

Development of the Structured Catalysts for the Exhaust Gas Treatment

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Experimental and theoretical investigation of NO decomposition in a catalytic monolith reactor has been performed. Preparation of the monolith catalyst, composed of cordierite substrate as an inert carrier and copper containing ZSM-5 zeolite as catalytic washcoat, is described in details. The reaction was examined in the temperature range from 573 K to 773 K and at different flow rates.

One-dimensional (1D) heterogeneous model was applied to describe a single channel of the monolith. The model included the processes of external mass transfer and chemical reaction on the surface of the catalyst. Mass transfer coefficient was estimated from correlation available in the literature. Kinetics of NO decomposition was described by Langmuir-Hinshelwood type of rate equation.

The reactor model was verified by comparing experimental data with theoretical predictions. Generally, good agreement has been achieved. However, the rate constant was found to increase with the increase in the thickness of the catalytic washcoat. Consequently, the internal mass transfer, even within a very thin layer of the catalytic washcoat, must also be included in the reactor model for the monolith channel to adequately describe behavior of such a reactor system.

Key words:

Catalytic decomposition of NO, Cu/ZSM-5 zeolite, mathematical model, monolith catalyst, washcoat

Introduction

Monolithic catalysts, also referred to as honeycomb catalysts, are nowadays widely used in several environmental applications. Cleaning of automotive exhaust gases, selective catalytic reduction (SCR) of nitrogen oxide (NO_x) generated from the stationary sources, and catalytic abatement of volatile organic compounds (VOCs) from industrial processes, are some of their commercial uses. However, these catalysts still belong to less common reaction systems. This type of the so-called structured catalysts (reactors) can simultaneously meet special requirements, e. g. very low pressure drop, excellent mass transfer properties, high surface-to-volume ratio, short diffusion resistance, absence of the need for a catalyst separation, easy scale-up, etc. Therefore, monolith reactors are attractive alternatives to conventional multi-phase reactors (slurry and packed-bed reactors).^{1–8} Nowadays, particular interest is being focused on their application in three-phase catalytic reactions. This has resulted in several processes that are currently under development. Monolith catalysts have also good prospects in the field of catalytic fuel combustion.^{9–11} The

most important feature of catalytic combustion is insignificant formation of thermal nitrogen oxides.

Despite great opportunities for practical application of monolith catalysts, the articles describing details of their preparation are very scarce. One of the few contributions is an excellent book by Cybulski and Moulijn published recently.¹²

It is known, that the removal of NO_x from the exhaust gas is one of major issues in environmental protection. A demand for new and more efficient catalytic systems for NO_x reduction has encouraged extensive research in this area. Due to the fact that over 90 % of NO_x appear in the form of NO, direct decomposition of NO has been for decades a model system for evaluation of the activity of various catalytic materials.^{13–17} Our previous works report on the results of the kinetic study of catalytic NO decomposition, performed over powder Cu/ZSM-5 catalyst, and propose an appropriate kinetic model for the reaction.¹⁸ This work deals with a monolithic catalyst, used in the same reaction system. Preparation of the monolith catalyst, composed of cordierite as an inert carrier, and copper containing ZSM-5 zeolite as catalytic washcoat, is described in

details. One-dimensional heterogeneous model is used to describe behavior of the monolithic reactor. Particular emphasis is put on justifying suitability of such a reactor model.

Experimental

Characteristics of the support

Monolithic catalysts were made of ceramic honeycomb substrate (cordierite) and copper containing ZSM-5 zeolite used as catalytic layer (washcoat). Cordierite substrate was supplied by Engelhard Corporation. Table 1 shows the main physical parameters of honeycomb support.

Table 1 – Properties of cordierite honeycomb support

channel structure	square
number of channels, channels/cm ²	31
channel spacing (pitch), mm	1.8034
wall thickness, mm	0.2667
wall porosity, %	35
hydraulic diameter, mm	1.5367
geometric surface area, m ² m ⁻³	1.9055 · 10 ³
open frontal area, %	73.21
bulk density, g m ⁻³	0.4374

The commercial oval type of honeycomb was cut into square pieces, each with 4 channels. The samples 46–79 mm long were used for coating of the catalytic layer.

