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Application of the monoliths in DeNO$_x$ catalysis

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Abstract

Air pollution abatement catalysis refers to catalytic technologies and processes for reducing emissions of environmentally unacceptable compounds. Major problems related to these catalytic clean-up technologies are mobile emission control, removal of nitrogen oxides (NO$_x$), sulphur compounds, volatile organic compounds (VOCs) and other pollutants generated by industry or by other stationary sources. Application of the monolith catalysts and/or reactors is a key solution to these problems. This overview describes basic features of the monolithic structures and discusses their development and application prospects focusing on DeNO$_x$ catalysis. The status and ongoing modeling of the monolithic reactors are outlined. Particular emphasis is put on experimental validation and practical applications of the mathematical models of a monolithic reactor.

Keywords: Air pollution; DeNO$_x$ catalysis; Monolith catalysts; Volatile organic compounds

1. Introduction

Monoliths belong to a new family of the so-called structured catalysts and/or reactors (the border between "catalyst" and "reactor" vanishes in these reaction systems) [1–3]. A monolith structure is sometimes referred to as a honeycomb structure [2], although in the technical context monolith has a much broader meaning, generally referred to as the large uniform block of a single building material. In heterogeneous catalysis it is applied mostly as a support of a catalytically active component or as a catalyst if a catalytic component is the integral part of the monolith structure. Monolith structures play important role in the integrated approach to environmental protection, which, among other, includes integration of various process operations such as chemical reaction, separation and heat exchange. The results of the process integration are reduced investment costs often associated with significant energy recovery and space saving [4]. According to some authors, monolithic catalysts and/or reactors appear to be one of the most significant and promising developments in the field of heterogeneous catalysis and chemical engineering of recent years.

1.1. Basic features of the monoliths

A monolithic catalyst has a honeycomb structure with long, parallel and usually straight channels or cells through which the gas flows. The channels' wall can be coated with a high surface area washcoat (e.g. γ-Al_2O_3 and other common metal oxides) that contains dispersed catalyst(s) [5]. Schematic presentation of a monolithic catalyst is shown in Fig. 1. The main monolithic construction can be either ceramic (mainly cordierite) or of metallic materials (stainless steel, metal alloys, etc.). In the second configuration, the monolith wall may contain the catalyst as an integral part of the structure (e.g. honeycomb catalyst based on zeolites, TiO_2, V_2O_5 and/or WO_3).

Basic monolith structure, depending on the purpose, varies in dimensions and shapes (most frequently it is oval (or elliptic) and square) [6]. Monolith channels or cells are hexagonal, rectangular or of other shapes. The ceramic monoliths used as catalyst supports in automobile exhaust purifier systems generally consist of a closely packed array of small square cells. The channels' wall can be of different thickness. Geometric and physical properties of the monoliths, such as their shape, channel size, thickness and porosity of the wall as well as thickness and microstructure of the catalytic layer depend on specific requirements of the process [2,6]. Development of metallic monoliths started in the 1960s, mostly for the needs of chemical industry. Their use in the

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Nomenclature

C_{A0}	initial concentration of NO (mol m^{-3})
$C_{A,f}$	concentration in the fluid phase (mol m^{-3})
$C_{A,s}$	concentration in the solid phase (mol m^{-3})
C_{O_2}	concentration of oxygen (mol m^{-3})
D_e	effective diffusion coefficient in the washcoat ($m^2\ s^{-1}$)
D_f	molecular diffusion coefficient ($m^2\ s^{-1}$)
k	rate constant ($m^3\ mol^{-1}\ s^{-1}$)
K	adsorption equilibrium constant ($m^3\ mol^{-1}$)
r	radial coordinate (m)
$r_{A,s}$	surface reaction rate (mol $m^3\ s^{-1}$)
r_{ch}	equivalent radius of the monolith channel (m)
R	overall radius ($r_{ch} + \delta_e$) (m)
T	temperature (K)
u	linear velocity of gas phase (m s^{-1})
y_i	molar fraction of compound i (dimensionless)
z	axial coordinate (m)
Z	length of the monolith (m)

Greek symbol

δ_e	equivalent thickness of the washcoat (m)

cleanup of the vehicles' exhaust gases came under consideration in the 1980s. Nowadays, monoliths continue to be the preferred support in environmental applications due to their unique properties, such as high geometric surface area, low pressure drop, high temperature durability, mechanical strength, ease of orientation in a reactor, easy scale-up, etc. [1,2,7].

Preparation of monolithic catalysts is beyond the scope of this paper. However, more information on this subject can be found elsewhere [7–9].

1.2. Development and application of monolithic structures in DeNO$_x$ catalysis

Monolithic structures are most commonly applied in environmental protection, especially for the abatement of air pollution. This covers their application in the processes such as cleaning of exhaust gases from cars, selective catalytic reduction (SCR) of flue gases generated by power stations, destruction of volatile organic compounds (VOCs), ozone abatement in the aircrafts, ozone destruction in automobile radiators and catalytic combustion [2,6,10–12]. Other applications of monolithic supports in chemical industry are limited only in a single large-scale process—the production of hydrogen peroxide using the anthraquinone process [7,14]. This paper focuses particularly on the application of monoliths in DeNO$_x$ catalysis. More information about other fields of their application can be found in literature [2,6,11–16].

Monolith catalysts in DeNO$_x$ catalysis are intended for removal of NO$_x$ from both mobile and stationary sources of emissions [15]. Generally, the existing methods for NO$_x$ control are broadly divided into two strategies: (a) primary or preventive measures to control combustion and reduce or avoid NO$_x$ formation and (b) secondary measures to clean up the flue gas containing NO$_x$ and other pollutants [16]. The unique features of the catalytic monolith structures allow their application in both approaches.

