

# **NON-UREA SCR PATHWAYS TO REDUCE NO<sub>x</sub> IN DIESEL ENGINES**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI  
OCTOBER 2019**

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# **NON-UREA SCR PATHWAYS TO REDUCE NO<sub>x</sub> IN DIESEL ENGINES**

*by*

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Submitted in fulfillment of the requirements of the degree of Doctor of Philosophy  
to the



**Indian Institute of Technology Delhi**

**October 2019**

*Dedicated to my parents...*

## Certificate

This is to certify that the thesis entitled “**Non-urea SCR pathways to reduce NO<sub>x</sub> in diesel engines**” being submitted by **Shephali Singh** to the **Indian Institute of Technology Delhi**, for the fulfillment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering is a record of bonafide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standards for the submission of the thesis. The research report and the results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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## Acknowledgements

I would like to express my sincere gratitude to my supervisor Dr. Divesh Bhatia for his continued support, guidance, and encouragement throughout my Ph.D. I am thankful to him for sharing his knowledge and being a patient advisor and wonderful teacher when I was struggling with learning different concepts in Chemical Engineering. Without his able guidance, this thesis would not have taken its present shape. I would also like to thank my review committee members, Prof. K.K.Pant, Prof. Sreedevi Upadhyayula, and Prof. K.A. Subramanian, for their great support and invaluable advice, scholarly inputs and consistent encouragements throughout the research work.

I would like to express my sincere thanks to the Department of Chemical Engineering for providing me the exposure to various advanced courses during my coursework at IIT Delhi. I would like to thank IIT Delhi and the Science and Engineering Research Board, Department of Science and Technology [Project No. SB/S3/CE/071/2014] for the financial support.

I gratefully acknowledge the cordial and generous support of my friends and labmates at IIT Delhi, Mr. Prateek Khatri, Ms. Shabina Ashraf, Ms. Sirisha Parvathaneni, Mr. Vaibhav Srivastava, Mr. Deepak Sharma, Mr. Arvind Kumar, Mr. Abhijeet Kumar, Ms. Sunita Sen, Ms. Shelaka Gupta, Ms. Uzma Anjum and Mr. Rohit Kumar. Mr. Prateek Khatri, in particular, has helped me a lot during my tough days at IIT Delhi through personal as well as scholarly interactions. I would also like to express sincere thanks to my friends Ms. Monalisha Nayak, Ms. Madhvi Gaur, and Ms. Neha Dhiman for their constant support and encouragement during my stay at IIT Delhi.

I have no words to thank my parents, Dr. Har Narayan Singh and Mrs. Shashi Bala Singh who encouraged and helped me at every stage of my life and without whose support I would not have

been able to finish my thesis. I thank my sister Dr. Nimisha Raghuvanshi and my brother-in-law Dr. Dushyant Kumar Thakaran for their constant guidance and advice throughout my thesis work. I also thank them for their motivation and support which helped me through my tough times. I thank my younger brother Shantanu for the fun sessions which helped me a lot during my stay at IIT Delhi.

Lastly, I dedicate this thesis to my dad for having faith in me and giving me courage during the low times in my life even in his absence which helped me to move forward irrespective of the failures encountered.

*Shephali Singh*

## Abstract

Reduction of nitrogen oxide ( $\text{NO}_x$ ) emissions from diesel engines is a major challenge due to their fuel-lean operating conditions. Selective catalytic reduction (SCR) is a commercial technology which is widely used in vehicles for the abatement of  $\text{NO}_x$ . The reduction of  $\text{NO}_x$  on a SCR catalyst occurs by utilizing the  $\text{NH}_3$  generated by the hydrolysis of urea solution. However, the onboard storage and regular refilling of the urea solution are the major challenges associated with the implementation of SCR technology. Alternatively, Lean  $\text{NO}_x$  trap (LNT) catalysts can work without the requirement of a storage space onboard the vehicle. However, the cost of the LNT catalyst and the formation of undesired products such as  $\text{NH}_3$  and  $\text{N}_2\text{O}$  during the reduction of  $\text{NO}_x$  limit the application of the LNT technology. LNT-SCR and hydrocarbon-SCR (HC-SCR) are alternate non-urea based technologies for the control of  $\text{NO}_x$  from diesel engines, which avoid the need of an external reductant supply system.

