DUAL-FUNCTIONAL $Ag/MgO/Al_2O_3$ AS A PASSIVE NO_x ADSORBER AND NO_x REDUCTION CATALYST FOR LEAN-BURN ENGINES: DEVELOPMENT AND MECHANISTIC INSIGHTS

PRATEEK KHATRI

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

APRIL 2022

DUAL-FUNCTIONAL Ag/MgO/Al_2O_3 AS A PASSIVE NO_x ADSORBER AND NO_x REDUCTION CATALYST FOR LEAN-BURN ENGINES: DEVELOPMENT AND MECHANISTIC INSIGHTS

by

Prateek Khatri

Department of Chemical Engineering

Submitted

in fulfillment of the requirements for the degree of Doctor of Philosophy

to the

Indian Institute of Technology Delhi

April 2022

Dedicated

to

My Family…

Certificate

This is to certify that the thesis entitled "**Dual-functional Ag/MgO/Al_2O_3 as a passive NO_x adsorber and NO_x reduction catalyst for lean-burn engines: Development and mechanistic insights**" being submitted by **Prateek Khatri** to the Indian Institute of Technology Delhi, for the fulfilment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering is a record of bonafide research work carried out by him. He 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.

(Divesh Bhatia)

Associate Professor

Department of Chemical Engineering

Indian Institute of Technology Delhi

Hauz Khas, New Delhi-110016

Acknowledgements

Prof. Divesh Bhatia has been an ideal teacher, mentor, and supervisor offering invaluable assistance and insights leading to the writing of this dissertation. I thank him for providing continuous guidance, support, and motivation throughout my Ph.D. tenure at IIT Delhi. Moreover, I would like to thank him for giving me freedom to carry out my research and helping me to improve my technical writing and editing skills. Further, I would like to thank my SRC committee members, Prof. K.K. Pant, Prof. M. Ali Haider and Prof. P. Talukdar, for their valuable inputs and helping in enhancing the quality of the work presented in this dissertation.

I would like to thanks all of my family members for their continuous support and encouragement to carry out my Ph.D. at IIT-Delhi. I am grateful to my parents for their constant motivation and unconditional love. Deepest thanks to my brothers for their fruitful advice and immense support throughout my life. I am thankful to my wife Rachna who constantly inspired and encouraged me during the latter stages of my Ph.D.

I thank Mr. Ashish Panda, Mr. Harshal Peshne, Mr. Rudra Narayan kandi, Mr. Anurag Mishra, Mr. Vikrant, Mr. Praveen Thakur, Mr. Debiprasad Nayak, and Mr. Deepesh, as well as all my pals in Kumaon hostel, IIT Delhi, for all the great times I had there. I'll miss the weekend cricket and tea gatherings that helped me relax. I would also like to thank my lab members including Mrs. Shephali Singh, Mr. Pranav V. Kherdekar, Ms. Marvi, Ms. Akshata Ramteke, and others for the scholarly interactions and constant support.

Abstract

Selective Catalytic Reduction (SCR) catalysts and Lean NO_x Traps are used to reduce the NO_x emissions from the exhaust of diesel and lean-burn gasoline engines. However, they operate efficiently only above a temperature of ~200 ºC, and hence cannot reduce the cold-start emissions. Passive NO_x adsorbers (PNAs) have been touted to address the low-temperature NO_x emissions. However, most of the studied PNA materials include expensive Pt and Pd, and there are only a limited number of studies on the development of non-PGM PNA materials.

This work is focused on studying the NO_x adsorption, desorption, and reduction characteristics of $Ag/MgO/Al_2O_3$. The NO_x storage activity over $Ag/MgO/Al_2O_3$ is comparable to that obtained by Pd-based PNAs, and is hypothesized to occur through a spillover mechanism. Mechanistic insights into the adsorption sites, the role of Ag and MgO, and the potential surface species formed during NO_x exposure to the PNA are obtained. It is deduced that the facile conversion of nitrites to nitrates occurs in the presence of H_2. The role of NO oxidation in NO_x storage is studied, and it is inferred that NO_x storage can take place even without the occurrence of NO oxidation. In addition, the contribution of NO oxidation and decomposition of stored NO_x species towards the NO_x release profiles is studied at various temperatures. In addition to the low-temperature NO_x adsorption characteristics, the catalyst is found to be active for NO_x reduction as well. The effect of various species such as H_2, NH_3, C_3H_6, CO_2, and H_2O on the NO_x adsorption, desorption, and reduction behaviour of the developed catalyst is studied for a wide temperature range. A significantly high NH_3-SCR activity with negligible N_2O formation is measured at 150 ºC, while C_3H_6-SCR activity is exhibited at higher temperatures. The presence of H_2 remarkably increases the low-temperature NO_x adsorption and binding strength, and is attributed to the significant formation of nitrates as opposed to the predominant formation of nitrites in the absence of H_2. CO_2 exhibits a strong inhibiting effect on the low-

temperature NO_x adsorption, which is explained by the reduced rates of NO_x spillover due to the formation of bicarbonates. The effect of H_2, CO_2, and H_2O on the NH_3-SCR activity is studied as well. Further, the effect of Ag and MgO loading on the structural characteristics as well as the activity of the catalyst towards C_3H_6 oxidation, NO oxidation, C_3H_6-SCR, NH_3-SCR, and NH_3 oxidation is studied.