1.2.1. Removal of NO$_x$ from stationary sources

1.2.1.1. Selective catalytic reduction of NO$_x$. Of various secondary measures, the selective catalytic reduction (SCR), using ammonia (NH_3) or urea ($CO(NH_2)_2$) as a reducing agent, is the most widely applied post-combustion technology for minimizing NO$_x$ emissions from stationary sources (such as power stations, waste incineration plants, chemical plants, cogeneration plants, etc.). Commercial SCR catalyst is usually a homogeneous mixture of titanium dioxide, tungsten trioxide (or molybdenum trioxide) and divanadium pentoxide, and is usually formulated in honeycomb shapes, especially for coal- or oil-fired units which might have particulates in the flue gas [17]. The plate-type catalyst and coated metal monoliths can also be applied in the SCR. The SCR monoliths and plates are assembled into standard modules and inserted into a reactor to form catalyst layers. Each catalyst layer contains individual, retractable catalyst elements. This kind of modular construction allows flexibility of use. The choice of the channel width in the catalyst elements is specific to the particular application. Dust content and maximum tolerable pressure drop in the flue gas are decisive in making the choice, since the channel width

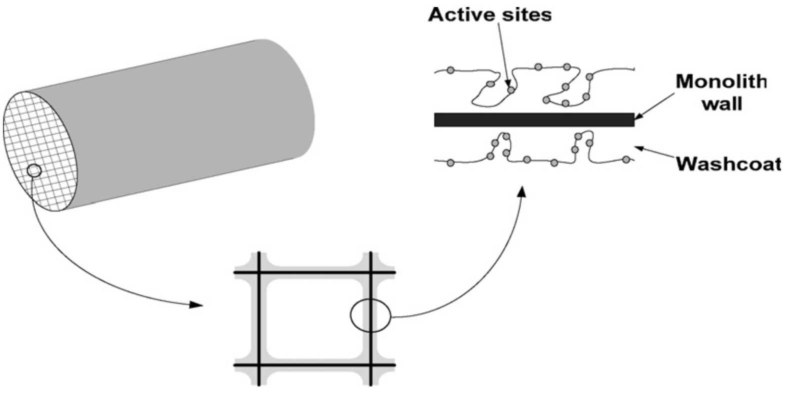

Fig. 1. Schematic representation of a honeycomb monolith catalyst.

influences total pressure drop in the flue gas purification system and thus capital and operating costs for the blower. The major drawbacks with SCR technology are high costs of catalysts and monitoring systems and the emission of unreacted (or slip) ammonia. The study of the effects of morphological and geometrical properties of the catalyst, of feed composition and of the interaction between $DeNO_x$ reaction and SO_2 oxidation has shown that there is additional space for improving both the catalyst and the reactor design [18].

1.2.1.2. Simultaneous removal of NO_x and other pollutants from the flue gases. Considerable effort has been made to develop the process for simultaneous removal of NO_x and other pollutants from the flue gas, such as SO_2, N_2O, VOCs, particulates, etc. Some examples of the combined NO_x/SO_x removal systems are SNO_x process (Haldor Topsoe), $DeSONO_x$ (Degussa), SO_x-NO_x-Rox Box process (Babcock & Wilcox Company) and other processes which combine $DeNO_x$ (mainly SCR) and $DeSO_x$ units. The so-called $BioDeNO_x$ process is a novel integrated physico-chemical and biological process for simultaneous removal of SO_2 and NO_x from the flue gases. $BioDeNO_x$ process is based on the reactive absorption, where mass transfer is enhanced by monolithic configuration [19,20]. Recently in 2003 the UOP, Paques and Monsanto Enviro-Chem have successfully completed a three-month demonstration of $BioDeNO_x$ technology by removing 99% of the particulates, 99% of SO_x and up to 95% of NO_x from a fluid catalytic cracking (FCC) plant [21].

A serious problem in the nitric acid industry is developing a catalyst for the combined removal of NO_x and N_2O. It has been found that combination of Fe-ZSM-5 and a $DeNO_x$ catalyst based on Co-ZSM-5 in a single reactor reduces at 573 K both N_2O and NO_x from the tail gases of nitric acid plants by more than 80% [22]. Suarez et al. [23] have reported a promising activity of Rh/γ-Al_2O_3-sepiolite monolithic catalysts for direct decomposition of N_2O traces. They found out that at 773 K this catalyst allows N_2O conversion in excess of 90%, even in the presence of oxygen, ammonia or water vapour in the stream.

The use of the monolithic or honeycomb systems opens the possibility of treating flue gases which contain solid particles. The ceramic wall flow filters enable removal of solid particles from waste gases. Their commonest application is in the treatment of the flue gases from waste incinerators, fluidized-bed coal combustors, diesel engines, etc. In some cases channels' wall of ceramic monoliths may contain a catalytically active component(s) (e.g. V_2O_5, V_2O_5-TiO_2, V_2O_5-Al_2O_3, etc.) that enable(s) simultaneous reduction and/or oxidation of gaseous pollutants such as NO_x, SO_x, VOCs, CO, etc. The main advantage of such integrated systems is a decreased number of process units, space and energy saving and, consequently, reduced overall process costs. Application of a catalytic filter in the SO_x-NO_x-Rox Box process and in similar processes is described in the patents [24,25].