In a combined LNT-SCR catalyst, the LNT and SCR catalysts can be arranged into a single unit such that the  $\text{NH}_3$  generated in a LNT can be used as an in-situ reductant in the SCR catalyst. In a combined LNT-SCR catalyst, LNT and SCR catalysts can be arranged in a sequential, dual-layer, or mixed configuration. However, there is no agreement between various research groups on the most effective configuration of the combined LNT-SCR catalysts. In the present work, mathematical models incorporating diffusional limitations in the washcoat are developed for various LNT-SCR configurations, and it is shown that the inclusion of  $\text{NH}_3$ -oxidation reactions in the LNT-SCR kinetic model results in a decrease in the  $\text{NO}_x$  reduction performance of the combined LNT-SCR configurations. It is highlighted that the  $\text{NH}_3$  oxidation activity of the LNT catalyst is potentially responsible for the different inferences drawn by various researchers on the

comparison of LNT-SCR configurations. In addition to  $\text{NH}_3$ , the hydrocarbons and CO present in the exhaust are potential reductants for  $\text{NO}_x$  over a SCR catalyst. In the present work, kinetic models are developed for the CO- $\text{NO}_2$  and  $\text{C}_3\text{H}_6$ - $\text{NO}_2$  interactions. These models are further combined with the  $\text{NH}_3$ -SCR kinetic model to predict the effect of CO and  $\text{C}_3\text{H}_6$  on the  $\text{NO}_x$  conversion during  $\text{NH}_3$ -SCR reactions on a commercial Cu-CHA SCR catalyst. The developed model captures the promotional effect of CO and  $\text{C}_3\text{H}_6$  on  $\text{NO}_x$  conversion at low temperatures and the inhibiting effect at high temperatures under  $\text{NO}_2$ -SCR conditions. The negligible effect of the presence of CO and the inhibiting effect of  $\text{C}_3\text{H}_6$  on the  $\text{NO}_x$  conversion under fast SCR conditions is also predicted.

Various reactions occurring on the LNT and SCR catalysts exhibit negative rate orders. Numerical issues are encountered while solving the diffusion-reaction equations for a negative-order reaction when the kinetic rate constants are high. An algorithm is developed in the present work to solve these equations for a catalyst slab when the reaction exhibits a negative rate order. It is shown that the proposed method works for a wide range of Thiele modulus and Biot numbers. The algorithm successfully captures the multiplicity of solutions as well as the transition from the kinetic/internal-diffusion controlled regime to the external mass-transfer controlled regime. The developed algorithm is further used to calculate the concentration profile in a monolith reactor. The developed algorithm is also used to calculate the concentration profile in a catalyst slab for a multi-component reaction system wherein the reaction exhibits both positive and negative order with respect to various species.

## सार

नाइट्रोजन ऑक्साइड ( $\text{NO}_x$ ) का कमी डीजल इंजनों से उत्सर्जन उनके ईंधन-दुबले ऑपरेटिंग परिस्थितियों के कारण एक बड़ी चुनौती है। चयनात्मक उत्प्रेरक कमी (SCR) एक व्यावसायिक तकनीक है जो वाहनों में व्यापक रूप से  $\text{NO}_x$  उन्मूलन के लिए उपयोग की जाती है। SCR उत्प्रेरक पर  $\text{NO}_x$  की कमी  $\text{NH}_3$  का उपयोग करके होती है जो यूरिया समाधान के हाइड्रोलिसिस द्वारा उत्पन्न किया जाता है। हालाँकि, वाहन पर भंडारण और यूरिया के घोल को नियमित रूप से भरना SCR प्रौद्योगिकी के कार्यान्वयन से जुड़ी प्रमुख चुनौतियाँ हैं। वैकल्पिक रूप से, LNT उत्प्रेरक वाहन पर एक भंडारण स्थान की आवश्यकता के बिना काम कर सकते हैं। हालाँकि, LNT उत्प्रेरक की लागत और इस प्रौद्योगिकी में  $\text{NO}_x$  की कमी के दौरान अवांछित उत्पादों जैसे कि  $\text{NH}_3$  तथा  $\text{N}_2\text{O}$  के गठन की वजह से LNT का उपयोग सीमित है। LNT-SCR और HC-SCR (एचसी-एससीआर) डीजल इंजनों से उत्सर्जित  $\text{NO}_x$  के नियंत्रण के लिए वैकल्पिक गैर-यूरिया आधारित प्रौद्योगिकियाँ हैं, जो बाहरी रिडक्टेंट आपूर्ति प्रणाली की आवश्यकता से बचती हैं।

