

Fundamental and Applied Catalysis

Isabella Nova
Enrico Tronconi *Editors*

Urea-SCR Technology for deNO_x After Treatment of Diesel Exhausts

 Springer

Fundamental and Applied Catalysis

Series editors

Martyn Twigg, Royston, UK

Michael Spencer, Cardiff, UK

For further volumes:

<http://www.springer.com/series/5964>

Isabella Nova · Enrico Tronconi
Editors

Urea-SCR Technology for deNO_x After Treatment of Diesel Exhausts

 Springer

Editors
Isabella Nova
Enrico Tronconi
Politecnico di Milano
Milan
Italy

ISSN 1574-0447
ISBN 978-1-4899-8070-0 ISBN 978-1-4899-8071-7 (eBook)
DOI 10.1007/978-1-4899-8071-7
Springer New York Heidelberg Dordrecht London

Library of Congress Control Number: 2014934157

© Springer Science+Business Media New York 2014

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law. The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

It is widely recognized that Diesel vehicles are sure to significantly increase their worldwide penetration, particularly in countries like the United States where the present market share is not remarkable in comparison to that of vehicles with gasoline engines. This is mainly due to Diesel engines being inherently more thermodynamically efficient than spark-ignition engines, thus offering the prospect of reducing emissions of carbon dioxide.

Diesels produce, however, higher emissions of nitrogen oxides (NO_x) and particulate matter (PM). The emissions levels which can be achieved depend on both the engine-out emissions and the performance of the emissions control system. For the engine-out emissions, there is a well-known trade-off between PM and NO_x. Such a trade-off is not, however, a constant relationship between the two pollutants. Developments in combustion systems, fuel injection equipment, turbocharging, and associated control systems have allowed and continue to allow the trade-off curve to move to lower values of both NO_x and PM. The trade-off thus gives engine developers the opportunity to combine the optimization of 'raw' emissions and fuel economy with the optimization of the emissions control system.

Improvements in combustion and/or alternative fuels can lead to lower NO_x emissions, but it is generally recognized by now that, in order to meet the current and forthcoming legislative emissions standards both in Europe and in the USA, the application of after treatment systems is required. Indeed, Diesel particulate filters (DPFs) are needed to achieve the PM emission levels regardless of the system used to reduce NO_x. But, most importantly, the significant CO₂ reduction (i.e., the improved fuel consumptions), that is also dictated by the upcoming regulations, are forcing a drastic decrease in the average temperature profile of the exhaust gases; in such conditions, the catalytic removal of NO_x becomes extremely challenging. In fact, a significant portion of the present test cycles (e.g., the NEDC, New European Driving Cycle, and the WHTC, World Harmonized Transient Cycle) is characterized by very low exhaust temperatures. This makes very difficult the fulfillment of NO_x emission limits.

Currently, the major deNO_x after-treatment technologies under consideration include the so-called Lean-NO_x Traps (LNT), which are used with direct injection gasoline and Diesel engines, and the Selective Catalytic Reduction (urea-SCR) process.

Urea-SCR was the European motor industry's technology of choice to meet Euro 4 and Euro 5 emissions requirements for heavy-duty Diesel engines and more recently was also applied to light-duty vehicles and passenger cars in the USA and in Europe, as well. An SCR system is designed to catalytically reduce NO_x emissions in the oxygen-rich environment of Diesel exhausts. To this purpose, the SCR system needs a chemical reagent, or reductant, to help convert the NO_x to nitrogen: in mobile applications, the preferred reductant is typically an aqueous solution of nontoxic urea, which is used as an ammonia source. In fact, the so-called Adblue[®] solution (or DEF, Diesel Emission Fluid) is injected into the exhaust system where it is decomposed to NH₃.

Usually, a Diesel Oxidation Catalyst is also present in the system configuration, upstream of the SCR converter, to partially convert NO to NO₂; this enriches the stream entering the SCR reactor with significant amounts of NO₂ in addition to NO, and thus enables the onset of the SCR deNO_x reactions at lower temperature in comparison to the case where most of the NO_x is composed of NO alone.

Urea-SCR was first brought to the market in 2005 for heavy-duty vehicle applications by Daimler AG (DaimlerChrysler at the time) under the trade mark BLUETEC[®], based on the use of extruded honeycomb monolith catalysts consisting of V₂O₅-WO₃-TiO₂, similar to those extensively used worldwide for the control of NO_x emissions from power stations and other stationary sources. Subsequently, we have seen a trend in the automobile industry to replace Vanadium-based SCR catalysts with a new generation of metal-exchanged zeolite-based systems in order to expand the operating temperature window and to solve the high temperature deactivation problems typical of the anatase-rutile TiO₂ transition. A variety of zeolites have been proposed for this purpose (e.g., ZSM-5, mordenite, beta, ferrierite, Y-zeolite, and more recently chabazite). Zeolites are generally promoted by transition metals, such as iron and copper: the resulting catalytic systems are associated with an excellent deNO_x activity, particularly in the case of the Cu-zeolites. Indeed, metal-promoted zeolites have rapidly become the class of automotive SCR catalysts of choice, making urea-SCR the leading deNO_x technology nowadays. In the last few years, the improvement of the critical low-temperature deNO_x activity has been impressive, primarily due to the development of a new generation of Cu-promoted catalysts based on small pore zeolites, which also exhibit unparalleled stability with time-on-stream. The fundamental reasons for such enhanced performance, however, are not fully understood yet: they currently represent the objective of many academic and industrial research efforts.

There are several additional complications in using urea-SCR, including for example. The need for efficient ammonia release from the urea solution, and the related risks of deposits in the exhaust system due to by-products formation. Another issue is the accurate ammonia dosage: there should be enough ammonia present on the catalyst to reduce all NO_x, but at the same time there must be no excess of ammonia, to prevent its slippage from the vehicle. In order to realize this balance, a deep understanding of the influence of the operating conditions on the amount of ammonia stored on the catalyst, and on the rates of ammonia

adsorption/desorption, is crucial for the design and particularly for the control of SCR catalytic converters for vehicles. Ammonia slip catalysts represent a recent development in this area. Another area of current development is related to the fact that the SCR catalyst is often placed downstream of the Diesel Particulate Filter (DPF), in order to meet the requirements on soot particle emissions. On one hand, this configuration exposes the SCR catalyst to very high temperatures during DPF regeneration, so that its hydrothermal stability is a major concern. On the other hand, the multifunctional combination of DPF and SCR in a single device (SCR catalyst coated onto the DPF) presents several advantages, and is receiving considerable attention.

Finally, mathematical modeling has been recognized since the early days as a critical tool for timely and cost-effective development of urea-SCR technology for vehicles. This has resulted in a significant evolution, wherein the initial simple empirical models have been progressively replaced by the present sophisticated, chemically and physically consistent models, used in many companies to generate reliable simulations of NO_x emissions in highly transient test cycles for a wide range of conditions and parameters. Further efforts are being devoted to incorporate more details of the SCR catalytic chemistry, and to relate them to the catalyst features.