1.2.1.3. Catalytic combustion of methane. Regarding primary measures, different alternatives can be considered to minimize NO_x formation during combustion. One of them is catalytic combustion of fuels in gas turbines, which results in ultra low levels of NO_x, CO and unburned hydrocarbons. The first commercial catalytic combustor for natural-gas-fired gas turbines was introduced in 2002 [26]. The advantages of catalytic combustors are the opportunity to perform combustion over a wide range of fuel-to-air ratios and the ability to operate at lower temperature than in conventional flame combustion (1373–1573 K versus 2073–2273 K). Thus, catalytic combustion does not require temperature decrease of the gaseous mixture at the outlet of combustion chamber. Catalytic combustors prevent generation of "thermal" NO_x (generated mostly at $T > 1673$ K). They also reduce constraints related to thermal stability of the construction materials, etc. The literature contains many scientific and technical works dealing with catalytic combustor systems [11,13,16,17].

Monolithic catalysts are used to ensure necessary conditions for catalytic combustion (e.g. high specific surface of the catalyst and simultaneous insignificant pressure drop through the catalytic layer). To date research in catalysts development has been conducted with ceramic and metallic monoliths that contain mostly Al_2O_3 as a secondary support, modified by the addition of Ba, La, Si and other elements to stabilize and improve chemical, thermal and other properties. The commonest catalytically active components are precious metals (Pt and Pd), oxides of transition metals, complex oxides (spinels-oxides type AB_2O_4, e.g. $MgAl_2O_4$; perovskite-oxides type ABO_3, e.g. $LaCoO_3$, etc.) and various hexa-aluminates and substituted hexa-aluminates ($BaO\cdot 6Al_2O_3$, etc.) [11,16]. However, so far studied catalysts are still lacking satisfactory stability and life at the temperatures of 1373–1773 K [11,16,27]. This necessitates further studies focused on upgrading of the catalyst thermal stability and stability in the presence of water steam, oxygen and other components (S, As and Pb) as well as simultaneous compliance with continuous operation for at least 1 year (ca. 8000 h). Cimino et al. [28] reported promising activity of the perovskite-based monolith catalysts for the catalytic combustion of methane. These materials have been proven to be resistant in the presence of H_2S and SO_2 or sulphur compounds present in natural gas and were shown to be applicable for the treatment of "fugitive emissions" from the iron and steel making industry [22].

Zwinkels et al. [11] and Thevenin et al. [16] state that the problems related to unsatisfactory activity and thermal stability of the catalyst under mentioned conditions can be partially settled with a hybrid combustion system, i.e. variously designed combustion chambers that enable controlled loading of the secondary fuel and/or air, and with a multilayer monolithic catalyst in the combustion chamber, etc.

1.2.2. Removal of NO_x from mobile sources

1.2.2.1. The three-way catalysts. In the mobile emission control applications, monolithic, either ceramic or metallic, catalyst supports have become the standard. They are normally called the three-way catalysts (TWCs), because they enable simultaneous removal of NO_x, CO and hydrocarbons (HCs). Since the introduction of catalytic converters, significant advances have been made in their design with regards to activity, selectivity and durability.

The first monolithic catalysts used in the treatment of exhaust gases from cars had ceramic monolith structure (mostly cordierite) with an active coating incorporating alumina, ceria and other oxides and combinations of the precious metals—platinum, palladium and rhodium. Subsequently, however, it was found out that catalyst efficiency depends on the motor operation. Actually, the efficiency is very low during cold start when also more than 80% of total emissions are generated. This is attributed to poor thermal conduction of ceramic material. Therefore, satisfactory operating temperature (ca. 523–623 K) of ceramic monolith catalysts is achieved after some time of motor operation and only then they exhibit satisfactory activity [29]. In order to overcome this problem Emitec [30], one of major world metallic monolith manufacturers, developed the treatment system for exhaust gases generated by unleaded gasoline combustion. The system has two parts: metallic monolith preheater (i.e. electrically heated catalytic converter, EHC) and basic ceramic monolith catalyst. The electrically heated converter is installed close to the entry to basic ceramic catalytic converter. This design reduces emissions during cold start, thus contributing to increase of the catalyst overall efficiency [29].

The main drawback with TWCs is the requirement for stoichiometric air–fuel ratio (14.5:1). Nowadays, the challenge is to reduce NO_x species under lean–burn conditions or at air–fuel ratios of 25:1 and above [31]. The pursuit of ‘‘lean $DeNO_x$’’ catalysis is currently a major research effort around the world, as this represents enabling technology for more widespread use of diesel fuels in passenger cars. This has prompted research on the development of a new catalyst technology—a NO_x storage-reduction catalyst (NSR catalyst) or lean NO_x trap (LNT) [32,33].

1.2.2.2. NO_x storage-reduction catalyst. The first NSR catalyst was developed and launched by Toyota in 1994 [34]. The basic concept of NSR catalysts is the possibility of using a catalytic material with the double function of acting as a sorption material and as a catalyst, with periodic switching between two functions. Obviously, this is another example of multifunctional possibilities of catalytic materials in the field of environmental catalysis.

Unlike conventional ‘‘steady-state’’ catalysts, these catalysts work continuously under periodic changes in feed composition from lean conditions (where NO_x is stored in the form of a nitrate, NO_3^-, in a barium-based storage material of the catalyst) and rich conditions (where the stored NO_x species are reduced to N_2 by the H_2, CO and hydrocarbons present in the gas). Possible mechanism of NO_x storage-reduction on the NSR catalyst is shown in literature [33–35]. The function of NO_x storage elements can be fulfilled by materials capable of forming sufficiently stable nitrates within the temperature range determined by lean conditions. Thus, especially alkaline, alkaline earths and to a certain extent also rare-earth compounds can be used. The main drawback of NSR catalysts is their high sensitivity to sulphur due to the fact that the NO_x storage component forms with SO_x a stable sulphate. To overcome this problem, new catalysts have been developed by Toyota based on $Pt/Rh/Ba/TiO_2/ZrO_2/\gamma\text{-}Al_2O_3$ supported on ceramic substrate with hexagonal cells [33]. Knowledge of the NO_x storage reduction mechanism and the SO_x deactivation mechanism is also important to achieve suitable catalyst for this reaction system. Further development and optimization of NSR catalysts is crucial for understanding of the unsteady-state behaviour of NSR catalyst.