एक संयुक्त LNT-SCR उत्प्रेरक में, LNT और SCR उत्प्रेरक को एक एकल इकाई में व्यवस्थित किया जा सकता है ताकि LNT में उत्पन्न  $\text{NH}_3$  का उपयोग SCR उत्प्रेरक में इन-सीटू रिडक्टेंट के रूप में किया जा सकता है। एक संयुक्त LNT-SCR उत्प्रेरक में, LNT और SCR उत्प्रेरक एक क्रमिक, दोहरी-परत या मिश्रित कॉन्फ़िगरेशन में व्यवस्थित हो सकते हैं। हालाँकि, संयुक्त LNT-SCR उत्प्रेरक के सबसे प्रभावी विन्यास पर विभिन्न अनुसंधान समूहों के बीच कोई समझौता नहीं है। वर्तमान कार्य में, वॉशकोट में विवादास्पद सीमाओं को शामिल करने वाले गणितीय मॉडल विभिन्न LNT-SCR विन्यासों के लिए विकसित किए गए हैं, और यह दिखाया गया है कि  $\text{NH}_3$  ऑक्सीकरण प्रतिक्रियाओं को LNT-SCR मॉडल शामिल करने से संयुक्त LNT-SCR कॉन्फ़िगरेशन की  $\text{NO}_x$  उन्मूलन में कमी होती है। यह रेखांकित किया गया है कि LNT उत्प्रेरक पर  $\text{NH}_3$  ऑक्सीकरण गतिविधि संभावित रूप से LNT-SCR विन्यास की तुलना पर विभिन्न शोधकर्ताओं द्वारा तैयार किए गए अलग-अलग निष्कर्षों के लिए जिम्मेदार है।  $\text{NH}_3$  के अलावा, निकास में मौजूद हाइड्रोकार्बन (HC) और CO भी एक SCR उत्प्रेरक पर  $\text{NO}_x$  उन्मूलन के लिए संभावित रिडक्टेंट्स हैं। वर्तमान काम में, CO- $\text{NO}_2$  और  $\text{C}_3\text{H}_6$ - $\text{NO}_2$  गतिज मॉडल को विकसित किया गया है। इन मॉडलों को आगे  $\text{NH}_3$ -SCR मॉडल के साथ संयुक्त किया गया है ताकि एक वाणिज्यिक Cu-CHA SCR उत्प्रेरक पर  $\text{NO}_x$  रूपांतरण के दौरान CO और  $\text{C}_3\text{H}_6$  के प्रभाव की भविष्यवाणी किया जा सकता है।

विकसित मॉडल  $\text{NO}_x$  रूपांतरण पर CO और  $\text{C}_3\text{H}_6$  के प्रचार प्रभाव की कम तापमान पर भविष्यवाणी करता है और उच्च तापमान पर  $\text{NO}_2$ -SCR के दौरान  $\text{NO}_x$  रूपांतरण पर अवरोधक प्रभाव को पकड़ता है। Fast-SCR के दौरान  $\text{NO}_x$  रूपांतरण पर CO की उपस्थिति का नगण्य प्रभाव और  $\text{C}_3\text{H}_6$  के निरोधात्मक प्रभाव का भी अनुमान लगाया गया है।

