NON-UREA SCR PATHWAYS TO REDUCE NO$_x$ IN DIESEL ENGINES

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by

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to the

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Dedicated to my parents…

Certificate

This is to certify that the thesis entitled "**Non-urea SCR pathways to reduce NO_x 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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Abstract

Reduction of nitrogen oxide (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 NO_x. The reduction of NO_x on a SCR catalyst occurs by utilizing the 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 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 NH_3 and N_2O during the reduction of 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 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 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 NH_3-oxidation reactions in the LNT-SCR kinetic model results in a decrease in the NO_x reduction performance of the combined LNT-SCR configurations. It is highlighted that the 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 NH_3, the hydrocarbons and CO present in the exhaust are potential reductants for NO_x over a SCR catalyst. In the present work, kinetic models are developed for the CO-NO_2 and C_3H_6-NO_2 interactions. These models are further combined with the NH_3-SCR kinetic model to predict the effect of CO and C_3H_6 on the NO_x conversion during NH_3-SCR reactions on a commercial Cu-CHA SCR catalyst. The developed model captures the promotional effect of CO and C_3H_6 on NO_x conversion at low temperatures and the inhibiting effect at high temperatures under NO_2-SCR conditions. The negligible effect of the presence of CO and the inhibiting effect of C_3H_6 on the 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 (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 NO_x उन्मूलन के लिए उपयोग की जाती है। SCR उत्प्रेरक पर NO_x की कमी 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। हालांकि, LNT उत्प्रेरक की लागत और इस प्रौद्योगिकी में NO_x की कमी के दौरान अवांछित उत्पादों जैसे कि NH_3 तथा N_2O के गठन की वजह से LNT का उपयोग सीमित है। LNT-SCR और HC-SCR (एचसी-एससीआर) डीजल इंजनों से उत्सर्जित NO_x के नियंत्रण के लिए वैकल्पिक गैर-यूरिया आधारित प्रौद्योगिकियां 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 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। हालांकि, 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 NH_3 ऑक्सीकरण प्रतिक्रियाओं को LNT-SCR मॉडल शामिल करने से संयुक्त LNT-SCR कॉन्फ़िगरेशन की NO_x उन्मूलन में कमी होती है। यह रेखांकित किया गया है कि LNT उत्प्रेरक पर 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। NH_3 के अलावा, निकास में मौजूद हाइड्रोकार्बन (HC) और CO भी एक SCR उत्प्रेरक पर NO_x उन्मूलन के लिए संभावित रिडक्टेंट्स हैं । वर्तमान काम में, CO-NO_2 और C_3H_6-NO_2 गतिज मॉडल को विकसित किया गया हैं। इन मॉडलों को आगे NH_3-SCR मॉडल के साथ संयुक्त किया गया है ताकि एक वाणिज्यिक Cu-CHA SCR उत्प्रेरक पर NO_x रूपांतरण के दौरान CO और C_3H_6 के प्रभाव की भविष्यवाणी किया जा सकता है।

विकसित मॉडल NO_x रूपांतरण पर CO और C_3H_6 के प्रचार प्रभाव की कम तापमान पर भविष्यवाणी करता है और उच्च तापमान पर NO_2-SCR के दौरान NO_x रूपांतरण पर अवरोधक प्रभाव को पकड़ता है। Fast-SCR के दौरान NO_x रूपांतरण पर CO की उपस्थिति का नगण्य प्रभाव और C_3H_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^3 washcoat-s)
$A_{l,f}$	pre-exponential factor for forward reaction l (mol/m^3 washcoat-s)
A_{Ω}	channel cross-sectional area open to flow (m^2)
Bi	Biot number
C	concentration of reacting species (mol/m^3)
$C_{BaO,f}$	concentration of fast NO_x storage sites in LNT catalyst (mol/m^3 washcoat)
$C_{BaO,s}$	concentration of slow NO_x storage sites in LNT catalyst (mol/m^3 washcoat)
C_{bulk}	bulk fluid-phase concentration of reactant species (mol/m^3)
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^3)
C_m^{in}	concentration of reacting species in the fluid phase at the inlet of monolith reactor (mol/m^3)
C_{Pt}	concentration of active Pt sites in LNT catalyst (mol/m^3 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^3 washcoat)
C_{SCR}	concentration of Bronsted acid sites in combined LNT-SCR catalyst (mol/m^3 washcoat)

C_{site}	concentration of active sites (mol/m^3 washcoat)
C_{Tm}	total molar concentration in fluid-phase of monolith reactor (mol/m^3)
D	diameter of the monolithic substrate (m)
D_e	diffusivity of species within the washcoat (m^2/s)
D_m	bulk diffusivity of species in the fluid phase (m^2/s)
$\mathrm{E}_{\mathrm{l,b}}$	activation energy for reverse reaction l (kJ/mol)
$\mathrm{E}_{\mathrm{l,f}}$	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^{-1})
k_c	external mass transfer coefficient (m/s)
$k_{l,b}$	kinetic rate constant for reverse reaction l (mol/m^3 washcoat-s)
$k_{l,f}$	kinetic rate constant for forward reaction l (mol/m^3 washcoat-s)
k_r	kinetic rate constant for a general n^{th} order reaction (mol^{1-n}m$^{3(n-1)}$/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^{-2}) 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_{Ω}	channel perimeter open to flow (m)
r_v	rate of reaction (mol/m^3-s)
R_{vl}	rate of reaction l in washcoat phase (mol/m^3 washcoat-s)
R_{Ω}	effective transverse diffusion length in fluid phase (m)
s	arc-length
Sh_{Ω}	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_x
$X_{j,m}$	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)
α'	independent variable in arc-length method
α	dimensionless concentration below which the reaction rate is linearized
ε	porosity of catalyst slab
ε_{wc}	porosity within the washcoat
δ	calculated error at the fluid-particle interface
δ_c	thickness of the catalyst slab (m)
δ_{LNT}	washcoat thickness of standalone LNT catalyst, upstream LNT catalyst in sequential configuration and inner LNT layer in dual-layer configuration (m)
δ_{SCR}	washcoat thickness of outer SCR layer in dual-layer configuration and downstream SCR catalyst in sequential configuration (m)
δ_{wc}	total thickness of the washcoat (m)
φ	Thiele modulus
φ_c	critical Thiele modulus above which solution to diffusion – reaction equations does not exist
λ	dimensionless position below which the reaction rate is linearized
ϑ_j	stoichiometric coefficient of species j in the reaction
ϑ_{lj}	stoichiometric coefficient of species j in the reaction l
σ_p	fractional contributtion of factor ‘p’ in the overall consumption of stored NH_3 during the lean phase

θ_j	fractional surface coverage of species j
θ_j^o	initial fractional surface coverage of species j
$\underline{\theta}$	vector of surface coverages of adsorbed species in the washcoat
θ_{S1-j}	fractional surface coverage of species j on Cu sites in Cu-CHA catalyst
θ_{S2-j}	fractional surface coverage of species j on Bronsted-acid sites in Cu-CHA catalyst
θ_{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
θ_{v1}	fraction of vacant Cu-sites in Cu-CHA catalyst
θ_{v2}	fraction of vacant Bronsted-acid sites in Cu-CHA catalyst
τ	tortuosity factor

Subscripts

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

q	qth 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_x Traps
MoRTH	Ministry of Road Transport and Highways
NSR	NO_x Storage and Reduction
PM	Particulate Matter
SCR	Selective Catalytic Reduction
SDPF	SCR-catalyzed Diesel Particulate Filter