1.2.2.3. Continuously regenerating filter (or trap). The problem related to simultaneous removal of solid particles and nitrogen oxides from the exhaust gases generated by diesel fuel combustion and regeneration of a catalytic filter, used in this system, has been overcome only recently, by development of continuously regenerating filters (CRT) [12,29]. They work in the following way: the first part of the filter has a ceramic monolith catalyst (Pt as a catalytically active component) that enables oxidation of CO and HC into CO_2 and H_2O, respectively. Simultaneously, nitrogen oxides (present in flue gases mostly as NO) oxidize to NO_2, while the remaining gas mixture passes through other part of the filter where solid particles or soot accumulate. Furthermore, reaction between the collected particulate matter and NO_2 (generated in the first part of the filter) causes oxidation, which enables continuous auto-regeneration of the filter. Regeneration is carried out below 523 K. Ceramic catalyst supports and filters for gasoline and diesel exhaust aftertreatment are described extensively by Gulati [36,37].

1.2.3. Other potential applications of monoliths

As already mentioned, monolithic units are currently used mainly for DeNOxification of the flue gases. However, some emerging applications have been also reported in literature, such as: hydrogen generation for fuel cell, steam reforming of hydrocarbons, water gas shift catalysts, preferential oxidation of CO and other chemical applications [6]. Monolithic reactors seem to be an attractive alternative to conventional multiphase reactors, such as slurry and packed-bed reactors. Particular interest is focused on application of monoliths in three-phase catalytic reactions [38,39].

Several options exist for application of monoliths in oil refineries. They include gas phase processes for removal of sulphur traces from gasoline and effluent gases, gas–liquid processes aimed at deep hydrodesulfurization, hydrodenitrogenation, dearomatization and hydrocracking (co- and counter-current flow) employing catalytic distillation, reactive stripping and reactive adsorption as well as gas–liquid–solid processes like moving bed application for hydrodemetallization and sulphur removal by reactive adsorption [40]. Obviously, chemical reaction engineering has a lot to offer in development of monolithic catalysts/reactors for practical use in the mentioned processes.

2. Modeling of the monolith reactors

2.1. Development of mathematical models

Mathematical modeling plays an important role in developing a new technology where catalytic reactor is used or in looking for the areas where the existing reactor designs can be improved. Modeling of the complex reaction systems, such as monolith reactors, is not an easy task. The performance of the monolith reactor is a complex function of design parameters (channel geometry, length and diameter of the channel, channel wall thickness), operating conditions (temperature, velocity) and the properties of both the catalyst (active species loading, washcoat loading, etc.) and the reaction mixture. In addition, complexities arise from continuously changing inlet conditions that require a transient description of the monolith reactor. Hence, the experimental investigation of the performance of the monolithic reactor is time-consuming and requires a large experimental setup. Mathematical models of the monolith reactors can be of different complexity, which generally depends on description of the reactants flow along the channels, kinetic models of the chemical reaction(s), heat and mass transfer in fluid and solid phases, etc. Excellent articles on the modeling of the monolith reactors can be found in literature [11,41–47]. Since publication of the classical paper of Hegedus and co-workers [48,49] on the design of monolith catalysts for power plant NO_x emission control, several papers associated with modeling of $DeNO_x$ monoliths have been reported in literature [50–58]. Recently, important contribution to this topic has been given by Balakotaiah and co-workers [59–61]. They reported the series of theoretical papers dealing with behaviour of the catalytic monoliths. Given the limited number of pages, the following text mentions only some aspects of the monolith reactor modeling and outlines future research priorities.

Detailed modeling and simulation of the monolith reactor may help understand complex interaction between various physical and chemical processes that occur within the channels of the monolith reactor (Fig. 2). At least one of these processes takes place at a molecular level. In a typical monolith reactor for purification of the automotive exhaust gases one has to consider the processes on several length-scales: monolith length and diameter of 10 cm; channel approximately 1 mm in diameter; 10–100 μm thick porous catalytic washcoat layer; particles forming the supporting material 1 μm in diameter; meso- and micro-pores of the supporting material 1–10 μm in diameter; active catalytic sites sized in nanometres and reactive molecules sized in Angstroms [62]. Apparently, modeling of the monolith reactor is a multi-scale problem [62,63].

In modeling of the monolithic reactors it is recommended to use a great deal of details if necessary or appropriate parameters are known, but whenever possible to avoid overdetailed descriptions, without sacrificing accuracy of the overall calculation. Phenomena identification at every scale and definition of all dominant mechanisms are of great significance for the analysis and modeling of such reaction systems. Main features of the mathematical models can be characterized by the specific focus on: identification of application areas, identification of the required level of sophistication of numerical methods and modeling in relation to a pre-specified accuracy level and available experimental data, and formulation of validation procedures.

There are various mathematical models which can be used to describe behaviour of a monolith reactor, such as one-dimensional (1D) [64–66], two-dimensional (2D) [67–69] and, in some cases, three-dimensional models [70–72]. They are always heterogeneous because of at least two phases in such reaction systems (i.e. catalyst—a solid phase and reactant(s)—a fluid phase). Accuracy of these models depends on approximations used in their development, number of spatial dimensions, details of transport processes and chemical kinetics. Usually, some simplifications are used to approximate the performance of the monolith reactors, such as steady-state, isothermal conditions, plug flow and identical properties in all monolith channels.