Coating of the catalytic layer on the monolith support

A detailed description of Cu/ZSM-5 zeolite preparation can be found elsewhere^{18,19}. Briefly, Cu/ZSM-5 zeolite (Si/Al = 40, *w* = 1.92 % Cu) was prepared by ion exchange of Na/ZSM-5 (10 g) with 0.01 mol dm⁻³ of aqueous solution of cupric acetate (1 dm³).

To washcoat the monolith, slurry was prepared by suspending 0.5 g of Cu/ZSM-5 zeolite per 2 cm³ of Al(NO₃)₃ · 9 H₂O (0.5 mol dm⁻³) aqueous solution. Slurry was introduced into the channels of the monolith by means of vacuum. Then monolithic catalyst was dried over 24 hours at room temperature. In some cases the procedure had to be repeated several times (each time after drying at room temperature) in order to increase the amount of the active phase on the monolith walls. The resulting monolithic catalysts were designated M-2, M-3 and

M-4. In some experiments, aqueous slurry was prepared by suspending zeolite in a commercial sodium silicate solution. The sample was designated M-1. The mass of the active phase on the monolith walls was determined gravimetrically and the obtained values presented in Table 2.

Table 2 – Properties of the monolithic catalysts

Monolith sample	l mm	m g	d_h mm
M-1	79	0.2520	0.94 ± 0.02
M-2	75	0.0776	1.50 ± 0.03
M-3	46	0.1510	0.94 ± 0.03
M-4	69	0.2600	0.54 ± 0.02

Experimental apparatus and procedures

The reactor system consisted of a tubular reactor (I.D. 6.5 mm, length 150 mm), electrical heater, thermocouple, flowmeter and gas analysis equipment.

The monolith catalyst was placed into the reactor. Empty space between the honeycomb catalyst (square geometry) and the reactor walls was filled with an inert material (SiO₂) to prevent bypass. Before reaction, the monolithic catalyst had been reduced *in situ* at 773 K for 2 hours under helium flow rate (50 cm³ min⁻¹) and cooled to the desired reaction temperature. Blank conversion, without the monolith catalyst, was measured and found to be negligibly low (below 2 %).

Catalytic decomposition of NO over monolithic catalysts was performed at 573–773 K under atmospheric pressure and at various flow rates (4–60 cm³ min⁻¹). Temperature of the reactant gas (4 % NO/He; Messer Griesheim) was monitored by the thermocouple (Ni-CrNi) placed at the exit of the monolith. Space times were changed by varying total flow rate of the reactant gas over constant volume of the monolith. The catalyst activity for NO removal was evaluated by conversion of NO into N₂ when the reaction reached steady state (30 minutes from the exposure to stream).

The reaction products were analyzed by GC (Varian 3300) using molecular sieve 5A, thermal conductivity detector and helium as carrier gas.

Results and discussion

Preparation of the catalyst

Deposition of the active catalytic layer on the inert monolithic support is known to be a critical step in preparation of the monolithic catalyst. Alu-

mina is the commonest washcoating material. Therefore, various methods have been reported to describe the washcoating of an alumina layer on the monolith surface.^{12,20} Recently, lots of efforts have been made to coat various zeolites on the monolith support. As pointed out by *Armor*,²¹ reports on the preparation of the zeolite-based monolith catalysts, have not been disclosed to wide public. Only a few papers^{22,23} give more details of it, but most procedures have been patented or treated as confidential industrial property.

