
❑ Perovskite As Automotive Catalysts

- Three way catalysts for gasoline application
  - HC, CO oxidations
  - NO/CO reactions
- "Intelligent" catalysts (TWC)
  - Pd self-regeneration
  - Limited cost reduction

NO Oxidation and NO_x Storage



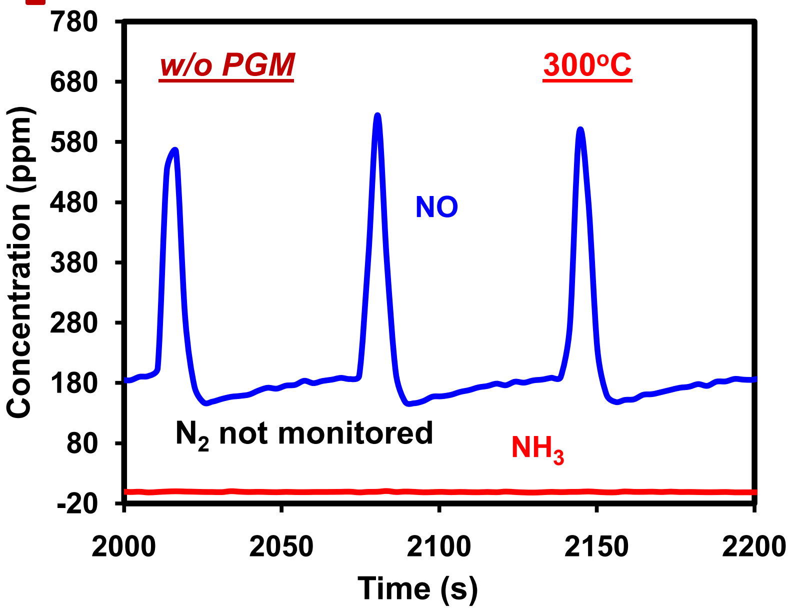


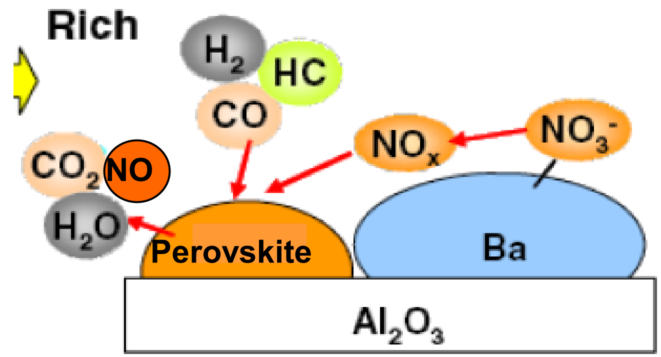


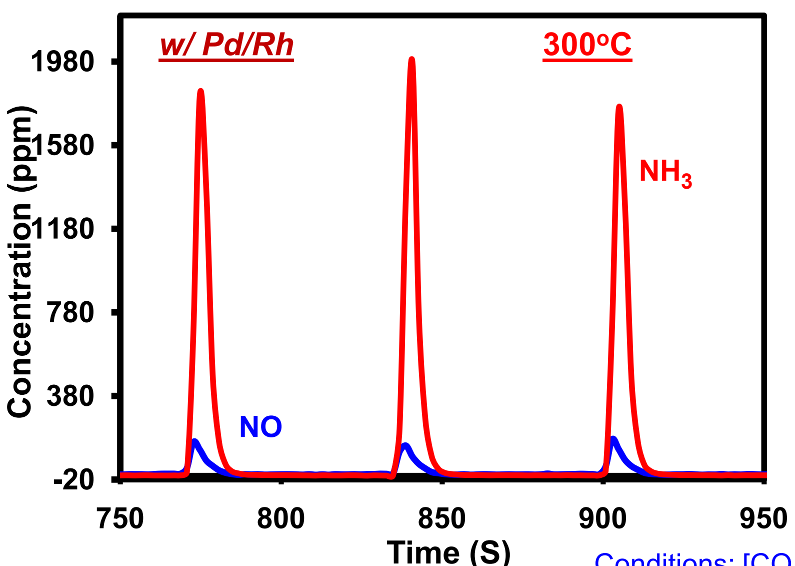
- Perovskite catalysts are active for NO oxidation to NO_2
- Perovskite based LNT shows good NO_x storage capacity in lean condition
- NO_x adsorption capacity: 0.75 g/L