Customary analysis of a monolith reactor is based on the 1D heterogeneous model, where the complexities of the radial interphase transport are lumped into the gas–solid mass and heat transfer coefficients [73]. This approach invokes analogy with the Graetz–Nusselt problem governing heat transfer into fluid under the laminar flow in a duct at constant wall temperature. However, this model is usable only if proper correlations for the appropriate heat and mass transfer coefficients are available, but usually this is not the case. Therefore, the 1D heterogeneous model can be useful only in evaluation of experimental kinetic parameters and in quantification of the effects of some design variables on performance of a monolith reactor [41,74]. It is important to note that this is possible only in the limited range of operating conditions.

A more comprehensive approach to modeling of a monolith reactor is based on the distributed heterogeneous mathematical models, account for all necessary spatial variations. These models allow reasonably accurate predictions of the monolith performance under diffusion-limited conditions, especially if they are based on experimentally determined parameters or meticulous calculations. The influence of heat and mass transfer phenomena on performance of the monolith reactor has

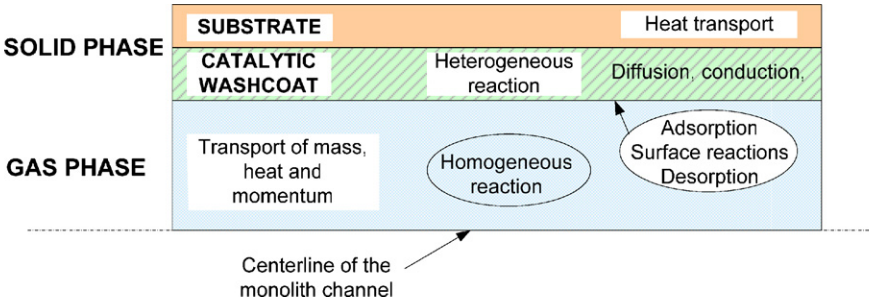

Fig. 2. Overview of heat and mass transfer phenomena in a monolith reactor channel.

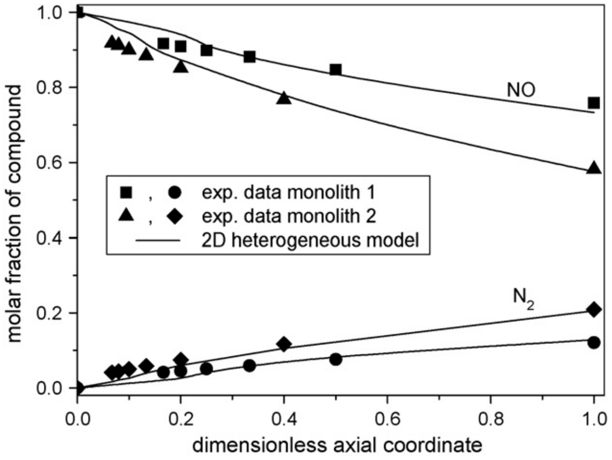

Fig. 3. Comparison between experimental data (points) and values predicted by the reactor model for the monoliths with different equivalent thicknesses of the catalytic layer.

been extensively investigated. Interested reader is referred to the articles by Holmgren and Andersson [75] and Hayes et al. [67,69,76,77].

An extensive study of direct decomposition of NO over a homemade zeolite-based monolith catalyst has been performed in our laboratories and the results are reported in various papers [78–80]. Our research was on the laboratory-scale and used various types of the monolith catalyst. The focus was on the mass transfer models accounting for the mass transport of species in the fluid phase and in the porous microstructure of the catalyst. Different heterogeneous models of the monolith reactors were used and analysed to elucidate the importance of mass transfer effects and to determine correct values of the local Sherwood numbers (*Sh*) and corresponding mass transfer coefficients inside the monolith reactor. The parameters of the monolith reactor model were estimated from the experimental data using the modified differential method and Nelder–Mead method of non-linear optimization.

Table 1
Governing equations of a 2D heterogeneous model of the monolith reactor

Model equation	
Mass balance equation (gas phase)	$u\frac{\partial C_{A,f}}{\partial z} - D_f\left(\frac{\partial^2 C_{A,f}}{\partial r^2}+\frac{1}{r}\frac{\partial C_{A,f}}{\partial r}\right)=0$
Mass balance equation (solid phase)	$D_e\left(\frac{\partial^2 C_{A,s}}{\partial r^2}+\frac{1}{r}\frac{\partial C_{A,s}}{\partial r}\right)-r_{A,s}=0$
Boundary conditions	$C_{A,s}=C_{A,f}=C_{A0}, \quad \text{at}\ z=0$ $\frac{\partial C_{A,f}}{\partial r}=0, \quad \text{at}\ r=0$ $D_f\frac{\partial C_{A,f}}{\partial r}=D_e\frac{\partial C_{A,s}}{\partial r}, \quad \text{at}\ r=r_{ch}$ $\frac{\partial C_{A,s}}{\partial r}=0, \quad \text{at}\ r=R$ $\frac{\partial C_{A,s}}{\partial z}=0, \quad \text{at}\ z=Z$
Kinetic model	$r_{A,s}=\frac{kC_{A,s}^2}{(1+\sqrt{KC_{O_2}})^2}$

Fig. 3 shows comparison between the experimental data obtained under conditions employed in our study and the values predicted by the 2D heterogeneous model based on a complete 2D description of both fluid and solid phase. A detailed presentation of the system of equations has been given elsewhere [79]. Here they are summarized in Table 1. Axial and radial profiles of the molar fraction of NO at the temperature of 673 K are shown in Fig. 4. It can be seen that the concentration gradients were much higher in the fluid phase than in the washcoat layer, indicating that the interphase mass transfer was probably a limited step in the overall reaction.

