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BOOK REVIEW

Isabella Nova, Enrico Tronconi: Urea-SCR Technology for deNOx Aftertreatment of Diesel Exhausts

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One of the most significant environmental undertakings in recent decades in the US and Europe included crafting the regulations and developing the technologies to mitigate and reduce emissions of nitrogen oxides (NOx) from Diesel engines by more than 90 %. This undertaking required momentous, synergized efforts amongst governments, academic and industry researchers to develop Diesel NOx reduction technologies to meet such landmark reductions.

Written by a collection of international experts amongst Diesel NOx reduction scientists and engineers, and edited by the two of the utmost authorities on the subject matter, this book is a comprehensive collection of intercontinental efforts to develop and apply Selective Catalytic Reduction (SCR) technologies to meet the new vehicular and stationary Diesel NOx emission limit regulations.

It covers a spectrum of topics beyond just the needs of SCR researchers: It also provides plenty of easy-to-digest, well-written, thorough information and insights for anybody seriously active in NOx reduction, including application engineers, catalyst chemists, emission system integrators, regulatory professionals, emission modelers, NOx reduction catalysts and emission system calibration engineers and the like.

The book is divided into eight parts. It first provides a primer on SCR technology, and next follows by covering catalytic aspects of vanadia, iron- and copper-zeolite SCR; metal oxides catalysts and H_2-SCR; mechanistic consideration of SCR for NOx such as discussions on active sites, role of NO, ammonia and O_2 (lean exhaust), transient mechanisms, the significant role of NO_2 in NOx reduction, and plenty of discussions on reaction kinetics in vanadia, iron-, and copper-zeolite SCR including their use in SCR control. Injection of urea (or, more correctly, urea water solution), spray quality, mixing, aftertreatment architecture, ammonia storage and release, N_2O formation, dual-layer ammonia slip catalysts, SCR synergy with NOx Storage Reduction (NSR) including on-board generation of ammonia, and integration of SCR into Diesel Particulate Filters (DPF) are amongst other useful topics discussed. The book ends with a thorough industry case study on integrating SCR technology into vehicle platforms (2010 Ford Diesel trucks). Discussions are enriched, where proper, by 0-D and 1-D SCR kinetics modeling and Computational Fluid Dynamics (CFD) within the context of few chapters; construction and use of a CFD model to identify catalyst configurations and control, and also to perform SCR aftertreatment system optimization is also covered in the end. Each chapter is closed with a summary of its discussions, a conclusion or an outlook.

The eight parts in the book encompass 22 chapters in all. Part 1 presents an overview on SCR technology in on-road and off-road vehicles in the first two chapters. It includes an introduction to the fundamentals of the technology, a primer on engine development activities from a NOx mitigation point of view, and SCR technologies for both light duty (passenger cars and light trucks) and heavy duty Diesel vehicles (large trucks). SCR as a system such as urea delivery (tank, injector, control, mixer, etc.) and the role of the oxidation catalyst and ammonia slip catalyst are also amongst the opening discussions. Chapter 1 ends with an outlook on the regulatory picture and an optimistic prediction for an ever-increasing role of SCR in the control of Diesel NOx in the decades to come. Chapter 2 extends the discussions into a thorough overview of SCR technology for large engines used in off-highway platforms, encompassing related off-road emission regulations, SCR systems for both high-speed engines (small ships, rail, gensets), medium and low speed engines and various aspects of system considerations including the impact of fuel sulfur and packaging aspects. The chapter ends with relevant discussions on SCR control issues and an outlook into further

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proliferation of aftertreatment systems in off-highway applications.

Part 2 is focused on various SCR catalyst technologies, namely vanadia, iron-zeolite and copper-zeolite. Focusing on vanadia SCR, Chapter 3 covers properties, reaction mechanisms, design, catalyst dimensioning, role of NO_2, and catalyst aging, amongst other analyses presented there within. Relative robustness of vanadia SCR to sulfur, oil poisons and hydrocarbons as well as its sensitivity to alkali metals (potassium, calcium, and others), bio-Diesel fuels, and its thermal deactivation due to prolonged exposure to high temperatures are discussed. System considerations such as the role of DOC and NO_2 in promoting fast SCR reactions are amongst the significant discussions included here. Chapter 4 focuses on iron-zeolite SCR catalyst; its beneficial performance at high temperatures, comparison with copper-zeolite, spatial variations of ammonia 'budgeting' (in slip, in reducing NOx, or taking part in secondary reactions) along the catalyst length, and its storage sensitivity to temperature and N_2O formation (hence concerns for GHG formation and regulatory noncompliance). The chapter ends with a worthwhile discussion on durability, aging and deactivation mechanisms in iron-zeolite SCR catalysts.