[NO] = 200 ppm, [CO_2] = [H_2O] = [O_2] =10%, SV=50,000 h^{-1}, ramp rate = 10 C/min, catalyst degreened at 700 °C for 2.5 hrs

Perovskite Based LNT Regeneration







$NO_x + H_2/CO$ —Perovskite (✗)→ N_2/NH_3

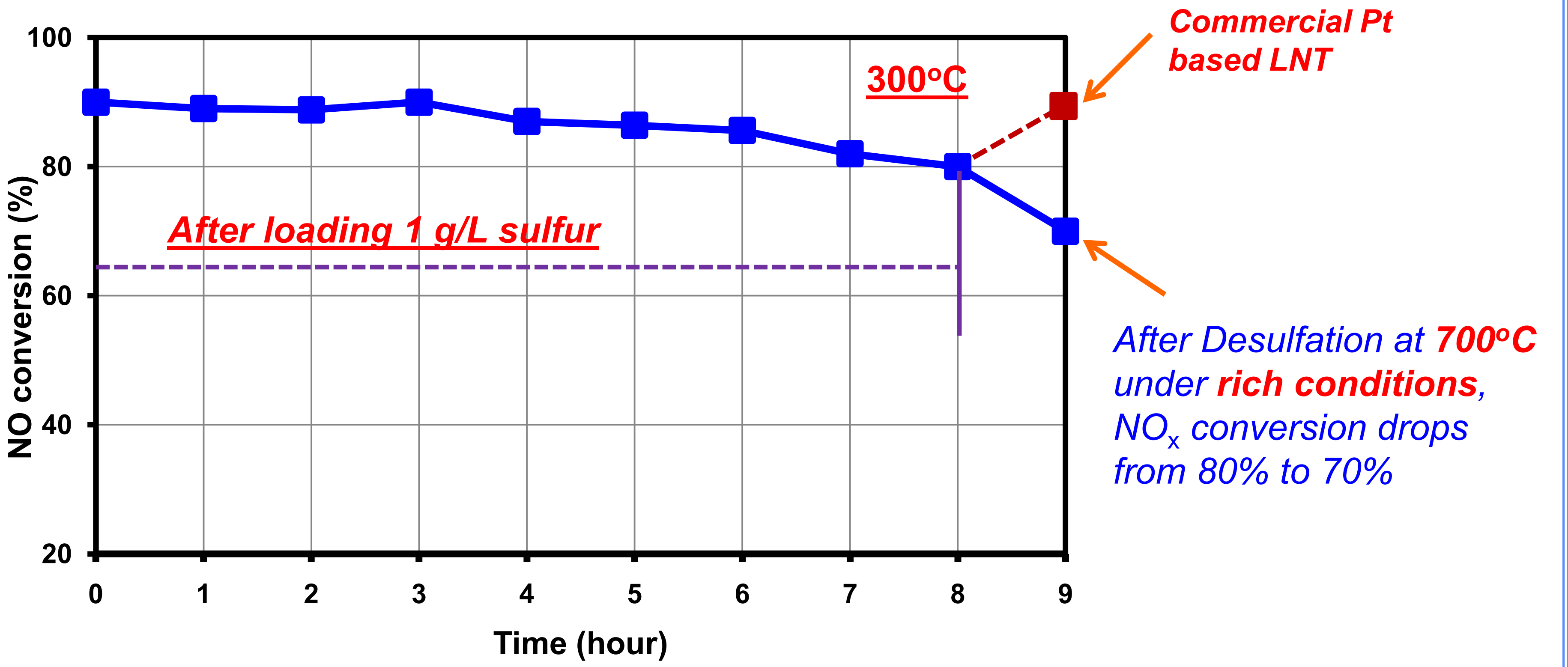
$NO_x + H_2/CO$ —Pd/Rh (✓)→ N_2/NH_3

- *Stored NO_x can not convert to N_2 or NH_3 in rich condition on perovskite based LNT without PGM*
