Stepwise Desulfation & its Impact on LNT Performance Study of CLEERS Reference Catalyst

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12th DOE CLEERS Workshop April 30, 2009 Dearborn, MI







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Goal is to obtain a thorough understanding of real LNT's response to sulfur

- Types, spatial distribution & stability of sulfur
- Impact on spatiotemporal distribution of reactions
 - NO oxidation
 - NO storage/reduction (NSR)
 - Oxygen storage capacity (OSC)
 - Reductant conversion & utilization
- Impact on global performance
 - Total NO_x capacity
 - NO_x conversion
 - NH₃ selectivity



Information relevant to modeling & developing LNTs with enhanced durability, reduced cost & fuel penalty



Last year we studied how S affects spatial reaction distribution & global LNT perform.

Spatial reaction distribution vs. S

Unsulfated





CLEERS LNT Global performance vs. S



- Sulfation of NO_x storage sites is plug-like vs. that of OSC sites less efficient (more dispersed)
- Plug-like deactivation of NO_x storage sites displaces "active" NSR zone downstream
 - $-NO_x$ conversion decreases when remaining unsulfated LNT length < NSR zone length
- NSR-zone displacement shortens downstream OSC-only zone
- Manage Distribution of upstream NSR-zone-formed NH₃ decreases: NH₃ selectivity increases for the U.S. Department of Energy



Conceptual model of spatial development of different sulfates was proposed consistent w/ performance trend



Various washcoat components form sulfates

- BaO, MgAl₂O₄, CeO₂-ZrO₂, Al₂O₃

NO_x storage sites showed highest affinity for sulfur

- Plug-like sulfation; hard to desulfate
- More analyses necessary to discriminate different sulfur types



This year we enhanced conceptual model by characterizing & assessing stepwise DeS

Various tools employed

Bench reactor

- Monolith core
- Performance evaluation
- Stepwise desulfation (TPR)



Micro reactor

- Powder
- CLEERS LNT + "components"
- Sulfation & desulfation (TPR)



Characterization

- Monolith core
- Microscopy/EPMA



- Refined understanding of LNT washcoat structure, composition & S distribution
- Impact of stepwise desulfation on LNT performance



Characterization continues revealing complex structure of CLEER LNT



• Washcoat is composed of various compositionally distinct domains - Pt, Pd, BaO, CeO₂-ZrO₂

 $BaO > CeO_2$ - ZrO_2 & $BaO < CeO_2$ - ZrO_2 imply existence of different Ba morphologies (e.g. surface vs. bulk)

- $-\operatorname{Pt},\operatorname{CeO}_2,\operatorname{MgAl}_2\operatorname{O}_4$
- $-\,\mathrm{Rh},\,\mathrm{Al_2O_3}$



Desulfation of LNT "components" performed to help interpret CLEERS LNT DeS (1/2)



All studied non-Ba components store sulfur w/ varying affinity to S

- $-\,\text{CeO}_2\text{-}\text{ZrO}_2\,\text{\&}\,\text{Al}_2\text{O}_3\,\text{support form mainly low-T sulfates}$
- $-AI_2O_3$ can also form medium-T sulfates
- MgAl₂O₄ leads to mainly high-T sulfates, but Pt incorporation (via impregnation or physical mixture) decreases high T-sulfates & increases significantly low- & medium-T sulfates



Desulfation of LNT "components" performed to help interpret CLEERS LNT DeS (2/2)



 Ba forms mainly high T sulfates; impregnating it on Al₂O₃ leads to sulfates more stable than those on CeO₂-ZrO₂

DeS of Pt/Ba/Ce-Zr+MgAl₂O₄ gives a S profile similar to CLEERS LNT

- CLEERS LNT's DeS window is wider at high T end (due to presence of bulk Ba phases?)



Estimated types & spatial distribution of S are consistent with performance trends



Results consistent w/ performance data presented last year

- $-NO_x$ storage poisoning (Ba) is plug-like
- Oxygen storage poisoning (Ce-Zr) is much less plug-like



Stepwise desulfation was performed to evaluate impact of different sulfur species





After each DeS step, different functions of CLEERS LNT were evaluated

Evaluated properties

- Total S removal from desulfation profiles
- Total NO_x storage recovery from long cycling at 400 °C (15-min lean/10-min rich)
- NO_x conversion & NH₃ selectivity from short cycling at 400 °C (60-s lean/5-s rich)

NSR cycling gas composition

	Gas Composition					
	NO	02	H ₂	H ₂ O	CO2	N ₂
Lean (storage)	300 ppm	10%	0%	5%	5%	Bal
Rich (regeneration)	0 ppm	0%	3.4%	5%	5%	Bal



Each step removes least stable S available



- Sulfur profiles do not match those of peak deconvolution
 - e.g. a lot larger 1st S peak
 - Indicates actual situation could be more complex than 4 sulfate-type scenario
- No sulfur evolution below maximum T of previous DeS step
 - Indicates there is no S redistribution from high T to low T sulfates



Roles of different S types were deduced from recovery trend of LNT



- Sulfation decreases total NO_x storage & NO_x conversion but increases NH₃ selectivity
- Stepwise desulfation reverses this trend but each step has distinct impact revealing roles of S:
 - 46% S recovered from 1st step: little impact w/ slight degradation of short cycling performance indicates association with components with insignificant NO_x storage capacity suggests low-T S from upstream can form higher-T S downstream (caution w/ incomplete DeS)
 - 26% S from 2nd+3rd steps: major impact on short cycling (NO_x conv. & NH₃ sel.) indicates association with NO_x storage components of practical relevance
 - – 28% S from 4th step w/ major impact on long cycling (total NO_x capacity)
 indicates association with NO_x storage components of little importance to short cycling

Pictorial representation of impact of stepwise DeS on S distribution & LNT performance



Medium & high-T sulfates: Ba, Mg-Al



- Some upstream released low-T S forms more stable sulfates
- Slight degradation of short cycling e.g. conv. decreases; NH₃ increases



- Practically relevant NO_x storage sites desulfated
- Short cycling performance
 almost fully recovered



- Most stable S removed
- Recovery of NO_x storage sites not relevant to short cycling

Low-T sulfates: Ce-Zr, Al, Mg-Al





Summary

- CLEERS LNT & model washcoat components have been characterized & evaluated in fresh, sulfated & desulfated states
 - Demonstrated complex WC structure: PtPd/Ba/Ce-Zr, Pt/Ce/Mg-AI, Rh/AI...
 - Clarified types, spatial distribution & stability of S species
- Sulfation & stepwise desulfation impact on LNT performance was rationalized based on spatial distribution of S & LNT functions
 - − Plug-like S of NO_x storage sites displaces NSR zone downstream: conv \downarrow , NH₃↑
 - Ce-Zr, Mg-AI & bulk Ba stores S delaying poisoning of relevant storage sites
 - Stepwise DeS reverses this trend but incomplete DeS could increase sulfation of relevant sites
- Future work
 - Experimentally confirm impact of stepwise DeS on spatial reaction distribution
 - Characterize CLEERS reference & LNT components after S & stepwise DeS
 - Contribute relevant info to modeling effort (see talk later by Larson, SNL)



Acknowledgments

- Research sponsored by DOE, Vehicle Technologies Program
 - Program Managers: Ken Howden, Gurpreet Singh

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- Catalyst from Umicore
 - Owen Bailey



Larry Walker









Thank You

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