Several years after its first commercial applications, the development of urea-SCR has now clearly turned into a success story, with positive and promising perspectives and still many opportunities for further improvements and breakthroughs in a number of areas. So now, it is probably a good time to review the status of the technology, and highlight the next challenges.

This book provides a complete overview of the selective catalytic reduction of NO_x by ammonia/urea (urea-SCR), drawing from the know-how of many leading experts in the field. The book begins with a discussion of the technology in the framework of the current context (legislation, market, system configurations), covers the fundamental aspects of the SCR process (catalysts, chemistry, mechanism, and kinetics) and eventually analyses its application to the real scale (modeling of full scale monolith catalysts, control aspects, ammonia/urea delivery systems and strategies, integration with other devices for combined removal of pollutants). The book concludes with case histories presented by two companies which have greatly and creatively contributed to make urea-SCR a well-established and crucial technology for the automotive industry.

The book is aimed primarily at researchers in industry and academia working on exhaust gas aftertreatment systems. Several chapters however provide reference material that will be useful for teaching general courses on catalytic processes for environmental protection, or dedicated courses on the Selective Catalytic Reduction of NO_x.

Finally, this book is the result of the work of a number of industrial and academic experts: all of these persons are to be congratulated for devoting their time and effort to the present volume.

Contents

Part I Selective Catalytic Reduction Technology

1	Review of Selective Catalytic Reduction (SCR) and Related Technologies for Mobile Applications	3
	Timothy V. Johnson	
1.1	Introduction	3
1.2	Regulatory Overview	4
	1.2.1 Heavy-Duty Truck Regulations	4
	1.2.2 Light-Duty Regulations	5
1.3	Engine Developments	6
	1.3.1 Heavy-Duty Engines	6
	1.3.2 Light-Duty Diesel Engines	8
1.4	SCR Technologies	10
	1.4.1 SCR System Introduction	10
	1.4.2 Urea Delivery System	12
	1.4.3 Alternative Sources for Ammonia and Systems	13
	1.4.4 DOC Overview	14
	1.4.5 SCR Catalysts	15
	1.4.6 Ammonia Slip Catalysts	19
1.5	SCR System Design	20
1.6	Onboard Generation of Ammonia Using Lean NOx Traps	23
1.7	Outlook	25
1.8	Conclusions	26
	1.8.1 Regulations and Engine Technologies	26
	1.8.2 Onboard Ammonia Delivery Systems and SCR Catalyst Systems	26
	1.8.3 Outlook	27
	References	27
2	SCR Technology for Off-highway (Large Diesel Engine) Applications	33
	Daniel Chatterjee and Klaus Rusch	
2.1	Introduction	33
2.2	Off-highway Emission Legislation	36

2.3	SCR Systems for High-Speed Engines	38
2.3.1	Small Ship Applications	39
2.3.2	Rail Applications	39
2.3.3	Gensets	40
2.4	Medium and Low-Speed Engines	42
2.4.1	Fuels and Sulfur	42
2.4.2	SCR Technology for Marine Applications	45
2.4.3	Low-Speed Engine Genset	45
2.5	Combined Systems	47
2.5.1	DPF + SCR	47
2.5.2	Combination of DeNoxiation and DeSulfurization	51
2.6	System Integration	51
2.6.1	Reductant Supply	51
2.6.2	Canning Concepts	55
2.7	Control Strategies	56
2.8	Outlook	58
	References	59

Part II Catalysts

3	Vanadia-Based Catalysts for Mobile SCR	65
	Jonas Jansson	
3.1	Introduction	65
3.2	Legislation	66
3.3	Main SCR Reactions	67
3.4	Urea Injection	68
3.5	Properties of Vanadia SCR Catalyst	68
3.6	Reaction Mechanism	71
3.7	Function/Principle Design	73
3.8	Dimensioning of SCR System	76
3.9	Effect of NO ₂	81
3.10	Aging of Vanadia SCR Catalysts	83
3.10.1	Thermal Aging	83
3.10.2	Impact of Sulfur	85
3.10.3	Alkali Metals and Alkaline Earth Metals	87
3.10.4	Oil Poisons	88
3.10.5	Hydrocarbons	90
3.10.6	Arsenic and Lead	91
3.10.7	Biofuel	91
3.10.8	In-use Aging Evaluation	92
3.11	Summary and Conclusions	92
	References	93

4	Fe-Zeolite Functionality, Durability, and Deactivation Mechanisms in the Selective Catalytic Reduction (SCR) of NO_x with Ammonia	97
	Todd J. Toops, Josh A. Pihl and William P. Partridge	
4.1	Introduction	97
4.2	Experimental Considerations in Evaluating and Aging Catalysts	99
4.3	Fe-Zeolite NO _x Reduction Characteristics	104
4.4	Durability, Aging Techniques, and Deactivation Mechanism Affecting Performance	111
4.5	Summary	118
	References	119
5	Cu/Zeolite SCR Catalysts for Automotive Diesel NO_x Emission Control	123
	Hai-Ying Chen	
5.1	Introduction	123
5.2	Chemistry and Functionality of Cu/Zeolite SCR Catalysts	124
5.3	Deactivation Mechanisms of Cu/Zeolite SCR Catalysts	126
5.3.1	Hydrothermal Deactivation	126
5.3.2	Hydrocarbon Storage, Inhibition, and Poisoning	132
5.3.3	Sulfur Poisoning	133
5.3.4	Urea and Urea Deposit Related Catalyst Deactivation	133
5.3.5	Chemical Poisoning	134
5.4	Development of Small-Pore Zeolite Supported Cu SCR Catalysts	135
5.5	Investigation on the Superior Hydrothermal Stability of Small-Pore Zeolite Supported Cu SCR Catalyst	140
5.6	Investigation on the Active Cu Sites in Small-Pore Zeolite Supported Cu SCR Catalysts	142
5.7	Summary	143
	References	144
6	Low-Temperature Selective Catalytic Reduction (SCR) of NO_x with NH₃ Over Zeolites and Metal Oxide-Based Catalysts and Recent Developments of H₂-SCR	149
	Gongshin Qi, Lifeng Wang and Ralph T. Yang	
6.1	Ammonia-SCR	149
6.1.1	Introduction	149
6.1.2	Catalysts and Mechanistic Aspects of the Low-Temperature Ammonia-SCR	151