Due to the combined NO_x adsorption/desorption and reduction activity, $Ag/MgO/Al_2O_3$ has the potential to significantly reduce NO_x emissions. An aftertreatment system consisting of $Ag/MgO/Al_2O_3$ and a commercial Cu/SSZ-13 catalyst is shown to achieve high NO_x conversions over a wide temperature range of 115-495 ºC. Thus, the Ag-based catalyst developed in this work can be coupled to an SCR or LNT catalyst, so as to lower the PGM loadings of these catalysts in aftertreatment systems. Moreover, the catalyst has the potential to be used in various industrial sectors where NO_x emissions need to be reduced over a wide temperature range. Further, the mechanistic insights obtained can be used to design more efficient dual-functional catalysts for NO_x adsorption and reduction.

सारांश

चयनात्मक उत्प्रेरक कमी (SCR) उत्प्रेरक और Lean NO_x trap डीजल और lean-burn गैसोलीन इंजन के निकास से NO_x उत्सर्जन को कम करने के लिए उपयोग किया जाता है। हालांकि, वे केवल ~ 200 ºC के तापमान से ऊपर कुशलतापूर्वक काम करते हैं, और इसलिए कोल्ड-स्टार्ट उत्सर्जन को कम नहीं कर सकते हैं। निष्क्रिय NO_x adsorbers (PNAs) को कम तापमान NO_x उत्सर्जन को संबोधित करने के लिए कहा गया है। हालांकि, अध्ययन किए गए अधिकांश पीएनए सामग्रियों में महंगे पीटी और पीडी शामिल हैं, और गैर-पीजीएम पीएनए सामग्री के विकास पर केवल सीमित संख्या में अध्ययन हैं।

यह काम NO_x सोखना, desorption, और $Ag/MgO/Al_2O_3$ की कमी विशेषताओं का अध्ययन करने पर केंद्रित है। $Ag/MgO/Al_2O_3$ पर एनओएक्स भंडारण गतिविधि पीडी-आधारित पीएनए द्वारा प्राप्त की गई तुलना में तुलनीय है, और एक स्पिलओवर तंत्र के माध्यम से होने की परिकल्पना की जाती है। सोखना साइटों में यंत्रवत अंतर्दृष्टि, एजी और एमजीओ की भूमिका, और पीएनए के लिए एनओएक्स एक्सपोजर के दौरान गठित संभावित सतह प्रजातियां प्राप्त की जाती हैं। यह अनुमान लगाया गया है कि नाइट्रेट्स में नाइट्राइट का सरल रूपांतरण H_2 की उपस्थिति में होता है। NO_x भंडारण में NO ऑक्सीकरण की भूमिका का अध्ययन किया जाता है, और यह अनुमान लगाया जाता है कि NO_x भंडारण NO ऑक्सीकरण की घटना के

बिना भी हो सकता है। इसके अलावा, एनओएक्स रिलीज प्रोफाइल की ओर संग्रहीत एनओएक्स प्रजातियों के नो ऑक्सीकरण और अपघटन के योगदान का विभिन्न तापमानों पर अध्ययन किया जाता है। कम तापमान NO_x सोखना विशेषताओं के अलावा, उत्प्रेरक NO_x कमी के लिए भी सक्रिय पाया जाता है। विकसित उत्प्रेरक के NO_x सोखना, desorption, और कमी व्यवहार पर H_2, NH_3, C_3H_6, CO_2, और H_2O जैसी विभिन्न प्रजातियों के प्रभाव का अध्ययन एक विस्तृत तापमान सीमा के लिए किया जाता है। नगण्य N_2O गठन के साथ एक काफी उच्च NH_3-SCR गतिविधि को 150 ºC पर मापा जाता है, जबकि C_3H_6-SCR गतिविधि को उच्च तापमान पर प्रदर्शित किया जाता है। H_2 की उपस्थिति उल्लेखनीय रूप से कम तापमान NO_x सोखना और बाध्यकारी ताकत को बढ़ाती है, और H_2 की अनुपस्थिति में नाइट्राइट के प्रमुख गठन के विपरीत नाइट्रेट्स के महत्वपूर्ण गठन के लिए जिम्मेदार ठहराया जाता है। CO_2 कम तापमान NO_x सोखना पर एक मजबूत बाधा प्रभाव प्रदर्शित करता है, जो बाइकार्बोनेट के गठन के कारण NO_x स्पिलओवर की कम दरों द्वारा समझाया गया है। NH_3-SCR गतिविधि पर H_2, CO_2 और H_2O के प्रभाव का भी अध्ययन किया जाता है। इसके अलावा, संरचनात्मक विशेषताओं पर एजी और एमजीओ लोडिंग के प्रभाव के साथ-साथ C_3H_6, नो ऑक्सीकरण, C_3H_6-HCR, NH_3-SCR और NH_3 ऑक्सीकरण की ओर उत्प्रेरक की गतिविधि का अध्ययन किया जाता है।

