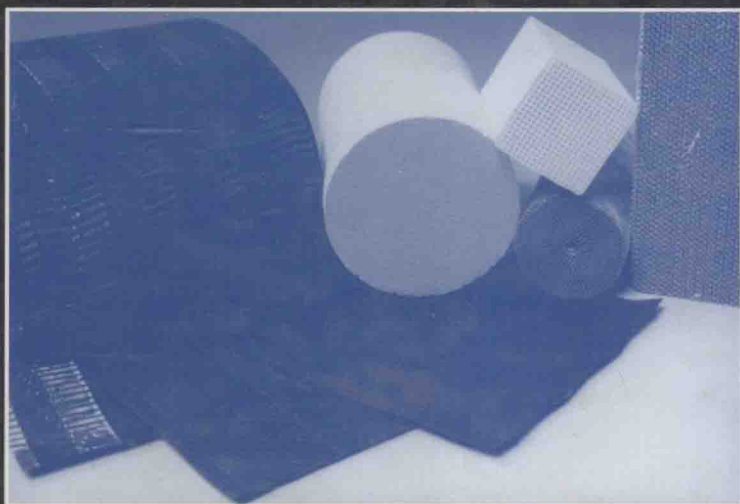# STRUCTURED CATALYSTS AND REACTORS

edited by
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STRUCTURED CATALYSTS AND REACTORS

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Preface

Heterogeneous catalytic processes are among the main ways to decrease the consumption of raw materials in chemical industries and to decrease the emission of pollutants of all kinds to the environment via an increase in process selectivity. Selectivity can be improved by the modification of catalyst composition and surface structure and/or by the modification of pellet dimensions, shape, and texture, i.e., pore size distribution, pore shape, length, and cross-sectional surface area (distribution). Until recently, the limiting factor in the latter modifications has been the particles' size, to which the length of diffusion in pores is related. The size should not be too small because of the significantly higher pressure drop for such small particles. Shell catalysts, which contain catalytic species concentrated near the outer particle's surface, are a remedy for improving selectivity, keeping pressure drop at a reasonable level. Pressure drop can be the limiting factor even for such catalysts, e.g., when large quantities of raw materials must be processed or when the higher pressure drop results in the significantly higher consumption of raw materials. For instance, converting huge amounts of natural gas in remote areas would require equipment characterized by low pressure drop. Otherwise the cost of processing would be too high to make the process economical. Too high a pressure drop in catalytic car mufflers would result in an increase in fuel consumption by several percent. This would mean a several-percent-higher consumption of crude oil for transportation. An inherent feature of conventional packed-bed reactors is their random and structural maldistributions. A structural maldistribution in fixed-bed reactors originates from the looser packing of particles near the reactor walls. This results in a tendency to bypass the core of the bed, even if the initial distribution of fluid(s) is uniform. The uniformly distributed liquid tends to flow to the walls, and this can drastically alter its residence time from the design value. Random maldistributions result in: (1) a nonuniform access of reactants to the catalytic surface, worsening the overall process performance, and (2) unexpected hot spots and thermal runaways of exothermic reactions (mainly in three-phase reactions).

Structured catalysts (reactors) are promising as far as the elimination of these drawbacks of fixed beds is concerned. Three basic kinds of structured catalysts can be distinguished:

1. *Monolithic catalysts (honeycomb catalysts),* in the form of continuous unitary structures that contain small passages. The catalytically active material is present on or inside the walls of these passages. In the former case, a ceramic or metallic support is coated with a layer of material in which active ingredients are dispersed.

2. *Membrane catalysts* are structures with permeable walls between passages. The membrane walls exhibit selectivity in transport rates for the various components present. A slow radial mass transport can occur, driven by diffusion or solution/diffusion mechanisms in the permeable walls.

3. *Arranged catalysts.* Particulate catalysts arranged in *arrays* belong to this class of structured catalysts. Another group of arranged catalysts are *structural catalysts*, derived from structural packings for distillation and absorption columns and static mixers. These are structures consisting of superimposed sheets, possibly corrugated before stacking. The sheets are covered by an appropriate catalyst support in which active ingredients are incorporated. The structure is an open cross-flow structure characterized by intensive radial mixing.