6.2	H ₂ -SCR	163
6.2.1	Introduction	163
6.2.2	Catalysts and Mechanistic Aspects of H ₂ -SCR	165
6.3	Challenges and Prospective	171
	References	172
 Part III Mechanistic Aspects		
7	Active Sites for Selective Catalytic Reduction	181
	Wolfgang Grünert	
7.1	Introduction	181
7.2	Strategies and Methods for the Identification of Active Sites.	182
7.3	Supported Vanadia Catalysts	193
7.4	Zeolite-Based Catalysts	198
7.4.1	Fe Zeolites.	198
7.4.2	Cu Zeolites	206
7.5	Recent Catalyst Development.	208
7.6	Concluding Remarks	210
	References	211
8	Mechanistic Aspect of NO–NH₃–O₂ Reacting System.	221
	Masaoki Iwasaki	
8.1	Introduction	221
8.2	Steady-State Reaction Analysis	221
8.2.1	NH ₃ /NO/O ₂ , NH ₃ /O ₂ , and NO/O ₂ Reactions	221
8.2.2	Apparent Activation Energy.	223
8.2.3	Apparent Reaction Orders	224
8.2.4	Relationship with NO Oxidation Activity	227
8.2.5	Effect of Coexisting Gases and Poisoning	230
8.3	Transient Reaction Analysis.	233
8.3.1	Periodic NH ₃ Supply.	233
8.3.2	NO Pulse Reaction	237
8.3.3	In Situ FT-IR Analysis	238
8.4	Reaction Mechanisms	240
8.4.1	Vanadium-Based Catalysts.	240
8.4.2	Fe- or Cu-Exchanged Zeolite Catalysts	242
8.5	Conclusions	244
	References	244
9	The Role of NO₂ in the NH₃–SCR Catalytic Chemistry	247
	Enrico Tronconi and Isabella Nova	
9.1	Introduction	247
9.2	Experimental	248

9.3	Surface Storage of NO _x	249
9.3.1	NO ₂ Adsorption/Desorption	249
9.3.2	FTIR in Situ Study of NO ₂ Adsorption	250
9.3.3	Effect of the Catalyst Redox State on NO ₂ Adsorption	251
9.4	The Role of Surface Nitrates in the Fast SCR Mechanism.	253
9.4.1	NH ₃ + NO _x Temperature Programmed Reaction (TPR) Runs	253
9.4.2	Role of Nitrates in the NO/NO ₂ -NH ₃ SCR Mechanism.	255
9.5	Mechanistic Studies by Transient Response Methods	255
9.5.1	Reactivity of Surface Nitrates with NO and with NH ₃	256
9.5.2	The Role of Nitrites	257
9.5.3	Overall Mechanistic Scheme	258
9.5.4	Ammonia Blocking of Nitrates Reduction	259
9.5.5	Considerations on the Red-ox Nature of the NH ₃ -SCR Mechanisms	260
9.5.6	Higher Temperatures: The NO ₂ -SCR Reaction	261
9.5.7	Selectivity Issues: The Formation of NH ₄ NO ₃ , N ₂ O	262
9.6	Feeding Nitrates: The Enhanced SCR Reaction	263
9.6.1	The Boosting Action of Ammonium Nitrate	263
9.6.2	Analysis of the Enhanced SCR Chemistry	267
9.7	Summary and Conclusions.	268
	References	269

Part IV Reaction Kinetics

10 Kinetics of NH₃-SCR Reactions Over

	V₂O₅-WO₃/TiO₂ Catalyst	273
	Isabella Nova and Enrico Tronconi	
10.1	Introduction	273
10.2	Methods	274
10.2.1	Experimental Rig and Procedures	274
10.2.2	Mathematical Model of the Microreactor for Kinetic Tests.	275
10.3	NH ₃ /O ₂ Reacting System.	276
10.4	NH ₃ -NO/O ₂ Reacting System	282
10.5	NH ₃ -NO/NO ₂ Reacting System	294
10.6	Conclusions	308
	References	308

11 Lean NO_x Reduction by NH₃ on Fe-Exchanged Zeolite and Layered Fe/Cu Zeolite Catalysts: Mechanisms, Kinetics, and Transport Effects.	311
Michael P. Harold and Pranita Metkar	
11.1 Introduction	311
11.2 Reaction System Performance Features	312
11.2.1 NO Oxidation and NO ₂ Decomposition.	315
11.2.2 NH ₃ Oxidation	316
11.2.3 Selective Catalytic Reduction of NO _x	317
11.3 Kinetics and Mechanistic Considerations.	324
11.3.1 NO Oxidation	325
11.3.2 Standard SCR Reaction.	331
11.3.3 Ammonia Inhibition	333
11.3.4 Selective Catalytic Reaction with NO and NO ₂	334
11.4 Reaction and Transport Interactions	343
11.5 Reactor Modeling Developments	348
11.6 Concluding Remarks.	353
References	354
12 Kinetic Modeling of Ammonia SCR for Cu-Zeolite Catalysts	357
Louise Olsson	
12.1 Introduction	357
12.2 Kinetic Models for Ammonia and Water Storage Over Cu-Zeolites	358
12.2.1 Global Kinetic Model for Ammonia Storage and Desorption.	361
12.2.2 Detailed Kinetic Model for Ammonia and Water Storage	362
12.3 Kinetic Models for Ammonia Oxidation Over Cu-Zeolites	364
12.3.1 Global Kinetic Model for Ammonia Oxidation	364
12.3.2 Detailed Kinetic Model for Ammonia Oxidation	364
12.4 Kinetic Models for NO _x Storage and NO Oxidation Over Cu-Zeolites	365
12.4.1 Detailed Kinetic Model for NO Oxidation.	365
12.4.2 Global Kinetic Model for NO Oxidation.	369
12.5 Kinetic Models for SCR Reactions Over Cu-Zeolites	371
12.5.1 Global Kinetic Models for SCR Over Cu-Zeolites	371
12.5.2 Detailed Kinetic Models for SCR Over Cu-Zeolites	376
12.6 Conclusions	381
References	381

Part V Modeling and Control

13 SCR Reactor Models for Flow-Through and Wall-Flow Converters 385
 Dimitrios Karamitros and Grigorios Koltsakis

13.1 Introduction 385

13.2 Fundamentals of Flow-Through Catalyst Modeling. 386

 13.2.1 Balance Equations 387

 13.2.2 Washcoat Internal Diffusion Modeling 389

 13.2.3 Multidimensional Model Extension. 391

13.3 Reaction Modeling 392

 13.3.1 Adsorption Model. 392

 13.3.2 de-NO_x Reactions. 394

 13.3.3 Parameter Calibration 397

13.4 Importance of Washcoat Diffusion Modeling. 397

 13.4.1 Experimental Results 398

 13.4.2 Simulation Study and Effective Diffusivity Investigation 398

13.5 From Lab Reactor Tests to Real-World System Modeling. 400

 13.5.1 Overview of Model Parameterization Approaches 400

 13.5.2 Microreactor and Monolith Reactor Tests 400

 13.5.3 Real-World Full-Scale Applications 402

13.6 Fundamentals of SCR on DPF Modeling. 403

 13.6.1 Wall-Flow Filter Model. 403

 13.6.2 SCR Kinetic Model and Soot Oxidation Kinetics 406

 13.6.3 Wall-Flow Versus Flow-Through Monoliths 407

 13.6.4 Interactions Between Soot and de-NO_x Activity. 408

13.7 Integrated Exhaust System Modeling 412

 13.7.1 Model-Based DPF + SCR System Optimization 413

 13.7.2 Combined LNT-SCR Concepts. 416

 13.7.3 Combined SCR-ASC Concept 418

13.8 Conclusion: Perspectives 419

References 422

14 Diesel Engine SCR Systems: Modeling, Measurements, and Control 425
 Ming-Feng Hsieh and Junmin Wang

14.1 Introduction 425

14.2 SCR Control-Oriented Modeling 426

 14.2.1 Introduction 426

 14.2.2 Main SCR Reactions. 426

 14.2.3 Control-Oriented SCR Model. 427

14.3 SCR Sensing and Estimation Systems. 430

 14.3.1 NO_x Sensor NH₃ Cross-Sensitivity 431

14.3.2	SCR Catalyst Ammonia Coverage Ratio Estimation	437
14.4	SCR Control	441
14.4.1	Control-Oriented SCR Model	442
14.4.2	Controller Design and Architecture	443
14.4.3	Experimental Setup	444
14.4.4	Experimental Results of US06 Test Cycle	446
14.5	Conclusions	448
	References	449