- *Perovskite based LNT containing Pd/Rh looks promising*

Conditions: $[CO_2] = [H_2O] = 10\%$, 200 ppm NO, SV=50,000 h^{-1}; Lean/Rich = 60s/5s; Lean 10% O_2; Rich 3%CO+1%H_2

Sulfur Poisoning and Desulfation

NO conversions as a function of sulfur loading

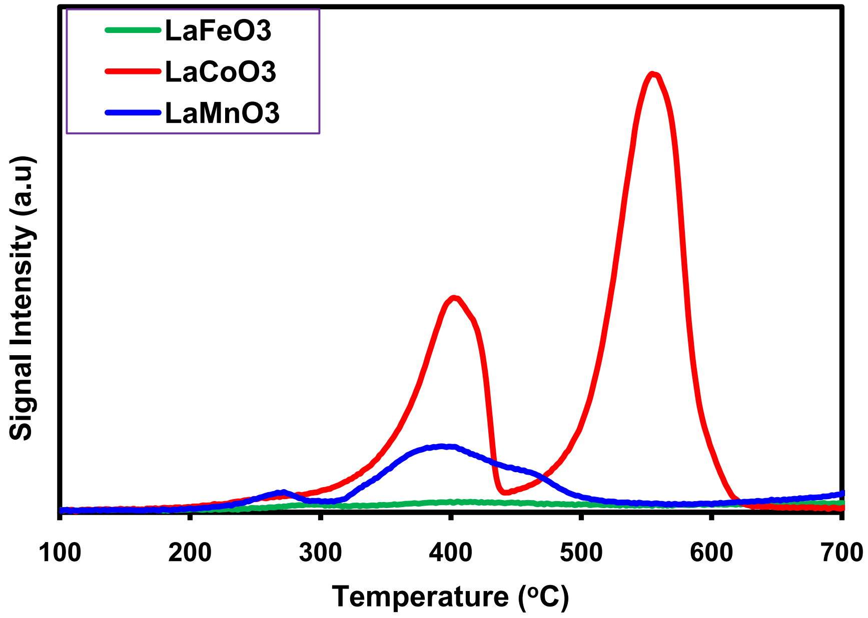


❑ $La_{0.9}Sr_{0.1}CoO_3$ -based LNT can not recover activities after desulfation