संयुक्त NO_x सोखना/desorption और कमी गतिविधि के कारण, $Ag/MgO/Al_2O_3$ में NO_x उत्सर्जन को काफी कम करने की क्षमता है। $Ag/MgO/Al_2O_3$ और एक वाणिज्यिक Cu/SSZ-13 उत्प्रेरक से मिलकर एक aftertreatment प्रणाली को 115-495 ^oC की एक विस्तृत तापमान सीमा पर उच्च NO_x रूपांतरण प्राप्त करने के लिए दिखाया गया है। इस प्रकार, इस काम में विकसित Ag-आधारित उत्प्रेरक को एक एससीआर या एलएनटी उत्प्रेरक के साथ जोड़ा जा सकता है, ताकि उपचार के बाद की प्रणालियों में इन उत्प्रेरकों के PGM लोडिंग को कम किया जा सके। इसके अलावा, उत्प्रेरक में विभिन्न औद्योगिक क्षेत्रों में उपयोग करने की क्षमता है जहां NO_x उत्सर्जन को एक विस्तृत तापमान सीमा पर कम करने की आवश्यकता है। इसके अलावा, प्राप्त यांत्रिक अंतर्दृष्टि का उपयोग NO_x सोखना और कमी के लिए अधिक कुशल दोहरी-कार्यात्मक उत्प्रेरक डिजाइन करने के लिए किया जा सकता है।

Table of Contents

List of Figures

List of Tables

Nomenclature and Abbreviations

DOC	diesel oxidation catalyst
$F_{in}^{NO_x}$	inlet NO_x mole fraction
$F_{out}^{NO_x}$	outlet NO_x mole fraction
IAT	initial adsorption temperature (ºC)
IAt	initial adsorption time (s)
LNT	lean NO_x trap
m	mass of the catalyst (g)
N_{NOx}	total moles of NO_x adsorbed per gram of catalyst (mol/g)
$[NO_x]_{in}$	NO_x concentration at the inlet of catalyst bed (mol/m^3)
$[NO_x]_{out}$	NO_x concentration at the outlet of catalyst bed (mol/m^3)
$[NO_2]_{out}$	NO_2 concentration at the outlet of the catalyst bed (mol/m^3)
$[NH_3]_{in}$	NH_3 concentration at the inlet of catalyst bed (mol/m^3)
$[NH_3]_{out}$	NH_3 concentration at the outlet of catalyst bed (mol/m^3)
$[N_2]_{in}$	N_2 concentration at the inlet of catalyst bed (mol/m^3)
$[N_2]_{out}$	N_2 concentration at the outlet of catalyst bed (mol/m^3)
$[N_2O]_{in}$	N_2O concentration at the inlet of catalyst bed (mol/m^3)
$[N_2O]_{out}$	N_2O concentration at the outlet of catalyst bed (mol/m^3)
NSE	NO_x storage efficiency (%)

NDE	NO_x desorption efficiency (%)
PNA	passive NO_x adsorber
SCR	selective catalytic reduction
S_{N_2}	selectivity towards N_2 (%)
$\dot{\vartheta}$	total volumetric flow rate (m^3/s)
t	time (s)
t_{ads}	NO_x storage time (s)
t_{T_0}	time at which temperature T_o is achieved (s)
t_T	time at which temperature T is achieved (s)
T_i	initial temperature considered for evaluating cumulative NO_2/NO_x ratio (ºC)
T_f	final temperature considered for evaluating cumulative NO_2/NO_x ratio (ºC)
X_{NO_x}	steady-state NO_x conversion (%)
β	fraction of the total NO_x desorbed till a particular temperature
η	cumulative NO_x adsorption and reduction efficiency (%)
$\left[\frac{NO_2}{NO_x}\right]_{cum}$	cumulative NO_2/NO_x ratio