Part VI Ammonia Supply

15	DEF Systems and Aftertreatment Architecture Considerations. . .	455
	Ryan Floyd, Levin Michael and Zafar Shaikh	
15.1	Role of Engine and Dosing Calibration	459
15.2	Overview of Injection Technology and Spray Quality	461
15.3	Overview of SCR System Mixing Devices	467
15.4	SCR System Mixing Devices: Ford Practical Example	471
15.5	Aftertreatment Architecture	474
15.6	Deposit Mitigation: Practical Example	479
15.7	Concluding Remarks	483
	References	483
16	Ammonia Storage and Release in SCR Systems for Mobile Applications	485
	Daniel Peitz, Andreas Bernhard and Oliver Kröcher	
16.1	Introduction	485
16.2	Urea as Ammonia Precursor Compound	486
16.2.1	Solid Urea	486
16.2.2	Urea Solution	487
16.2.3	Urea Thermolysis and Evaporation	487
16.2.4	Urea Decomposition Byproducts and Catalyst Deactivation	489
16.2.5	Catalytic Urea Decomposition	491
16.3	Alternative Ammonia Precursor Compounds	493
16.3.1	Cyanuric Acid	493
16.3.2	Ammonium Formate	494
16.3.3	Ammonium Carbamate	495
16.3.4	Metal Ammine Chlorides	496
16.3.5	Methanamide	498
16.3.6	Guanidinium Salts	499
16.3.7	Catalytic Decomposition of Alternative NH ₃ Precursor Compounds	499
	References	501

17 Modeling the Gas Flow Process Inside Exhaust Systems: One Dimensional and Multidimensional Approaches	507
Gianluca Montenegro and Angelo Onorati	
17.1 Introduction	507
17.2 1D Models for the Prediction of Gas Flows.	508
17.2.1 Modeling the Thermal Aspects.	510
17.2.2 Thermal and Hydrolytic Decomposition of Urea	516
17.2.3 Kinetic Model	517
17.3 Multidimensional Models	521
17.3.1 Governing Equations.	521
17.3.2 Modeling the UWS Injection	526
17.3.3 Modeling the Formation of Liquid Film	532
17.3.4 Discretization of Source Terms and Equations	535
17.3.5 Examples of CFD Application	538
References	547

Part VII Integrated Systems

18 Dual-Layer Ammonia Slip Catalysts for Automotive SCR Exhaust Gas Aftertreatment: An Experimental and Modeling Study	553
Isabella Nova, Massimo Colombo, Enrico Tronconi, Volker Schmeißer, Brigitte Bandl-Konrad and Lisa Zimmermann	
18.1 Introduction	554
18.2 Methods	556
18.2.1 Experimental	557
18.2.2 Modeling.	558
18.3 Derivation and Validation of the SCR Model.	561
18.3.1 Reaction Network and Kinetic Scheme Over the SCR Component	561
18.3.2 Kinetic Fit	566
18.3.3 Model Validation	567
18.4 Derivation and Validation of the PGM Catalyst Model	567
18.4.1 Reaction Network and Kinetic Scheme Over the PGM Component	567
18.4.2 Model Fit	573
18.4.3 Model Validation	573
18.5 Analysis and Modeling of SCR/PGM Interactions	575
18.5.1 Experimental Study of SCR/PGM Interactions	575
18.5.2 Predictive Simulations of the SCR/PGM Combined Systems	577

18.6	Modeling of Dual-Layer Monolith ASC	579
18.6.1	Development of a Dual-Layer Monolith Model	579
18.6.2	Validation of the Dual-Layer Monolith ASC Model	581
18.7	Conclusions	583
	References	584
19	NSR–SCR Combined Systems: Production and Use of Ammonia	587
	Fabien Can, Xavier Courtois and Daniel Duprez	
19.1	Introduction	587
19.2	NH ₃ Emission from NSR Catalysts.	588
19.2.1	The NSR Process	588
19.2.2	Ammonia Formation Pathways.	589
19.2.3	Influencing Parameters/Ammonia Reactivity	591
19.2.4	Conclusion.	596
19.3	Coupling of NO _x Trap and NH ₃ –SCR Catalysts.	596
19.3.1	Emergence and Development of the NSR–SCR Coupling Concept.	596
19.3.2	Coupling of Pt Catalysts with Zeolites	598
19.3.3	Coupling of Pt(RhPd)/BaO/Al ₂ O ₃ with Cu–Zeolite Catalysts	598
19.3.4	Coupling of Pt(RhPd)/BaO/Al ₂ O ₃ with Fe–Zeolite Catalysts	603
19.3.5	Other Systems Including Tungsten-Based Catalysts	606
19.4	Selective Catalytic Reduction of NO _x by Ammonia (NH ₃ –SCR)	608
19.4.1	Mechanistic Aspects of the SCR Reaction.	608
19.4.2	Effect of Zeolite Framework	610
19.4.3	Role of Acidic Sites	611
19.4.4	Active Sites and Performances of Cu–Zeolite, Fe–Zeolite, and Other Systems in NH ₃ –SCR	612
19.5	Conclusion and Perspective	614
	References	615
20	Integration of SCR Functionality into Diesel Particulate Filters.	623
	Thorsten Boger	
20.1	Introduction	624
20.2	Diesel Particulate Filter Technologies	626
20.2.1	Diesel Particulate Filter Designs and Materials	626
20.2.2	Catalyst Coatings for Diesel Particulate Filters.	629

- 20.3 Performance Considerations for SCR Integrated Diesel
 - Particulate Filters 630
 - 20.3.1 Pressure Drop and Permeability 630
 - 20.3.2 Filtration 636
 - 20.3.3 Filter Regeneration, Thermal Management,
and Durability 640
 - 20.3.4 DeNOx Efficiency 643
- 20.4 Modeling of SCR Integrated Particulate Filters 645
- 20.5 Application Examples 648
 - 20.5.1 Light Duty 648
 - 20.5.2 Heavy Duty 650
- 20.6 Summary 651
- References 652