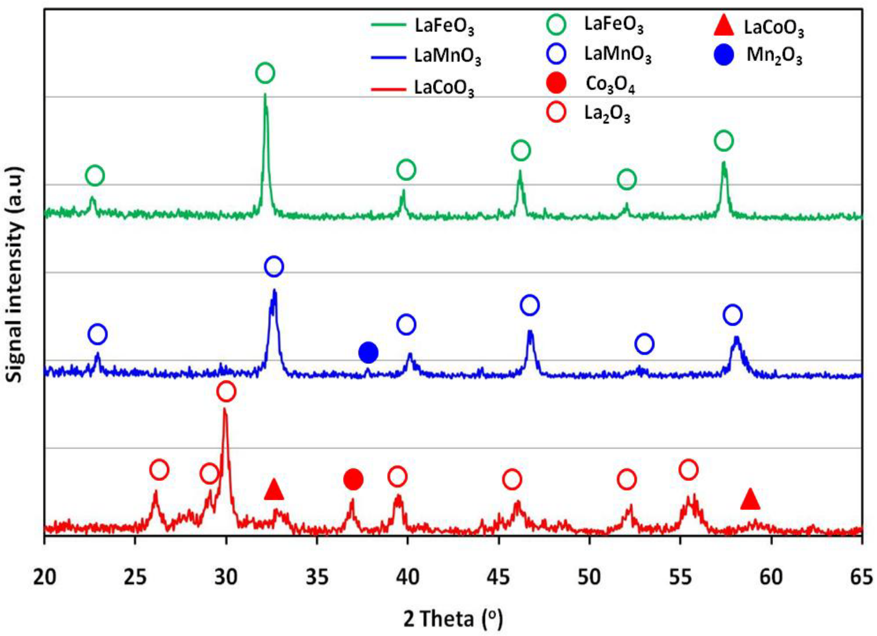
Conditions: lean-rich cycles (60s/5s) with 2 ppm SO_2; 200 ppm NO, $[CO_2] = [H_2O]$ =10%, SV=50,000 h^{-1}; Lean 10% O_2; Rich 3%CO+1%H_2

TPR/XRD of Perovskites

H_2-TPR of $LaMO_3$(M = Fe, Co, Mn)



XRD patterns of $LaMO_3$ (M = Fe, Co and Mn)

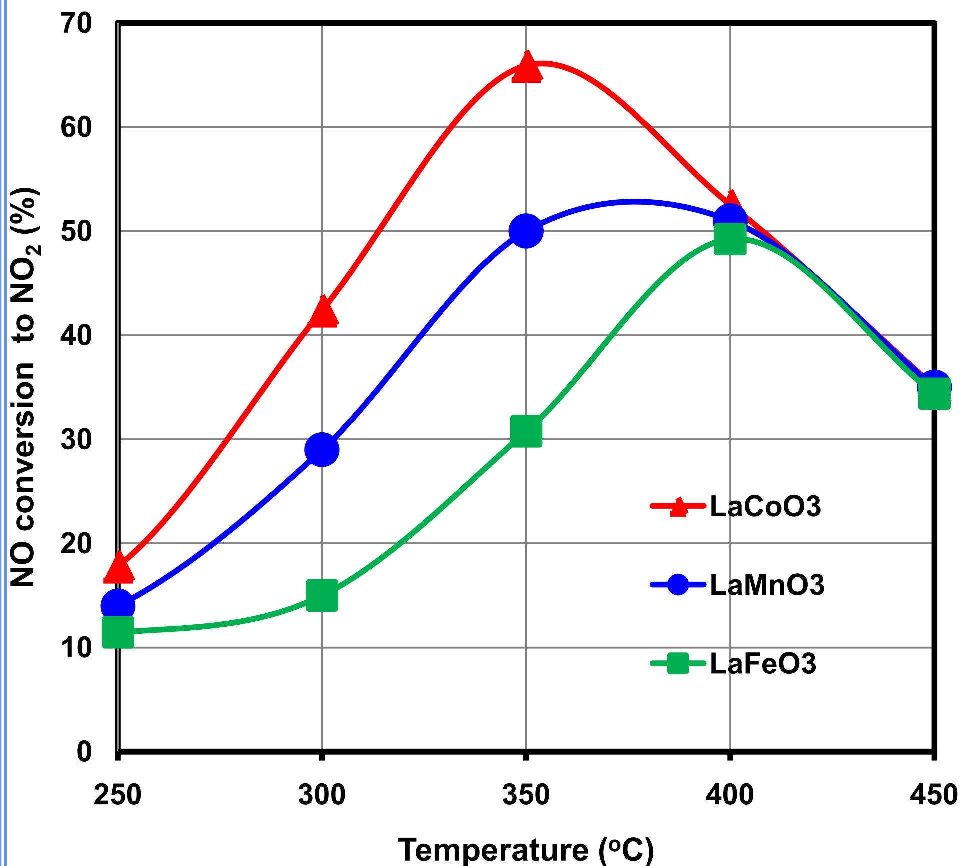


- ❑ *$LaCoO_3$ is not stable at 700°C in 5%H_2/N_2, likely needed for desulfation*
- ❑ *$LaMnO_3$/$LaFeO_3$ could be stable at 700°C in 5%H_2/N_2*