Usually, structured catalysts are structures of large void fraction ranging from 0.7 to more than 0.9, compared to 0.5 in fixed beds. The path the fluids follow in structured reactors is much less twisty (e.g., straight channels in monoliths) than that in conventional reactors. Finally, structured reactors are operated in a different hydrodynamic regime. For single-phase flow the regime is laminar, and the eddies characteristic of packed beds are absent. For multiphase systems various regimes exist, but here also the eddies typical of packed beds are absent. For these reasons, the pressure drop in structured catalysts must be significantly lower than that for the randomly packed bed of particles. Indeed, pressure drop in monolithic reactors is up to two orders of magnitude lower than that in packed-bed reactors.

Catalytic species are incorporated either into a very thin layer of a porous catalytic support deposited on the structured elements or into the thin elements themselves. The short diffusion distance inside the thin layer of the structured catalysts results in higher catalyst utilization and can contribute to an improvement of selectivity for processes controlled by mass transfer within the catalytic layer. Contrary to conventional fixed-bed reactors, the thickness of the catalytic layer in monolithic reactors can be significantly reduced with no penalty paid for the increase in pressure drop. Membrane catalysts provide a unique opportunity to supply reactants to the reaction mixture gradually along the reaction route or to withdraw products from the reaction mixture as they are formed. The former mode of carrying out complex reactions might be very effective in controlling undesired reactions whose rates are strongly dependent on the concentration of the added reactant. The latter mode might result in higher conversions for reversible reactions which are damped by products. The use of catalytic membranes operated in any of these modes can also contribute to significant improvement in selectivity.

The regular structure of the arranged catalysts prevents the formation of the random maldistributions characteristic of beds of randomly packed particles. This reduces the probability of the occurrence of hot spots resulting from flow maldistributions. Scale-up of monolithic and membrane reactors can be expected to be straightforward, since the conditions within the individual channels are scale invariant.

Finally, structured catalysts and reactors constitute a significant contribution to the search for better catalytic processes via improving mass transfer in the catalytic layer and thus improving activity and selectivity (also using membrane catalysts), decreasing operation costs through lowering pressure drop, and eliminating maldistributions.

Structured catalysts, mainly monolithic ones, are now used predominantly in environmental applications, first of all in the cleaning of automotive exhaust gases. Monolithic reactors have become the most commonly used sort of chemical reactors: several hundred

million small monolithic reactors are moving with our cars! Monolithic cleaners of flue gases are now a standard unit. Monolithic catalysts are also close to commercialization in the combustion of fuels for gas turbines, boilers, heaters, etc. The catalytic combustion reduces NO_x formation, and the use of low-pressure-drop catalysts makes the process more economical. Some special features of monolithic catalysts make the burning of LHV fuels in monolithic units much easier than in particulate catalysts. There are some characteristics that make structured catalysts also of interest for three-phase reactions. Several three-phase processes are in the development stage. One, the hydrogenation step in the production of H_2O_2 using the alkylanthraquinone process, has already reached full scale, with several plants in operation.

Interest in structured catalysts is steadily rising due to the already proven, and potential, advantages of the catalysts. Some review articles regarding different aspects of structured catalysts have been published in the last decade [see A. Cybulski and J. A. Moulijn, *Catal. Rev.-Sci. Eng. 36*(1):179–270 (1994); H. P. Hsieh, *Catal. Rev.-Sci. Eng. 33*(1&2):1–70 (1991); S. Irandoust and B. Andersson, *Catal. Rev.-Sci. Eng. 30*(3):341–392 (1988); L. D. Pfefferle and W. C. Pfefferle, *Catal. Rev.-Sci. Eng. 29*(2–3):219–267 (1987); and G. Saracco and V. Specchia, *Catal. Rev.-Sci. Eng. 36*(1):305–384 (1994)]. These articles do not cover the whole area of structured catalysts and reactors. Moreover, the science and applications of structured catalysts and reactors are developing very fast. The time has come to devote an entire book to structured catalysts and reactors. In this compilation an attempt is made to give detailed information on all structures known to date and on all aspects of structured catalysts and reactors containing them: catalyst preparation and characterization, catalysts and process development, modeling and optimization, and finally reactor design and operation. As such, the book is dedicated to all readers who are involved in the development of catalytic processes, from R&D to process engineering. A very important area of structuring in catalysis is that directed at a catalytic surface, microstructure, and structuring the shapes and size of the catalytic bodies. This area is essentially covered by publications concerning more fundamental approaches to heterogeneous catalysis. A lot of the relevant information is scale independent and, as a consequence, is not unique to structured catalytic reactors. Therefore these activities are described only briefly in the book.