Part VIII Case Histories

- 21 Development of the 2010 Ford Diesel Truck Catalyst System 659**
 - Christine Lambert and Giovanni Cavataio
 - 21.1 Introduction 660
 - 21.2 Early Research at Ford on Lean NOx Control
for Diesel Vehicles 661
 - 21.3 Ford’s Research Program on a Prototype Light-Duty
Diesel Truck 663
 - 21.3.1 SCR System Design 663
 - 21.3.2 DOC Development for SCR Systems 664
 - 21.3.3 SCR Catalyst Formulations 666
 - 21.3.4 Vehicle System Results 666
 - 21.4 Migration of Research into a Production Vehicle Program 668
 - 21.4.1 Vehicle Program Needs for Lean NOx Control 668
 - 21.4.2 Catalyst and System Design Options 669
 - 21.5 Development Challenges Associated with SCR
Catalyst Systems 670
 - 21.5.1 Thermal Stability of the DOC 670
 - 21.5.2 Thermal Stability of the SCR Catalyst 671
 - 21.5.3 Ammonia Storage Management 674
 - 21.5.4 HC Poisoning/Coking of Zeolitic SCR Catalysts 676
 - 21.5.5 Precious Metal Poisoning 679
 - 21.5.6 Sulfur Effects on Catalysts 681
 - 21.5.7 Urea Injection/Mixing 682
 - 21.5.8 Urea Specifications and Refill 682

21.6	Environmental Impact of Medium-Duty Diesels:	
	Current and Future	683
21.6.1	NO _x Emissions	683
21.6.2	Greenhouse Gas Footprint (CO ₂ , CH ₄ , N ₂ O)	684
21.6.3	Use of Base Metals, Pd Rich Catalysts	684
21.7	Conclusion.	686
	References	687
22	Model-Based Approaches to Exhaust Aftertreatment	
	System Development.	691
	Michel Weibel, Volker Schmeißer and Frank Hofmann	
22.1	Introduction	692
22.2	Modeling of the Exhaust Gas Aftertreatment System	693
	22.2.1 Total System Simulation	693
	22.2.2 Model Structure	694
	22.2.3 Kinetics and Parameterization	695
22.3	Simulation Methods in the Development Process	696
	22.3.1 Demands of the Development Process.	696
	22.3.2 The Virtual Testbench Concept	697
	22.3.3 Development of an AdBlue [®] Dosing Control Strategy	697
22.4	Outlook: On-board Model-Based SCR Control.	704
22.5	Summary	705
	References	706
	About the Editors	709
	Index	711

Part I
Selective Catalytic Reduction Technology

Chapter 1

Review of Selective Catalytic Reduction (SCR) and Related Technologies for Mobile Applications

Timothy V. Johnson

1.1 Introduction

NO_x is formed when air is heated to very high temperatures, and is thus emitted from combustion and engines. The most prevalent NO_x species from engines is NO. It will oxidize in the atmosphere to form NO₂, and also react with many hydrocarbons (HCs) to form ozone; both ozone and NO₂ are toxic and strong oxidants. Thus, NO_x is a criteria pollutant and is regulated. NO_x is very effectively controlled from gasoline engines with three-way catalysts (TWCs) (CO, HCs, NO_x), but they only operate under stoichiometric conditions. For lean diesel conditions, selective catalytic reduction (SCR) is the leading method of remediation. The reductant, ammonia (NH₃), which needs to be added to the exhaust, selectively reduces the NO_x rather than being oxidized by the excess oxygen, as do the innate exhaust reductants, CO and HCs.

This chapter will set the stage for the other chapters in the book by providing a representative review of the regulations, general engine trends, and key developments in SCR catalyst technology. It is not intended to be all-encompassing and comprehensive. Representative papers and presentations were chosen here that provide examples of new, key developments, and direction. For a more detailed review of SCR technologies, and diesel emission control technology trends and developments in general, the reader is referred to Johnson [1–3].

T. V. Johnson (✉)

Emerging Technologies and Regulations, Corning Environmental Technologies, Corning Incorporated, HP-CB-3-1, Corning, NY 14831, USA
e-mail: JohnsonTV@Corning.com

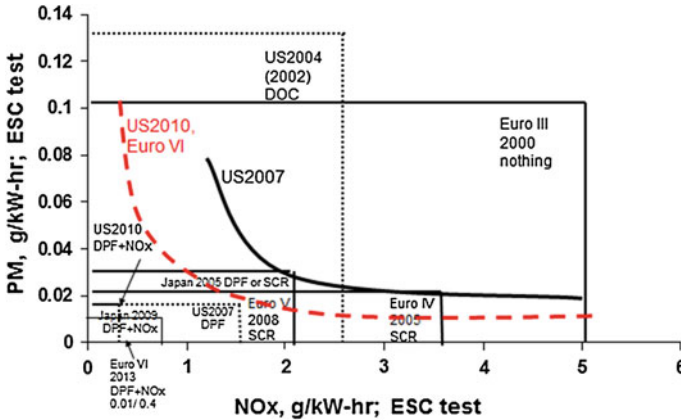


Fig. 1.1 Overview of key HD tailpipe regulations as measured on the ESC. The *dashed* and *solid lines* represent an estimate of the best commercially viable engine-out emissions for engines in 2007 and 2010

1.2 Regulatory Overview

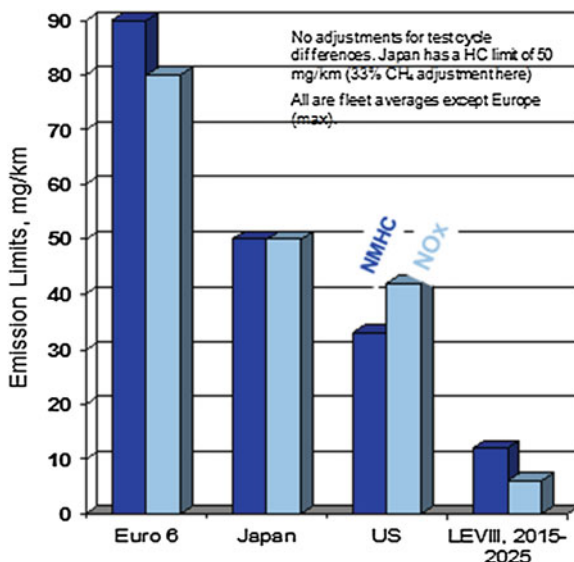
Although the first commercial lean deNO_x system was a lean NO_x trap (LNT) on the European Toyota Avensis in the early 2000s, and then on the US Dodge Ram truck (Cummins engine) in 2007, the first wide-scale use of deNO_x was the implementation of SCR for heavy-duty (HD) truck applications in Europe in 2005. The US Tier 2 and California Low Emission Vehicle (LEVII) regulations were the first to force SCR on light-duty (LD) applications in 2007. SCR did not make its way into NR applications until 2011 in both the US and Europe.

Following is a general overview of the HD, LD, and NR regulations pertinent to understanding the main drivers for SCR systems.

1.2.1 Heavy-Duty Truck Regulations

Figure 1.1 shows a summary of the key HD truck regulations in the world, along with estimates of the best commercially viable engine-out NO_x and particulate matter (PM) capabilities, as measured on the European Steady-State Cycle (ESC). The first vehicle regulation in the world that was attained with SCR systems was the Japan 2005 HD truck regulation in October 2004, shortly followed by Euro IV in January 2005. Although Euro IV was only a 30 % NO_x tightening from Euro III (2000), the PM regulation dropped ~80 %, and truck manufacturers generally elected to tune their engines for higher NO_x and lower PM and fuel consumption, and then use SCR to drop the tailpipe levels to within the NO_x (and PM) requirements. It is interesting to note that although the US2007 NO_x regulations

Fig. 1.2 Leading light-duty diesel NOx and non-methane hydrocarbon emissions



were 60 % lower than for Euro IV, and the PM regulations were about 35–55 % tighter (steady state and transient testing, respectively), the US manufacturers chose to meet the NOx regulations with engine technology (mainly exhaust gas recirculation (EGR)), and the PM regulations with diesel particulate filters (DPFs). The Japan 2005 regulation is intermediate between Europe and the US for both NOx and PM, and there was a split of approaches used in Japan, with trucks in high fuel consumption applications generally using a European SCR-only approach, and all others using a EGR + DPF approach.