One of the objectives of this study was to prepare monolithic catalysts, containing Cu/ZSM-5 zeolite as a washcoat, and to test their catalytic activity in NO decomposition. As mentioned before, adherent layer of the catalytic material was obtained in two ways. In both cases very thin layers of the washcoat (0.02–0.5 mm) were observed. A series of preliminary experiments was performed in the laboratory reactor to test catalytic activity of each sample in NO decomposition. Under similar conditions of the catalyst preparation (samples M-1 and M-3; thickness of the washcoat layer 0.3 mm), much better activity was achieved when washcoating of the catalytic layer was performed with the solution of aluminum nitrate. Poor activity of M-1 monolith catalyst might have been attributed to pore filling with sodium silicate, as already reported.²⁴ Thus, it was concluded that composition of slurry was critical in coating of the catalytic layer onto the surface of the monolith substrate.

Mathematical Model

Assumptions and model equations

Mathematical models of the monolith reactors can be of different complexity which, generally, depends on: (1) description of the reactant flow along the channels; (2) kinetic model of a chemical reaction; (3) heat and mass transfer in fluid and solid phases, etc. In this study, *one-dimensional (1D) heterogeneous model* was used to simulate one single channel of the monolith reactor (Fig. 1), i.e. a dependent variable (in our case NO concentration), depended on one dimension only (the reactor length), and two phases considered, a gaseous reactant and a solid catalyst.

The below 1D model equations (eq. 1–2) were derived according to the following assumptions, regarded as acceptable and convenient for the scope of the work:

1) steady-state and isothermal conditions

2) equal conditions within each monolith channel (thus, simulation of the whole monolith was reduced to the analysis of a single channel)

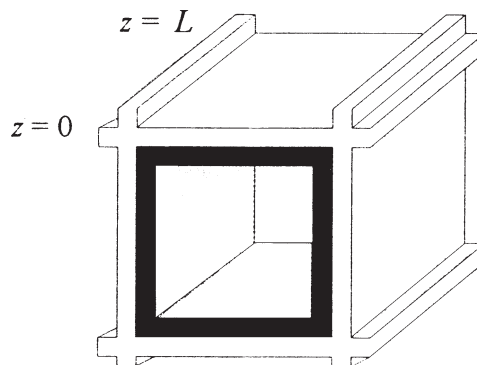


Fig. 1 – Scheme of square geometry of the single monolith channel

3) ideal flow in a single channel, since the length to diameter ratio for the channel was large enough (> 50)

4) negligible pressure drop along the monolith channel ($< 12 \text{ Pa m}^{-1}$)

5) square geometry of the channel after washcoating (due to a thin layer of the washcoat), and

6) negligible pore diffusion resistance within the thin catalytic layer, deposited on the monolith substrate.

It had been shown beforehand that despite various simplifying assumptions invoked in the development, such model described essential features of the monolith reactors employed under typical conditions of the gas turbine combustor operations.²⁵

According to the above assumptions, the following equation could be derived for the reactant concentration in the fluid phase:

$$u \frac{dc_A}{dz} = k_g a_v (c_A - c_{As}) \quad (1)$$

where c_A and c_{As} were concentrations of the gaseous reactant in the bulk and the catalyst surface respectively, a_v was geometric surface area per unit volume of the reactor, and k_g was the external mass transfer coefficient.

Concentration, c_{As} , on the catalyst surface was computed from the following algebraic equation:

$$k_g a_v (c_A - c_{As}) = r_A \quad (2)$$

where r_A was the reaction rate, given by the mechanistic kinetic model, as will be discussed later. Equations (1) and (2) had to be solved simultaneously, taking into account the inlet condition:

$$c_A = c_{As} = c_{A0}, \quad z = 0 \quad (3)$$

Equation (2) implicitly assumed kinetic control in the catalyst layer and only external mass transfer limitation for the catalytic reaction. That assump-

tion is justified when catalytic active layer is sufficiently thin and porous.

As mentioned earlier, it had been assumed that the reaction of NO decomposition occurred under isothermal conditions. Our previous work²⁴ confirmed that assumption by calculating temperature sensitivity of the reaction rate, which at 733 K yielded $2.75 \cdot 10^{-2} \text{ K}^{-1}$. Thus, energy balance equations were not included in our analysis.