LNT और SCR उत्प्रेरक पर होने वाली विभिन्न प्रतिक्रियाएं ऋणात्मक दर के आदेशों का प्रदर्शन करती हैं। जब काइनेटिक रेट स्थिरांक अधिक होते हैं, तो ऋणात्मक-क्रम प्रतिक्रिया के लिए प्रसार-प्रतिक्रिया समीकरणों को हल करते समय संख्यात्मक मुद्दों का सामना किया जाता है। एक उत्प्रेरक स्लैब के लिए इन समीकरणों को हल करने के लिए वर्तमान कार्य में एक एल्गोरिथ्म विकसित किया गया है जब प्रतिक्रिया एक नकारात्मक दर आदेश प्रदर्शित करती है। यह दिखाया गया है कि प्रस्तावित विधि थिएल मापांक और बायोट संख्या की एक विस्तृत श्रृंखला के लिए काम करती है। एल्गोरिदम सफलतापूर्वक समाधानों की बहुलता को कैप्चर करता है और साथ ही बाहरी द्रव्यमान-स्थानांतरण नियंत्रित शासन को गतिज/आंतरिक-प्रसार नियंत्रित शासन से संक्रमण करता है। विकसित एल्गोरिथ्म आगे एक अखंड रिएक्टर में एकाग्रता प्रोफ़ाइल की गणना करने के लिए उपयोग किया गया है। विकसित एल्गोरिथ्म का उपयोग एक बहु-घटक प्रतिक्रिया प्रणाली के लिए उत्प्रेरक स्लैब में एकाग्रता प्रोफ़ाइल की गणना करने के लिए भी किया गया है, जिसमें प्रतिक्रिया विभिन्न प्रजातियों के संबंध में सकारात्मक और नकारात्मक दोनों क्रम दिखाती है।

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# Nomenclature

$a$	width of monolith channel (m)
$A_{l,b}$	pre-exponential factor for reverse reaction $l$ (mol/m <sup>3</sup> washcoat-s)
$A_{l,f}$	pre-exponential factor for forward reaction $l$ (mol/m <sup>3</sup> washcoat-s)
$A_{\Omega}$	channel cross-sectional area open to flow (m <sup>2</sup> )
$Bi$	Biot number
$C$	concentration of reacting species (mol/m <sup>3</sup> )
$C_{BaO,f}$	concentration of fast NO <sub>x</sub> storage sites in LNT catalyst (mol/m <sup>3</sup> washcoat)
$C_{BaO,s}$	concentration of slow NO <sub>x</sub> storage sites in LNT catalyst (mol/m <sup>3</sup> washcoat)
$C_{bulk}$	bulk fluid-phase concentration of reactant species (mol/m <sup>3</sup> )
$c_{int}$	non-dimensional concentration at the fluid-solid interface
$c_m$	non-dimensional cup-mixing concentration of reactant species in the fluid phase
$C_{j,m}^{out}$	effluent cup-mixing concentration of species $j$ in the fluid phase (mol/m <sup>3</sup> )
$C_m^{in}$	concentration of reacting species in the fluid phase at the inlet of monolith reactor (mol/m <sup>3</sup> )
$C_{Pt}$	concentration of active Pt sites in LNT catalyst (mol/m <sup>3</sup> washcoat)
$c_s$	non-dimensional concentration of reactant species within the catalyst slab or monolith washcoat
$C_{S1-OH}$	concentration of active Cu sites in Cu-CHA catalyst (mol/m <sup>3</sup> washcoat)
$C_{SCR}$	concentration of Bronsted acid sites in combined LNT-SCR catalyst (mol/m <sup>3</sup> washcoat)