The book starts with an overview on structured catalysts (Chapter 1). The rest of the book is divided into four parts. The first three parts deal with structures differing from each other significantly in conditions for mass transfer in the reaction zone. The fourth part is dedicated to catalyst design and preparation.

Part I deals with monolithic catalysts. Chapters 2 and 3 deal with configurations, microstructure, physical properties, and the manufacture of ceramic and metallic monoliths. Monolithic catalysts for cleaning the exhaust gas from gasoline-fed engines are dealt with in Chapter 4, including fundamentals and exploitation experience. Chapter 5 is devoted to commercial and developmental catalysts for protecting the environment. Fundamentals and applications of monoliths for selective catalytic reduction are given. Unconventional reactors used in this field (reverse-flow reactors, rotating monoliths) are also discussed. Materials, activity, and stability of catalysts for catalytic combustion and practical aspects of applications of monolithic catalysts in this area are discussed in Chapter 6. The use of monolithic catalysts for noncombustion and nonenvironmental purposes is discussed in Chapter 7. Chapter 8 is devoted to the modeling of monolithic catalysts for two-phase processes (gaseous reactants/solid catalyst). Chapters 9–11 deal with three-phase monolithic processes. Both catalytic and engineering aspects of these processes are discussed.

Arranged catalysts allowing for convective mass transfer over the cross section of the reactor are discussed in Part II. Conventional particulate catalysts arranged in arrays are dealt with in Chapters 12 and 13. Current and potential applications of ordered structures of different kinds (parallel-passage and lateral-flow reactors, bead-string reactor) are mentioned. Chapter 14 is devoted to structural catalysts derived from static mixers and column packings, typified by low pressure drop. Configurations, methods of incorporation of catalytically active components into the structure, commercial and developmental catalysts, flow characteristics, mixing, mass and heat transfer, current and potential applications in two- and three-phase processes, reactor configurations, and design procedures are discussed. Chapter 15 deals with catalytic filters in general.

Part III of the book provides information about the structured catalysts of monolithic type with permeable walls, i.e., catalytically active membranes. Catalytic membranes create a unique opportunity to couple processes opposite in character (e.g., hydrogenation/dehydrogenation, endothermic/exothermic) via the combination of reaction and separation. Catalytic membranes can allow for the easy control of reactant addition or product withdrawal along the reaction route. Chapter 16 deals with membrane reactors with metallic walls permeable to some gases. The properties of metallic membranes, permeation mechanisms in metallic membranes, the preparation of membranes, commercial membranes, modeling and design, engineering and operating considerations, and finally current and potential applications of metallic membranes are discussed. Chapter 17 presents inorganic membrane reactors—materials, membrane microstructures, commercial membranes, cross-flow reactors, modeling and design, engineering and operating issues, current and potential applications. Chapter 18 is dedicated to the special sort of catalytic filters used for cleaning exhausts from diesel engines. Recent developments in the field of advanced membranes, in the form of zeolitic membranes, are discussed in Chapter 19. Cross-flow reactors are the subject of Chapter 20.

The last part of the book (Part IV) discusses techniques for incorporating catalytic species into the structured catalytic support (Chapter 21) and the computer-aided design of catalysts aiming at an optimal porous structure for the catalytic support (Chapter 22).

The amount of detail in this book varies, depending on whether the catalyst/reactor is in the developmental stage or has been commercialized. The know-how gained in process development has commercial value, and this usually inhibits the presentation of the details of the process/reactor/catalyst. Consequently, well-established processes/reactors/catalysts are described more generally. Projects at an earlier stage presented in this book are being developed at universities, which usually reveal more details. Each chapter was designed as a whole that can be read without reference to the others. Therefore repetitions and overlapping between the chapters of this book are unavoidable.

The authors of individual chapters are top specialists in their areas. They comprise an international group of scientists and practitioners (Great Britain, Italy, The Netherlands, Poland, Russia, Sweden, Switzerland, and the U.S.A.) from universities and companies that are advanced in the technology of structured catalysts. The editors express their gratitude to all of the contributors for sharing their experience. The editors also appreciate the administrative assistance of Mrs. Qwen Klis and the help of Ms. Annelies van Diepen in the preparation of the subject index.

