"Catalytic Air Pollution Control: Commercial Technology", 3rd Edition

By R. M. Heck (RMH Consulting, USA) and R. K. Farrauto (BASF Catalysts, USA) with S. T. Gulati (Consultant to Science and Technology Division, Corning Inc, USA), John Wiley & Sons, Inc, New Jersey, USA, 2009, 522 pages, ISBN: 978-0-470-27503-0, £73.00, €84.60, US$110.00

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Introduction

Thirty-five years ago the use of catalytic systems for controlling tailpipe pollutants from vehicles was virtually non-existent, yet now every new car in the major countries of the world is equipped with one or more emissions control catalysts. Over this time the autocatalyst industry has grown to become a multi-billion dollar worldwide business, and underpinning this success is the extremely high catalytic activity of the platinum group metals (pgms), especially rhodium and palladium as well as platinum itself.

On a vehicle, operating conditions are not smooth and steady as they are on a large single-stream methanol or ammonia plant (1). Low-temperature catalyst activity is vital during 'cold-starts' and very high temperatures (1000°C) can result from occasional engine misfires so very good catalyst thermal durability is a prerequisite. Conditions are highly transient – the gas flow rate changes often and it pulsates as exhaust gas is discharged from each cylinder in turn. The exhaust gas flow can be very high and the corresponding space velocity much higher than in a chemical plant, and there can be detrimental catalyst poisons such as sulfur and phosphorus species in the exhaust gas, as well as continuous physical vibration etc.

The primary pollutants from combustion of petrol, diesel and other hydrocarbon fuels such as liquefied petroleum gas (LPG) and compressed natural gas (CNG) are unburnt or partially oxidised hydrocarbons (HCs) and carbon monoxide (CO). Nitric oxide (NO) is also present, being formed from oxygen and nitrogen combining at the high-temperature flame front during combustion. Once in the air HCs and NO can undergo a series of photochemical reactions that lead to even more noxious secondary oxidising pollutants such as ozone (O_3) and organic compounds like peroxyacetyl nitrate (PAN) that are powerful and

very unpleasant lachrymators. So while cars and other vehicles with internal combustion engines have given society previously undreamt of mobility, they have also contributed to major undesirable environmental consequences (2,3). The approach for solving this problem has been to deal with the primary pollutants at their source and prevent them from entering the environment by catalytically oxidising HCs and CO, and catalytically reducing NO to small amounts of water (H_2O), carbon dioxide (CO_2) and nitrogen (N_2). And in the case of three-way catalysts (TWCs) these three reactions are done simultaneously.

Catalytic Air Pollution Control

Since their introduction the importance of catalytic control technologies has grown, and the first edition of the book "Catalytic Air Pollution Control" by Ronald Heck and Robert Farrauto (then with Engelhard Corporation), published in 1995 as a relatively slim volume with a little more than 200 pages, was a particularly significant contribution (4). Its appearance was timely and it provided a valuable easy-to-read reference for those working in the area of environmental control, and especially the catalytic control of tailpipe emissions from passenger cars. Seven years later there followed an enlarged second edition (5) with almost twice the number of pages. Suresh Gulti, formerly with Corning Incorporated, joined the two original authors and his contributions provided additional coverage of the 'chemical engineering' aspects of conventional flow-through monolithic catalysts, the design and sizing of ceramic diesel particulate filters and other related substrate details. The latest, third edition has 522 pages, and is again an enlargement and update over the previous edition and covers the recent developments.

The Third Edition

The present book is divided into four main sections: the first deals with 'Fundamentals' and is followed by sections entitled 'Mobile Sources', 'Stationary Sources', and 'New and Emerging Technologies'. The 'Fundamentals' section has been expanded to give more detailed background on kinetics of catalytic reactions, characterisation of catalysts and their modes of deactivation. In this section there are chapters on catalyst fundamentals, preparation of the components of monolithic-based catalysts, catalyst characterisation, the chemical engineering of catalysts, including the chemical kinetics of catalytic reactions, heat and mass transfer considerations, and pressure drop characteristics. The last chapter in this section deals with the various modes of catalyst deactivation including: thermally induced modes such as sintering; poisoning by, for example, sulfur species and lubrication additives such as calcium, zinc and phosphorus; and washcoat loss. Importantly it also covers the diagnostics used to identify the mode of deactivation in practical situations.