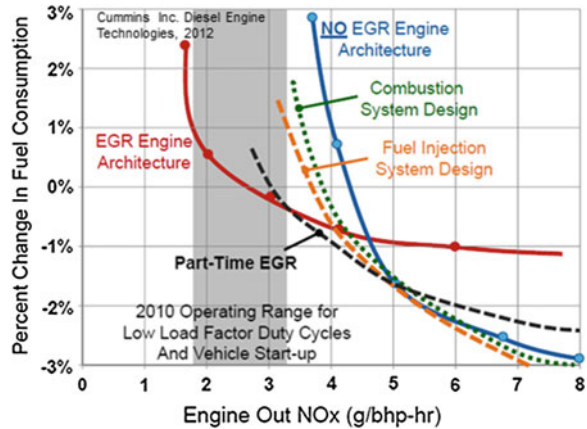
In the 2009+ time frame, Japan 2009, US2010, and Euro VI (2013) all require both SCR and DPF solutions. These regulations range from 0.26 to 0.7 g NOx/kW-h and 0.010 to 0.013 g PM/kW-h.

1.2.2 Light-Duty Regulations

The leading LD diesel non-methane HC and NOx regulations are graphically shown in Fig. 1.2. Only the US (Federal and California LEVIII) has the test-cycle and limit value combination to force NOx aftertreatment. All require a DPF (regulations not shown). By 2013, perhaps a dozen diesel models will be on the US market. However, the majority of Euro 6 applications will have NOx aftertreatment to minimize NO₂ emissions and fuel consumption.

One regulatory development that will drive SCR system design in Europe and elsewhere is emerging now in Europe: Real-World Driving Emissions (RDE). Investigators have found that NOx emissions from LD diesels can be 3–4X higher

Fig. 1.3 EGR can have fuel consumption benefits at low engine-out NO_x levels (<4 g/bhp-h or 5.2 g/kW-h), but at higher levels there is a fuel penalty versus SCR approaches with high deNO_x efficiency [4]



than the laboratory certification level. It is too early to note the details of these regulations, but they are likely to include portable emissions monitoring systems (PEMS) and require advance controls for cold start, high speed, and load conditions.

The regulatory trend in the US, Europe, and Japan is for very low-NO_x emissions. All HD trucks in these markets will have SCR systems by early 2014. These regulations are migrating into the NR machine sector, wherein most engines >70 kW will have SCR systems in 2014+. For passenger cars, all but the smaller diesels will have SCR systems in the three markets. Tighter regulations are foreseen for the developing markets, with Brazil leading the way, followed by China and India.

1.3 Engine Developments

This section will summarize HD and LD diesel engine technologies. We may see lean-burn gasoline engines in the market, and SCR is a viable option for these engines, but this is beyond the scope of this summary.

1.3.1 Heavy-Duty Engines

HD engine technology is in development to meet the next round of OBD (onboard diagnostics) tightening in the US for 2013 and the new CO₂ regulations in 2014. Concurrent with this, the Euro VI regulations come into play in 2013–2014.

Stanton [4] shows in Fig. 1.3 that the most effective engine means for reducing NO_x, EGR is an efficient approach and can have fuel consumption benefits if SCR

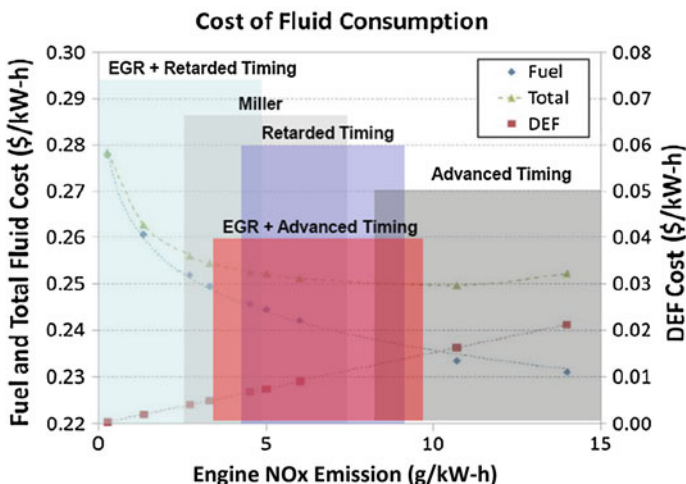


Fig. 1.4 General advance HD engine technologies and the resultant urea (DEF) and fuel cost curves, assuming DEF costs \$2.56 per gallon (\$0.69/l) and diesel fuel cost \$3.89/gallon (\$1.05/l). Fluid costs are minimized at 8–11 g/kW-h NOx [5]

efficiency requires low engine-out NOx levels (<2.5–5 g/kW-h NOx) in low-load operating regimes. However, if increased SCR deNOx efficiency allows higher NOx levels, EGR results in a fuel penalty. Given this, Stanton estimates that if SCR can attain a 98 % cycle-average deNOx efficiency, EGR can be eliminated. Furthermore, as shown in Fig. 1.3, running at higher engine-out NOx can return substantial fuel consumption benefits. In the high-NOx regimes, about 1 % fuel can be saved for every 1.2–1.5 % urea consumed (relative to fuel) to drop the NOx. This is beneficial for both CO₂ reductions and fluid cost savings (urea plus fuel).

Roberts [5] described some HD technologies for both high- and low-engine-out NOx approaches. A summary is shown in Fig. 1.4, wherein each point represents an engine hardware configuration that is optimized for low fuel consumption. As with previous such descriptions of advance engine technology packages [6], fuel consumption decreases as NOx increases, even out at >5 g NOx/kW-h. Roberts shows minimum fluid operating costs (top line) at 8–11 g/kW-h engine-out NOx. He assumes here that the urea (Diesel Exhaust Fluid (DEF)) is 65 % the cost of fuel. Emission control technologies (like SCR) would be needed to achieve at least 97–98 % efficiency to achieve this minimum fluid-consumption-cost calibration range, to meet the US 2010 regulations.

Zybell [7] also described some HD technology packages for meeting low emissions and fuel consumption, but mainly in the context of fuel injection technology. His slopes of fuel consumption versus NOx are not as steep as shown in Figs. 1.3 and 1.4, so his minimum cost range is in the 3–5 g/kW-h NOx range. However, when fuel injection pressure is increased from 1,800 to 2,400 bar, the fluid consumption drops about 0.6 % and the minimum calibration shifts to

2.5–4.0 g/kW-h NO_x. Continuing the trend, if injection pressure is increased to 3,000 bar, fluid consumption drops another 0.1 % and the minimum point shifts to 2.0–3.0 g/kW-h NO_x.