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Contents

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The Present and the Future of Structured Catalysts—An Overview

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I. INTRODUCTION

Conventional fixed-bed catalytic reactors have some obvious disadvantages, such as mal-distributions of various kinds (resulting in nonuniform access of reactants to the catalytic surface and nonoptimal local process conditions), high pressure drop in the bed, and sensitivity to fouling by dust. The search for means allowing for elimination of these setbacks has lead researchers to *structured catalysts*. Three basic kinds of structured catalysts can be distinguished:

1. *Monolithic catalysts.* These are continuous unitary structures containing many narrow, parallel straight or zigzag passages. Catalytically active ingredients are dispersed uniformly over the whole porous ceramic monolithic structure (so-called *incorporated monolithic catalysts*) or are in a layer of porous material that is deposited on the walls of channels in the monolith's structure (*washcoated monolithic catalysts*). The name *monolith* stems from Greek and means "composed of a single rock." However, the material of construction is not limited to ceramics but commonly includes metals, as well. Although not fully correct, we speak of ceramic and metallic monoliths. Initially, the cross section of channels in monoliths was like a *honeycomb structure*, and this name is still in common use.

2. *Membrane catalysts.* An interaction between the passages in the monolith can occur if the walls are permeable. Such catalysts are called *wall-through monolithic catalysts* or *membrane catalysts*. The catalytically active material is present on or inside the walls of these passages. Radial mass transport occurs by diffusion through the pores of the permeable walls. Consequently, mass fluxes through the walls are often rather small.

3. *Arranged catalysts.* Structured catalysts that allow for a relatively fast mass transport over the reaction zone in the direction perpendicular to flow are classified here as arranged catalysts. Particulate catalysts arranged in arrays belong to this class. Any other nonparticulate catalysts, such as packings covered with catalytically active material, similar in design to those used in distillation and absorption columns and/or static mixers, are also classified into this group.

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Table 1   Classification of Structured Catalysts

1. Design
    1.1 Monolithic catalysts; single-passage flow monoliths
    1.2 Membrane catalysts; wall-through catalysts
    1.3 Arrange catalysts
2. Support material
    2.1 Ceramics
    2.2 Metal
3. Mixing conditions
    3.1 A very limited radial mixing inside the channel and no mass exchange between individual channels with resulting zero mixing over the reactor (monolithic catalysts)
    3.2 An intense radial mixing over the cross section of the reactor (arranged catalysts)
    3.2 A very limited radial mixing inside the channel with a limited mass transfer between adjacent passages; a very limited radial mixing over the reactor (membrane catalysts)
4. Mode of operation
    4.1 Steady state (e.g., treatment of industrial off-gases)
    4.2 Nonstationary processes
       • periodic changes (e.g., catalytic mufflers, reverse-flow converters, rotating monoliths)
       • oscillations (e.g., Taylor flow of gas/liquid mixtures through channels)

It is clear from this classification scheme that by *structured catalysts* we mean regular structures free of randomness at a reactor's level, which is characteristic for a randomly packed bed of particles of various shapes. These structures are spatially arranged in a reactor. Structures at or below the level of particles (micropores in zeolites, macropores in MCM-41, or shaped pellets such as lobes, miniliths, and the like) are not dealt with in this book, since randomness of packing will always result in the lack of a uniform structure at the level of a reactor.

The most characteristic features of structured catalysts are given in Table 1. The main difference between the three types of structured catalysts we have just distinguished consists in the rates of radial mixing in the reactor containing the structured catalyst: from zero radial mass transfer in monolithic reactors to a very intense radial mass transfer in reactors with structural catalysts. For the sake of simplicity, reactors containing monolithic or membrane catalysts will be referred to as monolithic or membrane reactors, respectively.

II. MONOLITHIC CATALYSTS

The essence of monolithic catalysts is the very thin layers, in which internal diffusion resistance is small. As such, monolithic catalysts create a possibility to control the selectivity of many complex reactions. Pressure drop in straight, narrow channels through which reactants move in the laminar regime is smaller by two or three orders of magnitude than in conventional fixed-bed reactors. Provided that feed distribution is optimal, flow conditions are practically the same across a monolith due to the very high reproducibility of size and surface characteristics of individual monolith passages. This reduces the probability of occurrence of hot spots resulting from maldistributions characteristic of randomly packed catalyst beds.

Comprehensive reviews on catalytic combustion, including the use of monoliths for automotive converters, have been published in the last decades [1–5]. Reviews on mono-

liths including also nonenvironmental and noncombustion applications of monoliths were also published [6–8]. The steadily increasing interest in monolithic catalysts is reflected in the literature. This is illustrated by the results of the computer literature search in *Chemical Abstracts* (see Table 2). The first world conference on monolithic catalysts was organized in 1995 in St. Petersburg, Russia. As is usually the case in new developments, monolithic catalysts are covered by patents. This, along with the rather costly way of manufacturing them, has contributed to a relatively high price for monolithic catalysts (two to three times more expensive than particulate catalysts). However, the first patents are now close to expiration. Moreover, many ceramic and metallic supports can be manufactured in bulk, and this reduces their price, thereby increasing their accessibility for many applications. Therefore we expect that much cheaper monolithic catalysts will soon become available, not only in combustion processes that are stimulated by legislation but also for a number of typical chemical processes, just because of the technical and economic advantages of monolithic processes.