The second section deals with 'Mobile Sources' and forms the heart of the book, with some 270 pages and more than 500 cited references concerned with automotive catalysts and the substrates used to produce them (see Figure 1). The introduction of emissions control catalysts on cars is classified chronologically into different generations, and the most important

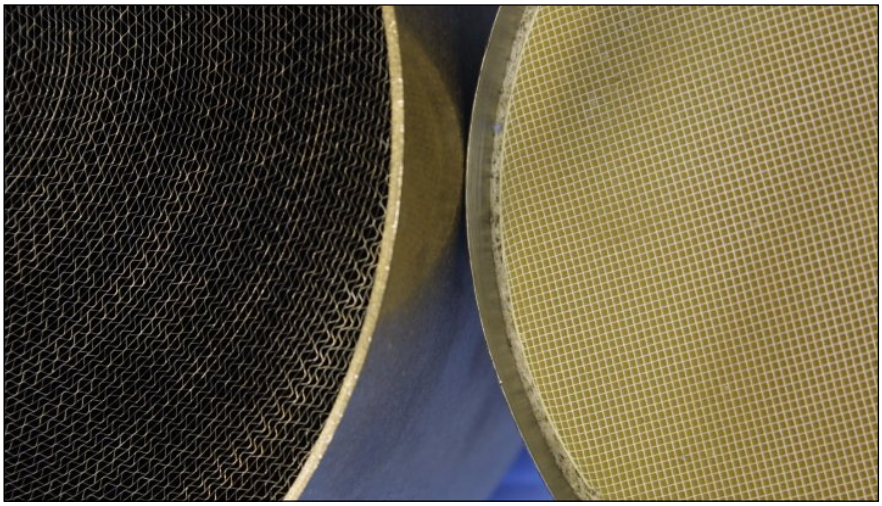

Fig. 1. Metal foil-based substrates (left) as well as extruded cordierite substrates (right) are used to manufacture three-way catalysts for gasoline engines and oxidation catalysts for diesel engines. NOx-trapping and selective catalytic reduction catalyst formulations for lean-NOx control are also coated onto flow-through substrates

areas of TWCs for controlling emissions from stoichiometric gasoline engines and oxidation catalysts and particulate filters for diesel engines (see Figure 2) are well covered. The control of NOx emissions under the lean conditions of a diesel engine is not straightforward and the technologies being implemented are NOx-trapping with a basic catalyst component such as an alkaline earth with periodic exhaust gas enrichments to convert stored nitrate to nitrogen, and selective catalytic reduction (SCR) with ammonia derived from an aqueous urea solution. Both approaches are now in series production. Some of the legislative emissions requirements are touched on in this chapter, and details of the test cycles used in different regions of the world are provided. However, the focus is mainly on chemical and catalytic technical aspects such as the stabilisation of alumina surface area, and details of engine-based cycles used to accelerate the ageing of catalysts during development work – an aspect that often has slight attention paid to it in academic studies, but is vital when developing practical catalysts that have to maintain high performance over 120,000 (or more) miles of use! Another technology that is often overlooked is the retaining of ceramic monolithic catalyst in a stainless steel can – here it is covered in considerable detail.The section concludes with a relatively short (17 pages) chapter on the catalytic decomposition of ozone in high-flying aircraft.

The next section deals with the control of pollutants from 'Stationary Sources', and is a third of the size of the previous one on mobile sources. It has four chapters concerned with 'Volatile Organic Compounds' (VOCs), 'Reduction of NOx', 'Carbon Monoxide and Hydrocarbon Abatement from Gas Turbines' and 'Small Engines'. The first chapter here includes emissions from sources such as catalytic incineration and wood burning stoves. Interestingly this is one of the few areas where deactivated catalysts are regenerated routinely. With modern pgm-based VOC oxidation catalysts sintering is not a problem and deactivation usually takes place through fouling or masking of the surface by material present in the flue gas. The most commonly used regeneration technique is to chemically wash the catalyst to dissolve the offending material without disrupting the structure of the underlying catalyst. Treatments often make use of mild acids and chelating agents, and if properly done catalyst lives may be extended to between five and ten years. However, in general the overall economics of catalyst regeneration mean that in some situations it might be more appropriate to replace old catalyst with new, depending on the time it takes to carry