Kobayashi et al. [8] gave a detailed account of their attempt to drop engine-out NO_x to 0.2 g/kW-h on a 10.5 l engine with the following features: 2,000 bar common rail fuel injection system, low-pressure (LP) and high-pressure (HP) EGR, variable valve actuation, 300 bar peak cylinder pressure, variable swirl, and advanced combustion chamber design. With a DPF, the engine achieved 0.8 g/kW-h NO_x on the JE05 Japanese HD transient cycle. At 1,200 RPM and 8 bar BMEP, substituting about 40–70 % LP-EGR instead of HP-EGR results in similar NO_x levels, despite 5–10 % higher total EGR rates, but with greatly reduced PM and fuel consumption. Also striving for high-efficiency and low-NO_x, Ojeda [9] reported that a prototype 13-l engine with 2-stage EGR cooling, 2-stage turbocharging, a 2,200 bar injection system, and optimized combustion system achieved 45 % BTE at road loads, with a 0.5 g/bhp-h NO_x (0.65 g/kW-h) NO_x level. This is higher efficiency than some 2,010 engines running with SCR at much higher NO_x levels. Although impressive, these studies show that achieving the engine-out NO_x levels required to meet the emerging tailpipe regulations, without NO_x after-treatment is quite difficult and could be very expensive.

Improved thermal management is increasing in importance, especially as it pertains to reducing urban NO_x from engines with SCR. The first evidence that this issue is being addressed on Euro VI engines was reported by Vermeulen et al. [10]. The 13-l prototype Scania engine had cooled-EGR to reduce low-load NO_x and intake throttling for thermal management. NO_x in-service conformity (ISC) was well below the 1.5X limit after allowable calibration adjustments, and NO_x emissions generally vary from 0.35 to 0.76 g/kW-h for most trips and segments. The SCR system was fully functional after 500 s of operation after a cold start at 3 °C.

Finally, US HD engine manufacturers described their future approaches to meeting the US Department of Energy (DOE) goal of demonstrating 50 % BTE (break thermal efficiency) on a HD engine [1]. All four US HD truck engine manufacturers get much of their efficiency improvements from combustion (chamber design, control, mixing, etc.), reduction of friction and parasitic losses, and Rankine cycle waste heat recovery (WHR). Improved SCR performance is also mentioned commonly (for higher NO_x calibrations).

Although HD NO_x regulations might be met by further advancements in engine technology, the best balance of low fuel consumption and low tailpipe NO_x emissions requires about 98+ % efficient SCR.

1.3.2 Light-Duty Diesel Engines

LD diesel engines are also improving to keep the efficiency advantage over gasoline. Pischinger [11] described future technologies for both diesel and gasoline engines to achieve 35 % CO₂ reductions. Major improvements in both platforms

include 25 % downsizing (7 % reductions), stop–start system (6 %), LP-EGR (3 %), and down-speeding (3 %). The approach can result in lower exhaust temperatures due to more turbocharging, and higher NO_x as the result of the same fuel amount burned in a smaller cylinder. However, for gasoline vehicles to meet the 95 g/km fleet average CO₂ emission requirement in Europe in 2020, Pischinger projects significant hybridization is needed. Diesel engines can meet the regulation with standard drivetrains.

In the US, to meet the tight LEV_{III} emissions, reduced cold start emissions are the key, requiring significant thermal management methods. Popuri et al. [12] use an intake throttle, bypass valves for the EGR, turbine, and LP-VGT (variable gate turbocharger), idle speed modulation, late cycle fuel injections, cylinder deactivation (fueling cut off), and an exhaust-manifold integrated diesel oxidation catalyst (DOC) to allow urea injection 125 s, earlier than for a baseline engine. Despite that the engine-out NO_x increased 20 %, and fuel consumption increased 5–7 % when the methods are used, Federal Test Procedure (FTP) Bag 1 deNO_x was an impressive 70 % and overall fuel efficiency increased 25 % compared to their baseline engine. A 4.5 l engine in a 5,000 pound (2,270 kg) vehicle achieved US Tier 2 Bin 5 standards at 25.5 MPG (9.1 l/100 km). Ruth [13] reported significant progress in the same program that reduces thermal management requirements and is now targeted to meet the LEV_{III} fleet average requirements (–70 % vs. Tier 2 Bin 5) by using a passive NO_x adsorber (PNA) that adsorbs NO_x at low temperature and releases it passively as temperature increases, a combination SCR + DPF (SCR catalyst coated onto a DPF), and gaseous NH₃ injection. The progress shows how critical advanced SCR technology is to improve feasibility of clean LD diesel engines.

Another LEV_{III} approach was reported by Balland et al. [14]. To address the challenge SCR and other deNO_x systems have in reducing high-load NO_x, the investigators report that a standard DOC can efficiently remove NO_x at stoichiometry, and thus run the engine in that mode during accelerations. The approach requires tight control of EGR, the turbocharger, and other engine parameters, and uses an “air-based control” approach similar to that of gasoline engines, rather than a fuel-based approach typical of diesel engines. Exhaust temperatures also increase substantially in the accelerations and the strategy is part of cold start thermal management.

Diesel engine costs have been a problem in competing with modern gasoline engines. Regner et al. [15] are updating the opposed-piston diesel engine, solving the historic problems using new materials and modern analytical techniques. Because it has no head or valve train, compared to a standard diesel engine, it has 40 % fewer parts, is 30 % lighter, and costs about 10 % less. Fuel consumption is 15–20 % lower than a state of the art 6.7 l diesel engine, but lube oil consumption and NO_x emissions are about double.

Contrary to HD applications, wherein deNO_x improvements are used to reduce fuel consumption and 98 % deNO_x is desired, modern LD diesel engines do not have as strong a relationship between NO_x and fuel consumption at the higher NO_x levels. In the US, all of the available deNO_x efficiency will be used to meet

the LD NO_x regulations. In Europe, deNO_x efficiencies of 50–70 % are needed to meet the regulations in the most efficient means.

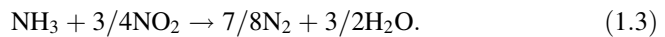
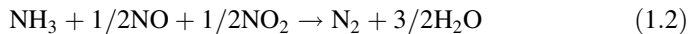
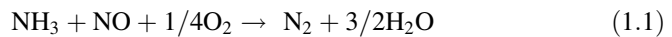
Lean NO_x control (lean deNO_x) technologies will be integral to meeting the emerging HD criteria pollutant regulations for diesel engines. Minimum removal efficiencies on the order of 85 % will be needed, but levels up to 97–98 % are desired to allow engines to operate in high-NO_x low-fuel consumption regimes. For LD applications, the efficiency is as important in the US, but light-off or low-temperature performance characteristics are even more so.