Monolithic catalysts have found many applications in combustion and environmental uses, e.g., as afterburners of engine exhausts and for removal of harmful compounds from industrial off-gases. The first important industrial applications of monolithic catalysts were for decolorization of nitric acid tail gas and for car exhaust emission control. Beginning in the late 1960s, investigations on monoliths were expanded by car manufacturers and the industries responsible for emissions of considerable amounts of gaseous air pollutants. The main reason for focusing research on monoliths was their low pressure drop. Through the Clean Air Act, legislators of California stimulated a search for effective afterburner catalysts that would not produce high pressure drop. Conventional particulate catalysts were sufficiently active in the removal of carbon monoxide, unburned hydrocarbons (UHC), and nitrogen oxides (NO_x). However, high pressure drop in catalytic mufflers filled with particulate catalysts resulted in a several percent increase in fuel consumption. The low pressure drop in monoliths was also important for off-gas cleaners. Usually there is an insufficient surplus of pressure before the stack to allow the installation of devices producing high pressure drop. Developments in the production of both ceramic and metallic monolithic supports resulted in an industrial production of monolithic catalysts of long lifetime that met the high requirements of units for efficient oxidizing of CO and UHC. By 1975 the first cars equipped with catalytic converters became available. In 1985 approximately 100 million catalytic mufflers were in use in the United States. Now several hundred million converters are in everyday operation, mostly in the United States and Europe.

Table 2 Results of Computer Search for Publications on Monolithic/Honeycomb Structures

Period	Number of publications	
	Patents and patent applications	Nonpatent papers
1967–1970	5	14
1971–1975	57	79
1976–1980	149	150
1981–1985	208	166
1986–1990	731	234
1991–1995	1035	507

A catalyst in the catalytic converter for engine exhaust treatment is subject to significant and frequent changes in flow rate, gas composition, and temperature. Ceramic refractory materials known in the late '60s were characterized by a rather high thermal expansion coefficient. Those materials could easily crack and rupture during frequent and large temperature changes. The lifetime of monolithic catalysts based on such materials would be impractically short. A breakthrough in the technology of monolithic catalysts for catalytic mufflers was that by Corning, Inc., who had developed monoliths made from cordierite. Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) appeared to have an almost zero thermal expansion coefficient, and this made it essentially insensitive to temperature changes. Together with an advanced extrusion technology for the monoliths' manufacture, this guaranteed Corning commercial success in the field of ceramic supports for catalytic mufflers. Monoliths made from other ceramic materials needed for other applications have been developed and became commercially available, e.g., mullite, titania, zirconia, silicon nitride, silicon carbide, and the like, all of them doped with other compounds if necessary. Manufacturers of ceramic monoliths can provide blocks of large size. Moreover the blocks can be stacked side by side and/or on top of one another to form a structure with the dimensions demanded. Monoliths with channels of ca. 1×1 mm are in predominant use with car converters. Monoliths with larger channels, up to 6×6 mm, are used if dusty gases are to be processed. Cordierite monoliths are discussed in more detail in Chapter 2 of this book.

The catalyst in automotive converters is inactive until it is warmed up to a certain temperature. During this period carbonaceous matter is deposited on active sites of the catalyst, decreasing its activity. Deactivation of this sort is reversible: The deposit is quickly burned off after the temperature reaches the level at which the catalyst becomes active in combustion processes. The warm-up period is on the order of a few minutes and depends on the thermal capacity of the catalyst. Up to 75% of air pollutants are emitted during the warm-up period. The lower the thermal capacity, the shorter the warm-up period becomes and, as a consequence, the lower is the emission of pollutants. This stimulated the tendency to decrease the mass of the monolith by lowering the thickness of the walls between adjacent channels. Modern cordierte monoliths have walls down to 150 μm thick. A further considerable decrease of wall thickness in ceramic monoliths is doubtful. Metallic monoliths are more promising in this respect. These monoliths are produced from sheets down to 40 μm thick, 50 μm being now the standard. The warm-up period for metallic catalysts has been shortened to several tens of seconds. The heat transfer characteristics of metallic monoliths is claimed to be superior to that of ceramic monoliths. It is comparable with that in packed-bed reactors. This creates a possibility to use metallic monoliths when a thorough control over temperature in tubular reactors is needed. Metallic monoliths are described in Chapter 3 of this book.