$C_{site}$	concentration of active sites (mol/m <sup>3</sup> washcoat)
$C_{Tm}$	total molar concentration in fluid-phase of monolith reactor (mol/m <sup>3</sup> )
$D$	diameter of the monolithic substrate (m)
$D_e$	diffusivity of species within the washcoat (m <sup>2</sup> /s)
$D_m$	bulk diffusivity of species in the fluid phase (m <sup>2</sup> /s)
$E_{l,b}$	activation energy for reverse reaction $l$ (kJ/mol)
$E_{l,f}$	activation energy for forward reaction $l$ (kJ/mol)
$f$	vector of non-linear equations
$F_{NO}^{in}$	inlet molar feed rate of NO during the lean phase (mol/s)
$F_j^{out}$	effluent molar feed rate of species $j$ (mol/s)
GHSV	gas hourly space velocity (h <sup>-1</sup> )
$k_c$	external mass transfer coefficient (m/s)
$k_{l,b}$	kinetic rate constant for reverse reaction $l$ (mol/m <sup>3</sup> washcoat-s)
$k_{l,f}$	kinetic rate constant for forward reaction $l$ (mol/m <sup>3</sup> washcoat-s)
$k_r$	kinetic rate constant for a general $n^{th}$ order reaction (mol <sup>1-n</sup> m <sup>3(n-1)</sup> /s)
$L$	length of monolith channel (m)
$n$	reaction order
$N$	number of unknown variables in arc-length method
$N_g$	total number of species in the fluid phase
$N_{ch}$	cell density (in <sup>-2</sup> ) of monolith reactor
$N_r$	number of reactions

$NH_3^{st}(t)$	amount of $NH_3$ stored on the Bronsted acid sites in combined LNT-SCR catalyst at any time $t$ (mol)
$[NH_3^{st}]_{SCR}$	amount of stored $NH_3$ utilized by SCR reactions (mol)
$[NH_3^{st}]_{Oxi}$	amount of stored $NH_3$ utilized by $NH_3$ oxidation reactions (mol)
$[NH_3^{st}]_{Gas}$	amount of $NH_3$ desorbed from the storage sites (mol)
$NO_x^{st}(t)$	amount of $NO_x$ stored on the LNT catalyst at any time $t$ (mol)
$[NO_x^{st}]_{lean}$	amount of $NO_x$ stored on the LNT catalyst during the lean phase (mol)
$P_{Tz}$	transverse Peclet number for monolith reactor
$P_{\Omega}$	channel perimeter open to flow (m)
$r_v$	rate of reaction ( $mol/m^3 \cdot s$ )
$R_{vl}$	rate of reaction $l$ in washcoat phase ( $mol/m^3$ washcoat-s)
$R_{\Omega}$	effective transverse diffusion length in fluid phase (m)
$s$	arc-length
$Sh_{\Omega}$	Sherwood number
$S_j$	selectivity of product $j$ during $NH_3$ oxidation reaction
$S_j^{cycle}$	cycle-averaged selectivity of species $j$
$t$	time (s)
$t_{begin}$	time corresponding to the beginning of the lean phase (s)
$t_{end}$	time corresponding to the end of the lean phase (s)
$t_{lean}$	duration of lean phase (s)
$t_{rich}$	duration of rich phase (s)
$T$	temperature of bulk fluid phase (K)

$T_m$	cup-mixing temperature of the fluid in monolith channel (K)
$T_s$	temperature of solid washcoat (K)
$\bar{u}$	average fluid velocity (m/s)
$u_{ref}$	fluid velocity in the uncoated monolith channel at standard conditions (m/s)
$\underline{x}$	vector of unknown variables in arc-length method
$x_j$	conversion of species $j$
$x_{NO_x}^{cycle}$	cycle-average conversion of NO <sub>x</sub>
$X_{j,m}$	cup-mixing mole fraction of species $j$ in fluid phase
$X_{j,m}^{in}$	inlet mole fraction of species $j$ in the fluid phase
$X_{j,m}^o$	initial cup-mixing mole fraction of species $j$ in fluid phase
$X_{j,wc}$	cup-mixing mole fraction of species $j$ in the washcoat
$X_{j,wc}^o$	initial cup-mixing mole fraction of species $j$ in the washcoat
$X_{j1,wc}$	cup-mixing mole fraction of species $j$ in the outer washcoat layer of the dual-layer LNT-SCR
$X_{j2,wc}$	cup-mixing mole fraction of species $j$ in the inner washcoat layer of the dual-layer LNT-SCR
$\underline{X}_{wc}$	vector of mole-fractions within the washcoat
$y$	length co-ordinate in the transverse direction of monolith channel (m)
$y'$	non-dimensional length co-ordinate along the depth of catalyst slab or monolith washcoat
$z$	length co-ordinate in the axial direction of monolith channel (m)