Condition: 50 mg $LaMO_3$(M = Fe, Co Mn), ramp rate = 10°C/min under 5%H_2/N_2

Oxidized at 550°C in air after reduction at 700°C in 5%H_2/N_2 for 30 min.

NO Oxidation over Perovskites



Lean

Rich

$NO + O_2$

NO_2

NO_3^-

BaO

CO/H_2

$N_2 + H_2O$

❑ LNT Catalyst

- Pd: 50g/ft^3
- Rh: 5g/ft^3
- Monolith: 400/4 cordierite substrate
- Aged at 750°C/72 hrs with10%H_2O/Air

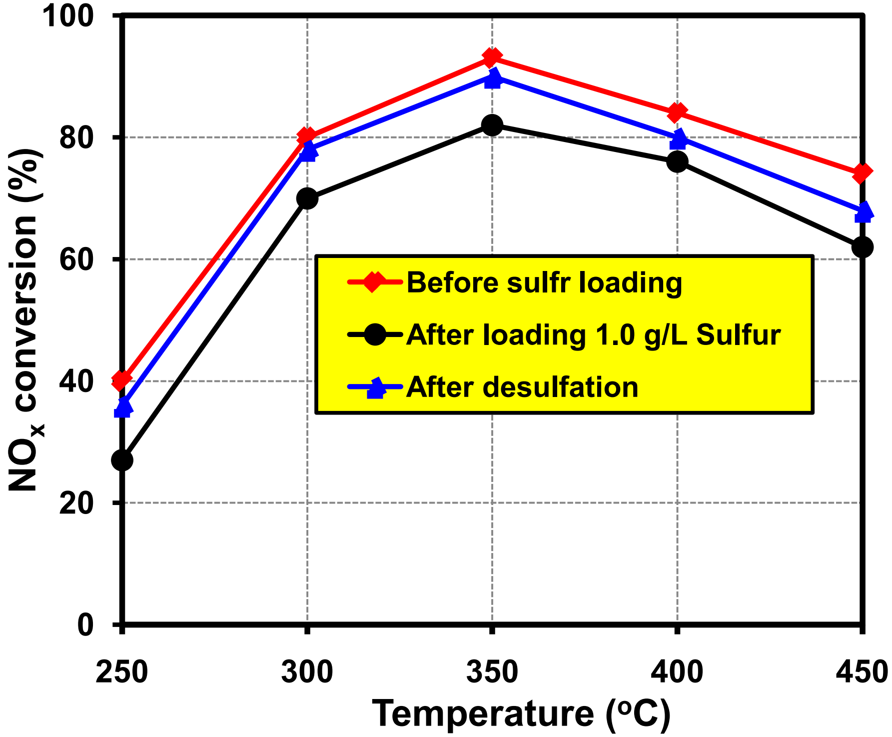
❑ *NO oxidation activity: $LaCoO_3$ > $LaMnO_3$ > $LaFeO_3$*

❑ *$LaMnO_3$ may be the best choice for LNT considering both NO oxidation efficiency and durability in rich conditions*