Part 2 continues with Chapter 5 focusing on copper-zeolite SCR catalysts. Chemistry and functionality of copper-zeolites are discussed, along with a thorough discussion on its deactivation mechanism due to hydrothermal aging, hydrocarbon storage, sulfur, and chemical poisoning such as due to lubricants. The role of urea deposits in reducing catalytic efficiency is also covered, along with closing discussions on small-pore zeolite-supported copper SCR, their superior hydrothermal stability and studies on active sites in copper-chabazite type zeolites. The important topic of low-temperature SCR performance and explorations on use of mixed-metal oxides in this regard is also included. This chapter concludes via a detailed review of H_2-SCR technology, its catalytic and mechanistic aspects and various roles of platinum and palladium within.

Part 3, covering three chapters, reviews mechanistic aspects of SCR technologies. SCR active sites are covered in Chapter 7, encompassing thorough discussions on methods to identify active sites, followed by such topics applied to vanadia- and zeolite-based (both copper and iron) catalysts and a related discussion on the most recent catalyst developments in this regard. Chapter 8 has a primary focus on standard-SCR reactions, discussing also activation energy and reaction order for the commonly-used vanadia, iron and copper SCR, ammonia-NO oxidation and acid site amount and effect of other gases in Diesel exhaust (CO_2, CO, HC, H_2O, SO_2 poisoning) on the said mechanisms in steady state operations; it further expands into transient reaction analysis and reaction mechanisms for all three SCR structures. The beneficial role of NO_2 and hence fast SCR reactions are covered in Chapter 9, articulating NO_2 adsorption and desorption mechanisms, effect of catalyst redox state, surface nitrate mechanisms, role of nitrites (ammonia blocking, redox consideration, high temperature effects and selectivity issues) and finally a discussion on 'enhanced SCR' reactions using nitrates, instead of 'fast SCR' via NO_2, is presented.

Encompassing Chapters 10, 11, and 12, Part 4 exclusively focuses on SCR reaction kinetics. Chapter 10 reviews kinetics of vanadia SCR; it reflects extensive laboratory studies of reactivity, mechanisms, chemistry, catalytic behavior and kinetics of a commercial vanadia SCR. Key topics are covered such as reliable experimental techniques, mathematical expressions for mass balance of species in adsorbed and gas phases, kinetics of ammonia oxidation, and reduction of NO both in the presence of and without NO_2. Following a careful methodology, attention is first given to modeling the adsorption-desorption process of ammonia and its higher-temperature reactions in the sole presence of oxygen; next, NO and finally NO_2 are introduced into the reactions; at each step, the kinetics and rate expressions are revisited and models are upgraded to adequately account for changes in reactions and redox kinetics. Extensive comparisons between experiment and models are included, demonstrating the full model's capability to predict, quite accurately, SCR of NOx under various operating conditions (low and high temperature, flow rates, and species concentration). Chapter 11 shifts the kinetics and mechanism focus to iron-zeolite and layered iron-copper-zeolite SCRs. Various SCR reactions and side reactions are discussed including ammonium nitrate formation, oxidation of ammonia and NO to NO_2, ammonia inhibition, transport properties and rate expressions. SCR of NO with and without NO_2 are presented and model comparison with experiments are demonstrated. Finally, Chapter 12 considers modeling SCR of NOx in copper-zeolite; it includes worthwhile and thorough discussions on the kinetics of ammonia and water storage and ammonia oxidation, both globally and via detailed fundamentals, including NOx storage, NO oxidation and their rate expressions. N_2O formation is also covered and other models in the literature are presented and discussed.

