Correlation between LNT NH₃ and N₂O selectivities under fast cycling conditions

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LNT can emit large amount of NH₃ & N₂O



- NH₃ & N₂O yields as high as 70 & 20%, respectively
- Highly dependent on reductant type & temperature
- Processes leading to these trends need to be understood
 - To control emissions & mitigate environmental and health impacts
 - To develop predictive models

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Transient chemistry details necessary to accurately describe performance trends

Example: bench reactor experiments at ORNL CLEERS reference LNT; 60/5-s lean/rich cycling; H₂ reductant



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Objective: clarify N₂O chemistry by probing NH₃ transformation

Transient surface



Presentation_name

Catalyst studied: CLEERS reference LNT

Lean GDI LNT (Umicore), 625 cpsi



• Large oxygen storage capacity (OSC: Ce/Zr mixed oxides)



Three types of experimental conditions

1. Lean/rich cycling

- 1. Lean (60 s): 300 ppm NO, 10% O₂
- 2. Rich (5 s): 3.4% reductant

2. Transient response

- 1. 300 ppm NH_3 (or 300 ppm $NH_3 + 0.5\% H_2$) pulse input
- 2. Initial LNT surface: reduced, oxidized or nitrated

3. Steady flow

- 1. 500 ppm NO + 0.5% H_2
- All experiments presented here conducted with
 - Base gas: 5% H_2O , 5% CO_2 , N_2 balance
 - SV: 30K h⁻¹

Time

NH₃ decomposition (2NH₃ = N₂ + 3H₂) is significant under transient conditions

Transient response experiment: NH₃ **pulse input** LNT pre-reduced with H₂ followed by inert (N₂) purge



- Very high initial rates: zero NH₃ slip at all temperatures
- Lower steady-state rates
- Steep leading edges of NH₃ breakthrough profiles indicate adsorption/storage
 - Not explained by NH₃ storage: minor role (small NH₃ desorption)

7 Managed by UT-Battelle for the U.S. Department of Hand Sorption or spillover Prese



Decomposition is inhibited by hydrogen



- Co-feeding H₂ suppresses both initial & steady-state NH₃ decomposition
 - Hydrogen inhibits NH₃ decomposition over precious metal
 - When "H-adsorption or storage capacity" is saturated



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NH₃ reduction of surface oxygen does not lead to N₂O formation

Transient response experiment : NH₃ **pulse input** LNT pre-oxidized with O₂ followed by inert purge



- NH₃ reduction of stored oxygen (CeO₂): very efficient (plug-like front)
- Extent of surface reduction highly dependent on temperature
- NH₃ reduction of CeO₂ not a major contributor to N₂O

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NH₃ decomposition & OSC reduction explain lower apparent yields at higher temperature



Pihl et al., SAE Technical Paper 2006-01-3441

- Steady rich flow experiments show higher NH₃ generation at higher T
- Another potential factor to consider:
 - Lower H_2/NO ratio (unfavorable for NH_3 formation) due to faster NO_x release

N_2O formation mainly due to NH_3 reaction with stored $NO_{\rm x}$



- NH₃ is efficient in reducing stored NO_x also
- Major contributor to N₂O



Gas-phase O_2 reaction with NH_3 at rich/lean transition can lead to additional N_2O

Transient response experiment: 200 °C, NH₃ pulse input with 0.5% H₂ LNT pre-oxidized with 0.5% O₂ followed by inert purge



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Time (min)



Light-off temperature is highly dependent on reductant type: H₂ < CO < C₃H₆ < C₃H₈



Conclusions

- NH₃ can be involved in various surface reactions
 - Decomposition & H-spillover (rich)
 - Adsorption (rich) & slow release (rich, subsequent lean)
 - Reduction of stored NO_x (rich), stored O (rich), gas-phase O₂ (rich/lean; lean)
- N₂O is formed as a result of NH₃ conversion
 - NH₃ reaction with stored NO_x (rich): major contributor
 - NH₃ reaction with stored oxygen (rich): negligible contribution
 - NH₃ oxidation with gas-phase O₂ (rich/lean, lean): minor contribution
- NH₃ & N₂O highest near light-off T for a given reductant type
 - Formation of NH_3 (reductant + stored NO_x) & N_2O (NH_3 + stored NO_x) maximized
 - NH₃+CeO₂ & decomposition minimized
- Findings can enhance model NH₃, N₂O capabilities
 - See following talk by Partridge/Kočí



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