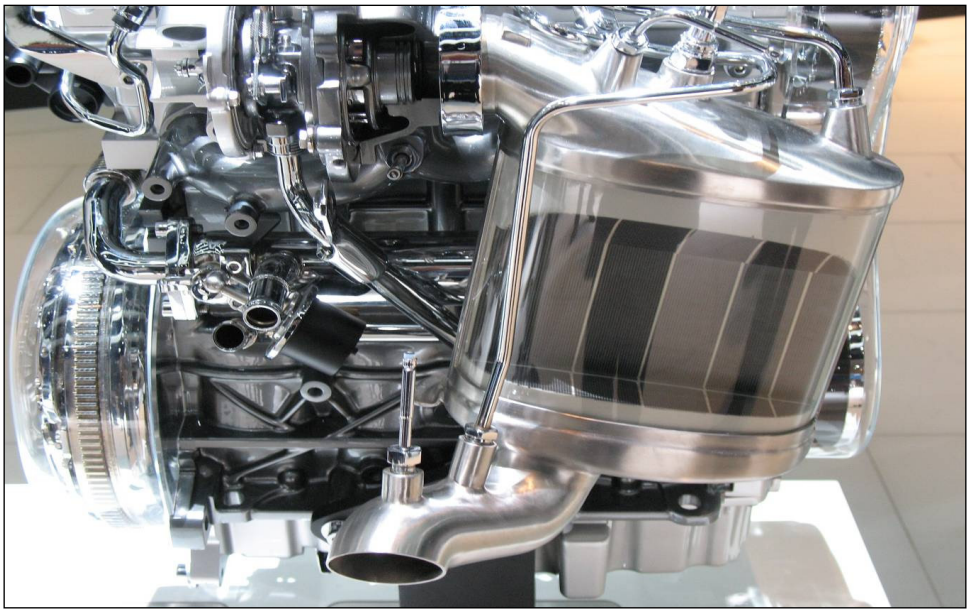

Fig. 2. Cutaway view of a catalysed soot filter (CSF) mounted directly on the turbocharger of a passenger car diesel engine. This cost-effective technology efficiently controls hydrocarbon, carbon monoxide and particulate emissions into the environment (Image copyright Martyn V. Twigg)

out the regeneration procedure and the economic penalty of not having the catalyst operating.

The final section on 'New and Emerging Technologies' is relatively small (49 pages) and includes on-vehicle ambient ozone decomposition by catalytic coatings on radiators. At first a platinum catalyst was suggested and later a particular form of manganese dioxide containing the complex anion called cryptomelane, $(Mn(IV)_6Mn(II)_2O_{16})^-$, which is more cost effective than platinum, went into series production on some cars. However, this technology has not been as widely adopted as was thought would be the case. A larger chapter then considers fuel cells and the generation of on-board hydrogen for mobile applications such as fuel cells. First, types of fuel cells are discussed, and the authors concentrate on the low-temperature proton exchange membrane (PEM) fuel cells that use pgms as electrocatalysts. Then routes to hydrogen are detailed. In the chemical industry this is done *via* steam reforming of hydrocarbons, especially natural gas, to form a mixture of hydrogen and carbon oxides (mainly CO) called synthesis gas, or syngas, that is used in large single-stream plants to manufacture ammonia and methanol (1). For mobile on-vehicle use methanol is a very convenient 'fuel' for hydrogen production *via* low-temperature steam reforming over copper-based catalysts (6). It will be interesting to see if these electrically-based power systems will have sufficient advantages to replace the highly refined ultra low emission internal combustion engines in the future.

Commercial Catalytic Systems

This book is unlike most textbooks on catalysis. The authors are industrial researchers who have been deeply involved in the development and application of innovative commercial catalytic emissions control systems for vehicles. They were responsible for many successful innovations that have benefited society, and in some ways their book gives a hint of the excitement of doing this. Throughout the book the emphasis is on the applied aspects and what is actually done industrially. Catalytic systems are included for both stationary and mobile sources and because the authors are from industry the topics are considered from a very practical point of view that is not found in standard textbooks. However, there are questions at the end of each chapter, rather in the form of a college textbook, and these would be of value to instructors using the book for specialist graduate courses. The cited references are collected together at the end of each chapter, and since there is no author index, tracking the work of a particular research group in different areas can be difficult. However, the titles of papers referred to are provided and this is helpful in identifying papers a reader might wish to pursue further. There is a subject index that usefully could be more exhaustive; it occupies only five pages.

Concluding Remarks

Overall this is a very good book that provides real technical insight into an important area of catalysis. Although there are occasionally some inaccuracies, for instance the mechanism of filtration with diesel particulate filters, this book will be of benefit to those working in the immediate area of catalytic pollution control, as well as those concerned with broader aspects of environmental chemistry both at the professional and student levels. Librarians are encouraged to ensure this volume is on their shelves.

References

1 "Catalyst Handbook", 2nd Edn., ed. M. V. Twigg, Manson Publishing, London, UK, 1996

2 "Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications", B. J. Finlayson-Pitts and J. N. Pitts, Jr., Academic Press, San Diego, USA, 2000

3 "Chemistry of Atmospheres", 3rd Edn., R. P. Wayne, Oxford University Press, Oxford, UK, 2000

4 "Catalytic Air Pollution Control: Commercial Technology", R. M. Heck and R. J. Farrauto, Van Nostrand Reinhold, New York, USA, 1995

5 "Catalytic Air Pollution Control: Commercial Technology", 2nd Edn., R. M. Heck and R. J. Farrauto with S. T. Gulati, John Wiley & Sons, New York, USA, 2002

6 M. V. Twigg and M. S. Spencer, *Top. Catal.*, 2003, **22**, (3–4), 191

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