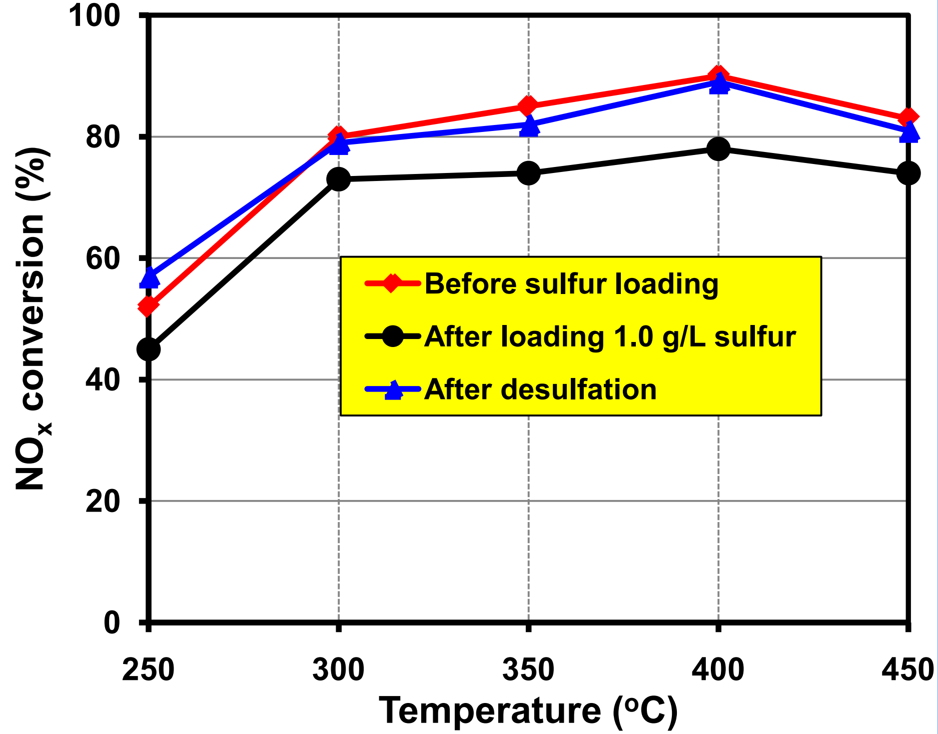
[NO] = 200 ppm, [CO_2] = [H_2O] = [O_2] =10%, SV = 50,000 h^{-1}.

Perovskite-based LNT vs. Platinum-based LNT

Pt/Pd/Rh: 0/50/5 g/ft^3



Pt/Pd/Rh: 45/8/5 g/ft^3

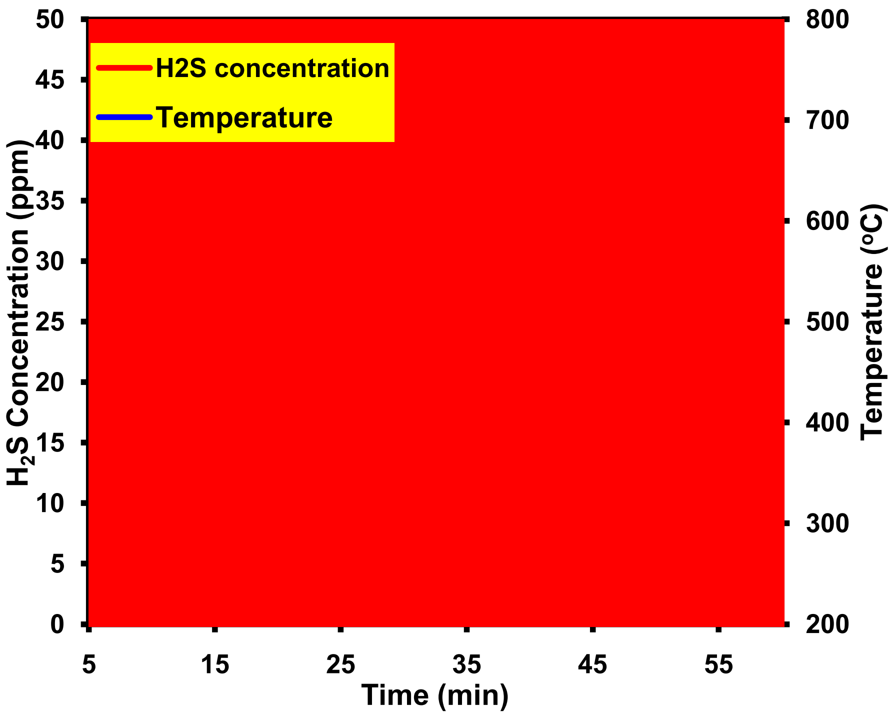


- ❑ *Comparable NO_x reduction performance*
- ❑ *Sulfur poisoning characteristics similar to a commercial LNT*