As explained previously [80,81], the important feature of multidimensional models is that they enable calculation of the local mass transfer coefficients along the length of the monolith channel under the reaction conditions. Mass transfer coefficients

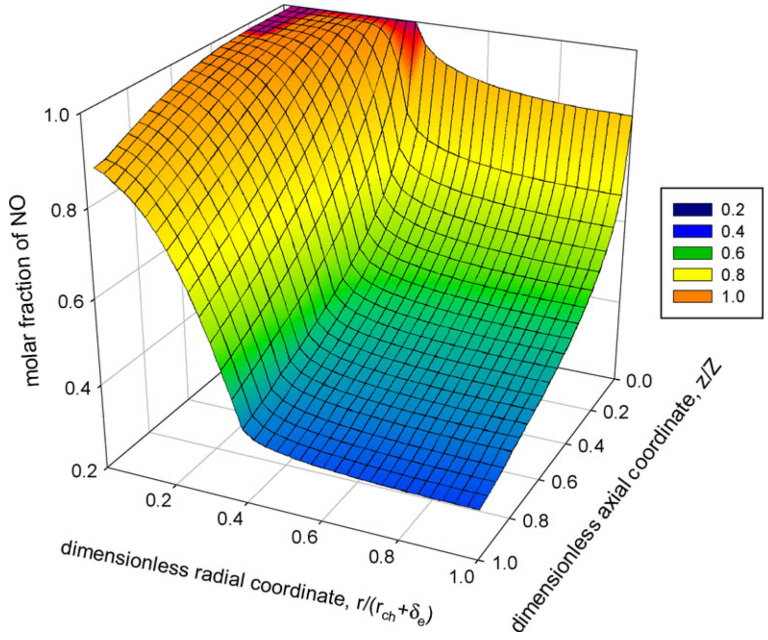

Fig. 4. Axial and radial profiles of the molar fraction of NO for the monolith catalyst at temperature of 673 K.

and especially the *Sh* number predicted by the model were very high at the entrance to the reactor and that their values decreased downstream the reactor. The explanation of such behaviour is given in literature [80].

Our present work was focused on setting up adequate experiments aimed at independent experimental measurement of the parameters of the monolith reactor model, such as the effective diffusion coefficients (D_e) in the catalytic layer. For this purpose the modified Wicke–Kallenbach cell was constructed. Preliminary results show good quantitative agreement between the experimentally obtained values of D_e and the values predicted theoretically with the use of the proposed mathematical models. However, confirmation of these results requires further experiments at wide range of the reaction temperatures. Finally, we believe that continued development and application of new reaction engineering tools will accelerate the development of monolithic structures and their application in $DeNO_x$ catalysis as well as in other fields.

2.2. Future research priorities in modeling of the monolith reactors

Nowadays, development and use of very complex models of the monolith reactors, reliable computation of many necessary parameters and finding numerical solutions are fairly feasible. The challenge for future is how to test and use these models effectively. It is, therefore, important to perform useful quantitative comparison between the experimental measurements and reactor model predictions. Under some circumstances, accuracy of the simulation is constrained primarily by the accuracy of the employed reaction rate parameters. In real combustion systems the number of chemical reactions occurring in the monolith reactor can be vast. The mechanism and kinetics of chemical reactions can be very complex. Some researches have attempted a detailed computer design of the chemical kinetic model and finding out an optimal method to reduce large kinetic models [81]. However, the existing methods for construction and analysis of the kinetic model are on the local level. Thus, considerable work still has to be done to generate kinetic models valid under a wide range of operating conditions.

Development of the heat and mass transfer models accounting for the energy and transport of species in the bulk flow as well as in the porous microstructure of the catalyst and support material of the reactor as a whole is also important in modeling of the monolith reactors. Obviously, further development of these devices will require intense and interdisciplinary research, from surface science to catalyst preparation techniques and engineering disciplines. The knowledge based on chemical engineering methodology will probably greatly contribute to meeting these expectations.

3. Conclusions

In future monolith catalysts and/or reactors will certainly maintain their major role in the abatement/avoidance of NO_x atmospheric emission and in resolving other environmental issues. According to some expectations, monolithic structures will be increasingly applied in chemical and biochemical processes, in mass production of chemicals, fine chemicals and specialty chemicals, treatment of fuel and flue gases, catalytic combustion of fuel and in multiphase processes in chemical industry. Obviously, materialization of these expectations requires further research that should, also, enable achievement of the following goals:

- development of the existing and new procedures for preparation of the monolithic catalysts taking into account process economics; upgrading of catalytical and physical properties (optimizing of chemical composition, structure, porosity and distribution of a catalytically active component(s), increasing of the oxygen storage capacity, etc.) and improvement of mechanical, thermal and other properties determining practical use of the monolithic catalysts/reactors;
- better distribution of fluids along the cross section of a monolith reactor in multiphase systems and development of corresponding mathematical models that describe fluid dynamics and complex processes performed in these systems. Optimization of the monolith reactor operation requires integral approach to the catalyst and reactor design. This approach is based on considering the catalyst in its multiscale components at the same time, which include active sites, solid architecture and texture, nano- and macrostructure.

Application of the basic methodology of chemical engineering along with the results of research and developments in the field of materials science will play important role in the achievement of the above goals.