$z'$	non-dimensional length co-ordinate along the axial direction of the monolith reactor
$\Delta z'$	non-dimensional length of the discretized element of the monolith reactor (m)
$\alpha'$	independent variable in arc-length method
$\alpha$	dimensionless concentration below which the reaction rate is linearized
$\varepsilon$	porosity of catalyst slab
$\varepsilon_{wc}$	porosity within the washcoat
$\delta$	calculated error at the fluid-particle interface
$\delta_c$	thickness of the catalyst slab (m)
$\delta_{LNT}$	washcoat thickness of standalone LNT catalyst, upstream LNT catalyst in sequential configuration and inner LNT layer in dual-layer configuration (m)
$\delta_{SCR}$	washcoat thickness of outer SCR layer in dual-layer configuration and downstream SCR catalyst in sequential configuration (m)
$\delta_{wc}$	total thickness of the washcoat (m)
$\varphi$	Thiele modulus
$\varphi_c$	critical Thiele modulus above which solution to diffusion – reaction equations does not exist
$\lambda$	dimensionless position below which the reaction rate is linearized
$\vartheta_j$	stoichiometric coefficient of species $j$ in the reaction
$\vartheta_{lj}$	stoichiometric coefficient of species $j$ in the reaction $l$
$\sigma_p$	fractional contribution of factor ‘ $p$ ’ in the overall consumption of stored $\text{NH}_3$ during the lean phase

$\theta_j$	fractional surface coverage of species $j$
$\theta_j^o$	initial fractional surface coverage of species $j$
$\underline{\theta}$	vector of surface coverages of adsorbed species in the washcoat
$\theta_{S1-j}$	fractional surface coverage of species $j$ on Cu sites in Cu-CHA catalyst
$\theta_{S2-j}$	fractional surface coverage of species $j$ on Bronsted-acid sites in Cu-CHA catalyst
$\theta_{NH_3}$	fractional surface coverage of $NH_3$ on Bronsted acid sites in combined LNT-SCR catalyst
$\theta_{NO_3^-,f}$	fractional surface coverage of $NO_x$ on the fast $NO_x$ storage sites
$\theta_{NO_3^-,s}$	fractional surface coverage of $NO_x$ on the slow $NO_x$ storage sites
$\theta_{NH_3,v}$	fraction of vacant Bronsted-acid sites in combined LNT-SCR catalyst
$\theta_{NO_3^-,vf}$	fraction of vacant fast $NO_x$ storage sites in LNT catalyst
$\theta_{NO_3^-,vs}$	fraction of vacant slow $NO_x$ storage sites
$\theta_{v1}$	fraction of vacant Cu-sites in Cu-CHA catalyst
$\theta_{v2}$	fraction of vacant Bronsted-acid sites in Cu-CHA catalyst
$\tau$	tortuosity factor

### Subscripts

$i$	axial position of any segment in a monolith reactor
$j$	$j^{\text{th}}$ species in a multi-component reaction system
$k$	$k^{\text{th}}$ species in a multi-component reaction system
$l$	$l^{\text{th}}$ reaction in a multi-reaction system

$q$	$q^{\text{th}}$ variable in the arc-length method
$r$	variable with maximum absolute value of derivative with respect to the arc-length

#### Abbreviations

BS	Bharat Stage
CPCB	Central Pollution Control Board
DOC	Diesel Oxidation Catalyst
HC	Hydrocarbon
HCV	Heavy Commercial Vehicle
HDV	Heavy-duty Diesel Vehicle
LCV	Light Commercial Vehicle
LDV	Light-duty Diesel Vehicle
LNT	Lean NO <sub>x</sub> Traps
MoRTH	Ministry of Road Transport and Highways
NSR	NO <sub>x</sub> Storage and Reduction
PM	Particulate Matter
SCR	Selective Catalytic Reduction
SDPF	SCR-catalyzed Diesel Particulate Filter