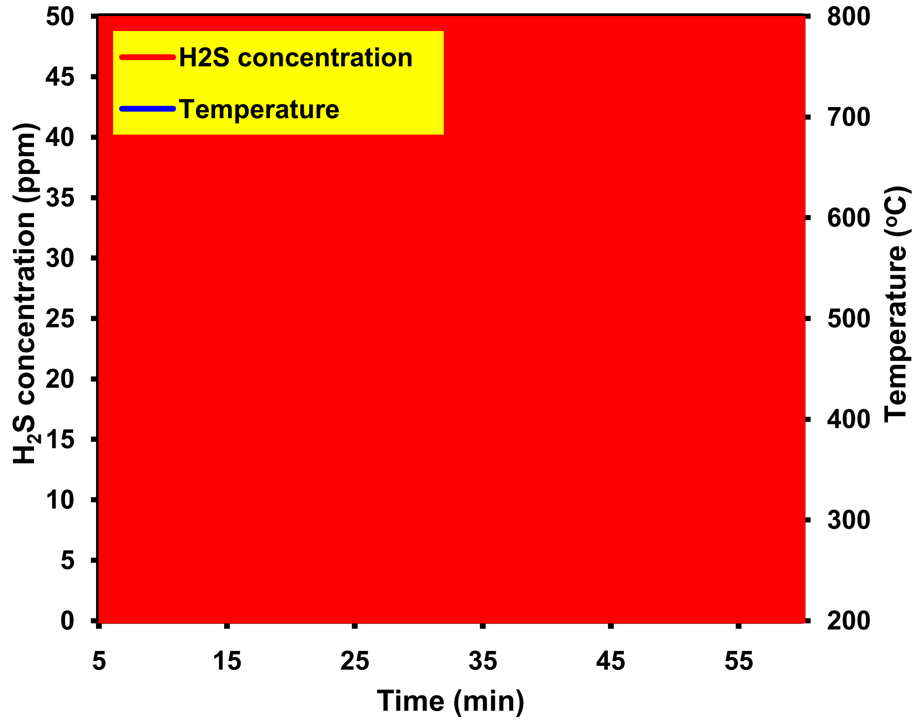
$[CO_2]$ = $[H_2O]$ =10%, SV=50k/hr; Lean: 200 ppm NO +10% O_2; Rich: 200 ppm NO+3%CO+1%H_2; Lean/Rich =60s/5s

Desulfation Comparison

Perovskite-based LNT



Pt-based LNT



- *Similar desulfation characteristics to a Pt-based LNT… most sulfur is likely adsorbed on BaO sites*

$[CO_2] = [H_2O] = 10\%$, SV=50k/hr; $3\%CO+1\%H_2$; temperature ramp 300-700C at 10C/min

Summary

- ***Co and Mn-based Perovskite oxides are active for NO oxidation to NO_2***
- ***Perovskite based LNT without PGM stores NO_x effectively under lean conditions; however, it is not effective in reducing NO_x to N_2/NH_3 under rich conditions***
- ***Integration of perovskite-based LNT with a TWC formulation leads to efficient NO_x conversions***
- ***$LaMnO_3$-based LNT shows similar sulfation and desulfation characteristics to a Pt-based LNT***
- ***This family of materials may offer significant PGM reduction opportunity for diesel catalysts***