1.4 SCR Technologies

1.4.1 SCR System Introduction

The TWC is the most effective NO_x reduction system on vehicles but requires the absence of oxygen. It has been in production for more than 30 years and is removing more than 99 % of the NO_x from modern engines. In this system, unburned CO and HCs are used to reduce NO_x on a rhodium catalyst. The key to this technology is the gas mixture control. It is critical to have a near-stoichiometric mixture, wherein the mixture of air and fuel are near-ideal and there is very little excess oxygen. If oxygen is present in the exhaust, the CO and HCs will react with it rather than with the NO_x. Diesel engines are lean-burn with plenty of excess oxygen. Practical and effective catalysts for selectively reducing NO_x with CO or HCs in a lean environment are not yet available, but selective catalysts using ammonia as the reductant have been commercialized in the stationary sector for decades.

The key SCR catalyst reactions are shown as



Reaction (1.1) is generally the “standard SCR reaction”. As NO₂ is always present in the exhaust to some extent (maybe 10 % of NO_x), Reaction (1.2) is also pertinent, and is in fact the fastest and preferred NO_x reduction reaction. To promote this “fast SCR reaction” a DOC is commonly used to form more NO₂ over platinum by the following reaction:



If too much NO₂ is produced in the DOC, more than 1:1 = NO:NO₂, then Reaction (1.3) becomes operative. This is undesirable because the “excess” NO₂ can yield N₂O, which is a strong greenhouse gas:

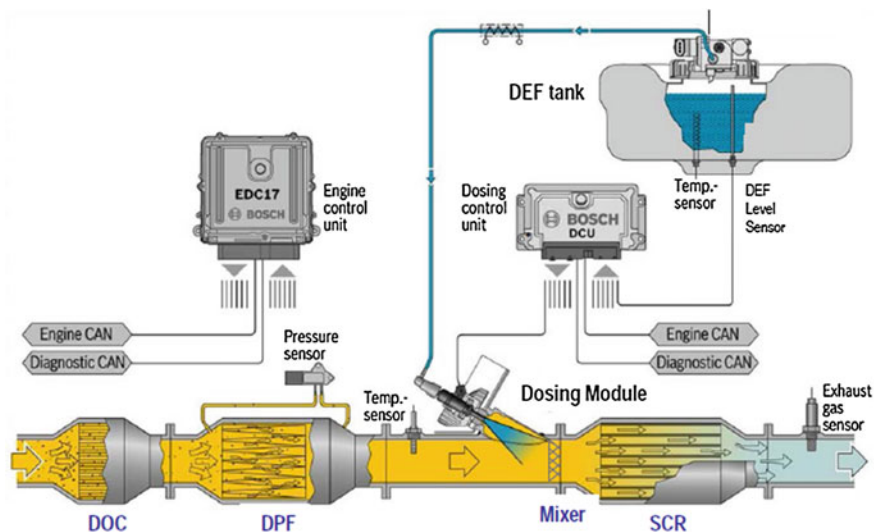
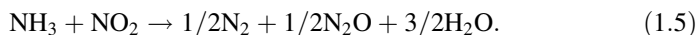
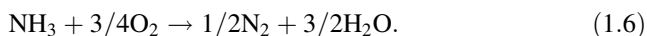


Fig. 1.5 Layout of a DPF + SCR system [16]



If the reactants are not well-mixed, if excess ammonia is injected to obtain high deNO_x efficiencies, or if ammonia stored on the SCR catalyst is released too fast, ammonia emissions can occur. To remediate this, an ASC is utilized:



SCR technology is entering its third or fourth generation since commercial introduction in Europe in 2003. Then, systems were removing upwards of 75 % NO_x over the European HD Transient Cycle to meet Euro IV regulations. To meet the US2010 and emerging Euro VI regulations in 2013, cycle-average deNO_x efficiencies approaching 95 % is realized. Work is continuing in the US to go even higher in efficiency to meet the current and emerging LD NO_x regulations. In both HD and LD applications, targets of 98 % test-cycle deNO_x efficiency are in the scope for future systems.

To achieve this high level of efficiency, all aspects of the system need to be optimized. An SCR system will generally comprise an ammonia delivery system, and the catalyst system itself comprises the DOC (and typically DPF), SCR catalyst, and the ammonia slip catalyst.

Casarella [16] shows the layout of a typical diesel emission control system incorporating the DPF, Fig. 1.5. In the US, the urea solution is referred to as DEF. In Europe, it is referred to as “AdBlue”.

In addition to the SCR catalyst system (DOC, SCR, ASC, mixer) and the DPF, the other main components of the system are the urea delivery system, comprising the storage tank (DEF tank) and sensors, the heated delivery line, pump, and

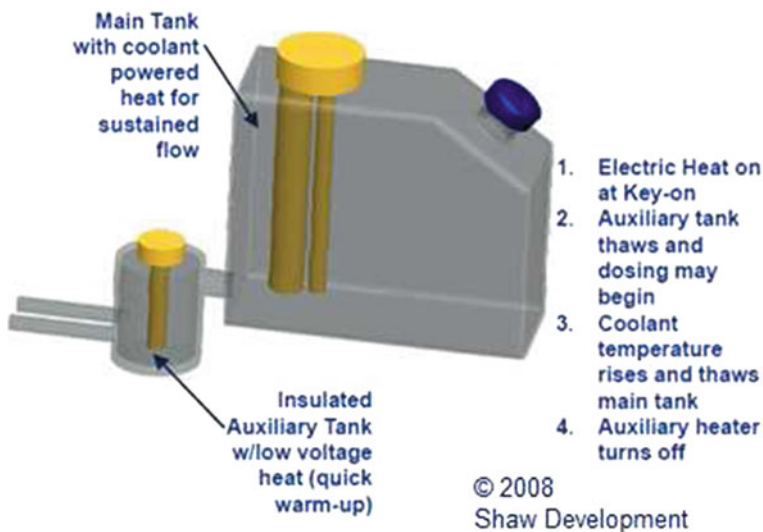


Fig. 1.6 Basic features of the heating system of a urea storage tank [17]

dosing module, including the injector and mixer; and the control system, comprising the sensors, dosing control module, engine control module, and controller area network (CAN) buses.

The following sections will provide more details on these subsystems.

1.4.2 Urea Delivery System

The urea tank, injector, controls, and mixer are significantly engineered systems. Ostertag [17] provides an example of the tank design alone. Figure 1.6 shows the heat-up features and basic designs. Urea is corrosive, so material selection is limited to stainless steel and plastic. Because urea solution (32.5 % urea, balance deionized water) will freeze at $-11\text{ }^{\circ}\text{C}$, the design has to allow for the 7 % expansion upon freezing and for rapid thawing to enable prompt use of the system. Further, internal components like heaters, level and temperature sensors, and fill and extraction lines need to be designed to withstand impact by solids in partially thawed systems. The design shown in Fig. 1.6 has all these components integrated into one unit (in yellow). Finally, and especially for NR applications, the draw point for liquid urea needs to accommodate different vehicle angles of operation.

The urea pump, dosing module, and injectors play a critical role. Designs have migrated from separate pumps and dosing modules to integrated designs [18]; from air-assisted to airless injection; and to systems with no return line. Injectors are designed to disperse fine droplets (20–100 μm mean size) into the exhaust, while minimizing contact with the exhaust pipe to minimize solid by-product formation.