Part 5 encompasses two complimentary chapters. Chapter 13 provides engineering models of SCR performance, relying primarily on global, reduced-step reactions and transport mechanisms, conservation principles and balance equations. Comparison of model prediction and experimental results are presented. The chapter also covers predictive models for SCR-on-DPF, its soot deposition and NOx reduction within. It is well known that NO_2-soot reactions (the so-called passive regeneration of soot) are diminished in SCR-on-DPF, due to stronger reactivity of NO_2 with ammonia, rather than with soot. This is well discussed in the chapter and also within the modeling context. Finally, system modeling challenges such as the role of the oxidation catalyst, DPF thermal inertia, and combined LNT-SCR and SCR-slip catalyst systems are covered. The following chapter in Part 5, Chapter 14, focuses primarily on SCR control and modeling. Zero-dimensional models for SCR control are discussed, taking into account ammonia storage as a function of temperature and using a continuous stirred tank reactor assumption, arriving at SCR dynamic equations in a state-space form. Challenges of model-based control due to catalyst aging are noted. The SCR sensing and system estimation discussion includes NOx sensor cross sensitivity to ammonia, the EKF model and its extension to capture non-linearities. Two observers for ammonia coverage ratio (for real-time urea injection control) and their simulations are shown. Finally, design and architecture of a SCR controller, its architecture, and an experimental set-up to validate the concept and to derive the system constants is shown and discussed.

No SCR system discussion is complete without an adequate analysis of urea delivery and injection systems. Part 6, composed of Chapters 15, 16, and 17, provides a thorough discussion of the on-vehicle Diesel Exhaust Fluid (DEF) delivery system to the SCR catalyst. Chapter 15 includes a summary of an industry attempt that successfully integrated and optimized a complex DEF injection system within the overall SCR architecture to achieve the desired NOx reduction. It covers the five cornerstones of such integration and optimization methodology: Engine calibration, aftertreatment architecture, mixer selection, injector spray quality and dosing calibration. The chapter benefits from discussions on the role of urea droplet size distribution, different mixers and an optimal two-mixer system, injector mounting options, packaging and space considerations, urea deposit formation and deposit mitigation strategies. Chapter 16 is an overview of various types of ammonia precursors; solid urea (and its thermolysis, hydrolysis and by-product formation), cyanuric acid, ammonium formate, ammonium carbamate, metal ammine chlorides, methanamide and guanidinium salts are discussed, along with their pros and cons and plenty of references to literature sources for the curious reader. Chapter 17 includes 1-D models, useful to track temperature evolution of both exhaust pipe wall and gas flow (including the moisture condensation impact during a cold start), thermolysis and hydrolysis of injected urea droplets and modeling of the related kinetics. The chapter then presents 3-D models for a full CFD calculation of droplet injection, heating, evaporation and transport processes, including modeling the liquid film and plenty of CFD calculation examples. While most urea injection systems include a mixer, this has not been considered in the models in this chapter; subsequently, the chapter could benefit from inclusion of a mixer and from integrating its impacts such as on secondary atomization of larger spray droplets and on droplet distribution. Overall, this chapter is light on chemistry (well covered in previous chapters) and heavy on transport processes.

Part 7 of the book expands the scope from SCR and urea delivery and injection components into integrated systems including ammonia slip catalyst, combined NOx Storage Reduction (NSR)-SCR systems and SCR-on-DPF. Discussions are provided on synergized SCR-ammonia slip catalyst in Chapter 18, along with experimental methodologies for their investigation (both powder and monolithic types), modeling, detailed kinetic schemes and rate expressions, kinetic fit, model validation, examples of predictive calculations, and plenty of discussions on the dual-layer slip catalysts, amongst others. Chapter 19 is a detailed discussion on ammonia formation in NOx Storage Reduction catalysts (also known as Lean NOx Trap/LNT) as a potential alternative to urea injection systems for smaller Diesel vehicles, and synergizing this ammonia formation capability with a SCR catalyst for total system NOx reduction. Discussions on ammonia formation pathways in a NSR are provided, along with various coupling concepts of a NOx trap with a copper-zeolite, iron-zeolite or tungsten-based SCR catalyst. The last chapter in Part 7, Chapter 20, focuses on one of the most recent undertakings in Diesel catalyst developments—Integration of SCR onto DPF. It first covers various DPF-related concepts such as materials (cordierite, silicon carbide and aluminum titanate), design (pore size, porosity, permeability, cell density, wall thickness, filtration,), catalyst coating, regeneration, durability and such, and next integrates such concepts within NOx reduction in a SCR-on-DPF. The literature is reviewed first with respect to modeling aspects of SCR-on-DPF and next with respect to development activities pertaining to both light and heavy duty platform use of SCR-on-DPF.