In general, both cordierite and metallic monoliths are unsuitable as catalytic supports. To process a monolith into an active monolithic catalyst, a layer of porous catalytic support must be deposited on the walls between channels. γ-Alumina appeared to be the most effective support for automotive catalysts. The alumina layer is deposited by sol-gel technique (so called *washcoating*). Adherence of γ-alumina to cordierite is relatively strong. However, to form the stable γ-alumina layer on a metallic surface, we need to use an appropriate alloy that is appropriately processed before the layer is deposited. Stainless steel containing chromium, aluminum, and yttrium subjected to thermal treatment under oxidizing conditions meets requirements of automotive converters. Aluminum in the steel is oxidized to form γ-alumina needles (*whiskers*) protruding above the metal

surface. Whiskers make adhesion of the γ-alumina deposited on such a surface sufficiently strong. The increasingly stringent regulation of emissions to the air made only noble metals suitable for the preparation of automotive catalysts. Platinum with an admixture of rhodium is now a standard catalytic species. Noble metals can be incorporated into the layer of γ-alumina by conventional methods known to those skilled in the art.

Low pressure drop, one of the greatest advantages of monoliths, is also one of the major drawbacks. Contrary to packed beds, monoliths do not damp nonuniformity of flow, which usually appears at the inlet due to the large changes in the diameters of inlet pipe and of the reactor. This nonuniformity is propagated throughout the reactor zone. Therefore, properly designed deflectors must be installed to equalize flow over the cross section before exhausts enter the monolith. To shorten the warm-up period, electrically heated monoliths are being implemented. Presently installed catalytic converters are active for more than 100,000 km. The manufacture and operational characteristics of automotive catalysts for gasoline engines are discussed in Chapter 4 of this book. More general aspects of the manufacture of monolithic catalysts for applications of all types are presented in Chapter 21. The computer-aided design of catalysts, including monolithic catalysts, is the subject of Chapter 22.

Another important environmental problem is the air pollution from stationary sources, such as the industrial plants of power plants. Flue gases from chemical plants contain organic pollutants that must be removed or destroyed. The polluting components of the gases are mainly hydrocarbons, carbon monoxide, sulfur dioxide, and nitrogen oxides. Catalytic oxidation is then a method expected to be efficient, and indeed is a well-established technique in this field. Again, monoliths, with their low pressure drop and a high resistance to plugging, have been found to be a very effective tool in the cleaning of such gases. Monolithic catalysts have been used to incinerate organic components and carbon monoxide in industrial off-gases from various plants, such as phenol plants, paper mills, phthalic and maleic anhydride plants, ethylene oxide plants, synthetic fiber plants, vegetable oil processing plants, and catalytic cracking reactors. Catalysts used for gas incinerations are essentially the same as those for afterburners. When bigger catalyst blocks are needed, individual monoliths are packed in a frame and a number of frames can be stacked together in a block.

Off-gases from power stations, steam generators, etc., where fuels are burned noncatalytically at very high temperatures, contain a lot of nitrogen oxides. NO_x removal is becoming more and more acute because of stricter regulations. Dutch regulations allow emissions of 75 and 60 ppm NO_x for furnaces operated on liquid and gaseous fuel, respectively. The southern Californian limit for gas turbines was cut to 9 ppm NO_x in 1993. Fuels, especially coal, also contain significant amounts of sulfur compounds which are converted to sulfur dioxide in the furnace.

It is important that subsequent oxidation to SO_3 not take place because of the formation of aerosols, which increases particulate emissions. Therefore the preferred mode of operation of selective catalytic reduction (SCR) of NO_x is such that SO_2 remains unoxidized. The gases cleaned in such a way need not be subject to troublesome treatment before they are emitted to atmosphere.

Monoliths of low cell densities (with openings ranging from 3 to 6 mm) are applied for deNOxification of gases at coal-fired power plants. This is due to the high content of dust in the gases. If dust particles were retained in the monolith, the pressure drop would increase greatly. Because of the abrasive action of the dust particles, incorporated-type catalysts are preferred. Often, WO_3 and V_2O_5 are incorporated into TiO_2 in the anatase