References

[1] A. Cybulski, J.A. Moulijn, Catal. Rev. Sci. Eng. 36 (1994) 179.
[2] A. Cybulski, J.A. Moulijn, Structured Catalysts and Reactors, Marcel Dekker, Inc., New York, 1998, p. 1.
[3] S.T. Sie, R. Krishna, Rev. Chem. Eng. 14 (1998) 159.
[4] G. Saracco, V. Specchia, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysts and Reactors, Marcel Dekker, Inc., New York, 1998, p. 417.
[5] A.E.W. Beers, I. Hoek, T.A. Nijhuis, R.S. Downing, F. Kapteijn, J.A. Moulijn, Top. Catal. 13 (2000) 275.
[6] R.M. Heck, S. Gulati, R.J. Farrauto, Chem. Eng. J. 82 (2001) 149.
[7] T.A. Nijhuis, A.E.W. Beers, T. Vergunst, I. Hoek, F. Kapteijn, J.A. Moulijn, Catal. Rev. 43 (4) (2001) 345.
[8] X. Xu, J.A. Moulijn, Transformation of a structured carrier unto structured catalyst, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysts and Reactors, Marcel Dekker, Inc., New York, 1998, p. 599.
[9] P. Avila, M. Montes, E.E. Miro, Chem. Eng. J. 109 (2005) 11.
[10] J.L. Williams, Catal. Today 69 (2001) 3.
[11] M.F.M. Zwinkels, S.G. Järås, P.G. Menon, Catalytic fuel combustion in honeycomb monolith reactors, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysts and Reactors, Marcel Dekker, Inc., New York, 1998, p. 149.
[12] E.S.J. Lox, B.H. Engler, Environmental catalysis, in: G. Eartl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Willey-VCH, Weinheim, 1997, pp. 1559–1633.
[13] F.J. Janssen, Environmental catalysis-stationary sources, in: G. Eartl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Willey-VCH, Weinheim, 1997, pp. 1633–1668.