Finally, Part 8, the book's last part, includes a Ford case study as a successful industry undertaking of SCR technology integration within the full powertrain system of an OEM's truck platform, captured in Chapter 21. Early NOx reduction technology comparison amongst HC-SCR, LNT and urea-SCR at Ford research laboratory is shown and the decision pathway to urea-SCR is described, indicating its robust NOx conversion efficiency and its superior fuel economy benefits. System architecture of the Ford truck DOC-SCR-DPF system is discussed, along with DOC and SCR thermal stability and aging considerations, ammonia storage, urea delivery, mixing, specifications and refill issues, HC, precious metal and sulfur poisoning of SCR, as well as historical observations on component evaluations from one formulation to another. Chapter 22, the book's last chapter, is contributed to using a model-based methodology in developing aftertreatment structure as a system. Simulation methods, benchmarks and deliverables, use of the model to predict ammonia injection rate for the urea dosing unit and its control, catalyst configuration optimization and on-board model-based control are amongst some of the topics discussed on how a model could be used for aftertreatment system development and optimization.

1 Concluding Remarks

This book presents a comprehensive overview of the Selective Catalytic Reduction of NOx by ammonia/urea in Diesel exhaust, both from component and system perspectives, and is immensely rich in content: In chemistry and kinetics, formulation, materials, engineering, math expressions, modeling and so on. It includes a reasonable balance of moderate to expert-level discussions. Fundamental research, development, testing protocols, modeling development, use and applications are covered, along with plenty of discussions on SCR catalytic kinetics and such for prevalent SCR catalyst technologies (zeolite- and vanadia-based) including thorough discussions on NO reduction both in the presence of and in absence of NO_2. Testing methodologies are covered and related technologies such as NOx Storage Reduction (NSR) and SCR-on-DPF are discussed and control aspects are included. The urea injection system and its integration within the full NOx reduction system is well covered, as well as ammonia storage models. SCR poisoning, aging and deactivation issues are discussed. Both on- and non-road uses of SCR are presented. Some topics, such as kinetics of SCR or SCR-on-DPF are reviewed by various authors from different points of view, hence providing diversified perspectives. Indeed, there is something useful for everybody in this book.

The book is also rich on modeling aspects of SCR of NOx within various chapters; it would have however benefited from providing a pros and cons discussion of various modeling approaches; at the present, such 'compare and contrast' is practically left to the reader. An extensive number of figures, tables and graphs (more than 400 in all, nearly 300 in color) are included throughout the book, creating a fine balance with its textual dimension. Nearly each chapter is accompanied by an extensive list of referenced citations. In all, more than 1500 citations from academic, industry and other sources have been referenced, covering fundamental research, development, production, performance, modeling and application of SCR of NOx and related topics, attesting to the richness, diversity, spectrum and depth of the collected materials in this book. Given such an extensive list of references, inclusion of a citation index in future editions is highly recommended; it would facilitate locating publications of interest to the curious reader. Chapter 15 would have benefited from a longer, richer list of references.

The book ends with an A-to-Z index of keywords, providing more than 2000-keyword references to various pages to conveniently locate topics of interests within the book. Though this index size may seem adequate, some significant keywords are however missing from the index, despite their presence within the book; there seems to exist room for including a more comprehensive index in future editions.

In conclusion, this book is a must for any library, organization or individual having a primary or even a secondary interest in Diesel NOx emission reduction, heterogeneous catalysis in Diesel emission mitigation or in related aspects such as delivery and injection of urea spray, emissions modeling, experiments and testing methodology, control, component or system considerations, future Diesel NOx mitigation strategies or regulations, calibration, onboard diagnostics and the like. Given the worldwide popularity and proliferation of Diesel engine use and their applications on one hand, and the developing world mostly following the regulatory footprint of emission reduction in the US and Europe on the other, it is fair to predict that this book will play a key role in transfusion of the lessons learned in the US and Europe to the developing countries, and hence in overcoming challenges in Diesel NOx mitigation in other regions around the globe.

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