[14] C.T. Berglin, W. Herrmann, US Patent 4,552,748, 1985 (assigned to EKA AB).
[15] H. Bosh, F. Janssen, Catal. Today 2 (1987) 1.
[16] P.O. Thevenin, P.G. Menon, S.G. Järås, CATTECH 7 (2002) 10.
[17] C.D. Cooper, F.C. Alley, Air Pollution Control—A Design Approach, third ed., Waveland Press, Inc., Long Grove, 1994, p. 512.
[18] A. Beretta, E. Tronconi, G. Groppi, P Forzatti, Monolithic catalysts for the selective reduction of NO_x with NH_3 from stationary sources, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysts and Reactors, Marcel Dekker, Inc., New York, 1998, p. 121.
[19] P. van der Maas, L. Harmsen, S. Weelink, B. Klapwijk, P. Lens, J. Chem. Technol. Biotechnol. 79 (2004) 835.
[20] http://www.milieutechnologie.wur.nl/uk/Research/Inorganic + Bioconversion/BioDeNOx.htm.
[21] www.uop.com/objects/UOPTechMoreMar2003.pdf.
[22] G. Centi, P. Ciambelli, S. Perathoner, P. Russo, Catal. Today 75 (2002) 3.
[23] S. Suarez, C. Saiz, M. Yates, J.A. Martin, P. Avila, J. Blanco, Appl. Catal. B: Environ. 55 (2005) 57.
[24] E.A. Pirsh (The Babcock & Wilcox Comp.), US Patent Application 4,220,633 (2 September 1980).
[25] J.B. Doyle, E.A. Prish, W. Downs (The Babcock & Wilcox Comp.), US Patent Application 4,793,981 (27 December 1988).
[26] Catalytica Energy Systems, http://www.catalyticaenergy.com/xonon/index.html.
[27] P. Forzatti, Catal. Today 62 (2000) 51.
[28] S. Cimino, R. Pirone, G. Russo, Ind. Eng. Chem. Res. 40 (2001) 80.
[29] M.V. Twigg, D.E. Webster, Metal and coated-metal catalysts, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysts and Reactors, Marcel Dekker, Inc., New York, 1998, p. 59.
[30] http://www.emitec.com/index.php?lang=en&mid=e4&doc=50.
[31] S. Matsumoto, CATTECH 4 (2000) 102.
[32] H. Shinjoh, N. Takahashi, K. Yokota, M. Sugiura, Appl. Catal. B: Environ. 15 (1998) 189.
[33] S. Matsumoto, Catal. Today 90 (2004) 183.
[34] S. Matsumoto, Catal. Today 29 (1996) 43.
[35] S. Matsumoto, Catal. Surv. Jpn. 1 (1997) 111.
[36] S.T. Gulati, Ceramic catalyst supports and filters for diesel exhaust aftertreatment, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysts and Reactors, Marcel Dekker, Inc., New York, 1998, p. 15.
[37] S.T. Gulati, Ceramic catalyst supports and filters for diesel exhaust aftertreatment, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysts and Reactors, Marcel Dekker, Inc., New York, 1998, p. 501.
[38] F. Kapteijn, T.A. Nijhuis, J.J. Heiszwolf, J.A. Moulijn, Catal. Today 66 (2001) 133.
[39] F. Kapteijn, J.J. Heiszwolf, T.A. Nijhuis, J.A. Moulijn, CATTECH 3 (1999) 24.
[40] M. Egorova, Dissertation, Swiss Federal Institute of Technology, Zurich, ETH No. 15376.
[41] E.M. Johanson, D. Papadias, P.O. Thevenin, A.G. Ersson, R. Gabrielsson, P.G. Menon, P.H. Björnbom, S.G. Järås, Catalytic Combustion for Gas Turbine Applications, Catalysis, vol. 14, The Royal Society of Chemistry, Cambridge, 1999, p. 183.
[42] G. Groppi, E. Tronconi, P. Forzatti, Catal. Rev. Sci. Eng. 41 (1999) 227.
[43] S.T. Kolaczkowski, Catal. Today 47 (1999) 209.
[44] S. Tischer, O. Deutschmann, Catal. Today 105 (2005) 407.
[45] R. Wanker, H. Raupenstrauch, G. Standinger, Chem. Eng. Sci. 55 (2000) 4709.
[46] R.E. Hayes, S.T. Kolaczkowski, W.J. Thomas, Comput. Chem. Eng. 16 (1992) 645.
[47] D. Leung, R.E. Hayes, S.T. Kolaczkowski, Can. J. Chem. Eng. 74 (1996) 94.
[48] F.P. Boer, L.L. Hegedus, T.R. Gouker, K.P. Zak, ChemTech 20 (1990) 312.
[49] J.W. Beekman, L.L. Hegedus, Ind. Eng. Chem. Res. 30 (1991) 969.
[50] E. Tronconi, P. Forzatti, AIChE J. 388 (1992) 201.
[51] E. Tronconi, P. Forzatti, J.P. Marin, S. Malloggi, Chem. Eng. Sci. 47 (1992) 2401.
[52] J. Svachula, N. Ferlazzo, P. Forzatii, E. Tronconi, Ind. Eng. Chem. Res. 32 (1993) 1053.
[53] E. Tronconi, A. Beretta, A.S. Elmi, S. Malloggi, A. Baldacci, Chem. Eng. Sci. 49 (1994) 4277.
[54] H. Choi, S. Ham, I. Nam, Y.G. Kim, Ind. Eng. Chem. Res. 35 (1996) 106.
[55] A. Bahamonde, A. Beretta, P. Avila, E. Tronconi, Ind. Eng. Chem. Res. 35 (1996) 2516.
[56] A. Santos, A. Bahamonde, M. Schmid, P. Avila, F. Garcia-Ochoa, Chem. Eng. Proc. 37 (1998) 117.
[57] B. Roduit, A. Baiker, F. Brettoni, J. Baldyga, A. Wokaun, AIChE J. 44 (1998) 2731.
[58] R. Khodayari, C.U.I. Odenbrand, Chem. Eng. Sci. 54 (1999) 1775.
[59] M. Bhattacharya, M.P. Harold, V. Balakotaiah, AIChE J. 508 (2004) 2939.
[60] K. Ramanathan, D.H. West, V. Balakotaiah, Catal. Today 98 (2004) 357.
[61] M. Dharma, M.P. Harold, V. Balakotaiah, Ind. Eng. Chem. Res. 44 (2005) 6264.
[62] F. Stepanek, M. Marek, J. Hanika, P.M. Adler, Catal. Today 66 (2001) 249.
[63] Z. Tian, Y. Xu, L. Lin, Chem. Eng. Sci. 59 (2004) 1745.
[64] E. Tronconi, P. Forzatti, J.P. Gomez-Martin, S. Mallaggi, Chem. Eng. Sci. 47 (1992) 2401.
[65] H. Choi, S.W. Ham, J.S. Nam, Y.G. Kim, Ind. Eng. Chem. Res. 35 (1996) 106.
[66] B. Liu, M.D. Checkel, R.E. Hayes, M. Zheng, E. Mirosh, Can. J. Chem. Eng. 78 (2000) 557.
[67] D. Leung, R.E. Hayes, S.T. Kolaczkowski, Can. J. Chem. Eng. 74 (1996) 95.
[68] R. Wanker, H. Raupenstrauch, G. Staudinger, Chem. Eng. Sci. 55 (2000) 4709.
[69] C.J. Bennett, R.E. Hayes, S.T. Kolaczkowski, W.J. Thomas, Proc. R. Soc. Lond. A 439 (1992) 465.
[70] D. Papadias, L. Edsberg, P. Björnbom, Catal. Today 60 (2000) 11.
[71] B. Roduit, A. Baiker, F. Bettoni, J. Baldyga, A. Wokaun, AIChE J. 44 (1998) 2731.
[72] R. Jahn, D. Šnita, M. Kubíček, M. Marek, Catal. Today 38 (1997) 39.
[73] G. Groppi, E. Tronconi, Chem. Eng. Sci. 52 (1997) 3521.
[74] D. Papadias, M.F.M. Zwinkels, L. Edsberg, P. Björnbom, Catal. Today 47 (1999) 315.
[75] A. Holmgren, B. Andersson, Chem. Eng. Sci. 53 (1998) 2285.
[76] R.E. Hayes, S.T. Kolaczkowski, Catal. Today 47 (1999) 295.
[77] R.E. Hayes, S.T. Kolaczkowski, P.K. Li, S. Awdry, Appl. Catal. B: Environ. 25 (2000) 93.
[78] V. Tomašić, S. Zrnčević, Z. Gomzi, Pol. J. Environ. Stud. 11 (2002) 23.
[79] V. Tomašić, S. Zrnčević, Z. Gomzi, Catal. Today 90 (2004) 77.
[80] V. Tomašić, Z. Gomzi, Chem. Eng. Proc. 43 (2004) 765.
[81] W.H. Green, P.I. Barton, B. Bhattacharjee, D.M. Mateu, D.A. Schwer, J. Song, R. Sumathi, H.-H. Carstensen, A.M. Dean, J.M. Glenda, Ind. Eng. Chem. Res. 40 (2001) 5362.