Rate equation

Intrinsic kinetic data on NO decomposition over Cu/ZSM-5 catalyst, ground to very fine particles (0.315–0.5 mm) so as to avoid internal diffusion limitations, have been published recently.^{18,24,26} The Langmuir-Hinshelwood type of rate equation was proposed:

$$r_A = \frac{k \cdot c_{As}^2}{\left(1 + \sqrt{K(c_{A0} - c_{As})/2}\right)^2} \quad (4)$$

It was derived assuming bimolecular surface reaction between the two adsorbed NO molecules as a rate-determining step.

External mass transfer coefficient

Mass transfer coefficient, k_g was estimated from the equation:

$$k_g = \frac{Sh D_{NO,He}}{d_h} \quad (5)$$

Values of Sh numbers were estimated from correlation derived for monoliths, proposed by *Hawthorn*:²⁷

$$Sh = B \left[1 + 0.095 Re Sc \frac{d_h}{l} \right]^{0.45} \quad (6)$$

where B was 2.976 for the square geometry of channels.

Molecular diffusion of NO in helium, $D_{NO,He}$ was calculated from Chapman-Enskog formula:²⁸

$$D_{NO,He} = 1.8583 \cdot 10^{-3} \frac{T^{3/2} (1/M_{NO} + 1/M_{He})^{1/2}}{p_t \sigma_{NO,He}^2 \Omega_{NO,He}} \quad (6)$$

Values of $D_{NO,He}$ were in the range from $2.1516 \cdot 10^{-4} \text{ m}^2 \text{ s}^{-1}$ at 573 K to $3.5588 \cdot 10^{-4} \text{ m}^2 \text{ s}^{-1}$ at 773 K. Hydraulic diameter of the monolith channel, d_h was taken as geometric characteristic of the monolith channel.

Solution method and model verification

By introduction of the following dimensionless variables:

$$x = z/l \quad C_A^* = c_A/c_{A0} \quad C_{As}^* = c_{As}/c_{A0} \quad (8)$$

the equations of the monolith model (eq. 1–2), along with the initial conditions, appeared in dimensionless form:

$$\frac{dC_A^*}{dx} = \tau k_g a_v (C_A^* - C_{As}^*) \quad (9)$$

$$k_g a_v (C_A^* - C_{As}^*) = r_A \quad (10)$$

$$x = 0, \quad C_A^* = C_{As}^* = c_{A0} \quad (11)$$

where τ was the reactor space time, defined as the ratio between the monolith length and the superficial velocity ($\tau = l/u$). Geometric surface area, a_v for square geometry of the monolith channel was defined as:

$$a_v = \frac{4}{d_h} \quad (12)$$

Equations (9) to (11) which contained previously calculated quantities k_g and a_v , were solved simultaneously for every monolith length, temperature and thickness of the catalytic layer. The values of kinetic quantities k and K from the equation (4), were estimated from experimental data. Kinetic quantities were assessed using modified differential method and Nelder-Mead method of nonlinear optimization.^{29,30} Inlet values used to estimate kinetic quantities were previously mentioned values for the powder Cu/ZSM-5 catalyst.^{18,24} The results are summarized in Table 3. For comparison purposes, there are also kinetic quantities for the powder zeolite catalyst. Some differences in the kinetic parameters for the powder zeolite catalyst and monolith containing zeolite washcoat, were recorded. They

Table 3 – Estimated kinetic quantities for powder Cu/ZSM-5 catalyst and monolith sample M-4 at various temperatures

T/K	Powder catalyst			Monolith catalyst		
	$\frac{k \cdot 10^{-2}}{\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\frac{K}{\text{m}^3 \text{ mol}^{-1}}$	$SD \cdot 10^2$	$\frac{k \cdot 10^3}{\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\frac{K \cdot 10^2}{\text{m}^3 \text{ mol}^{-1}}$	$SD \cdot 10^3$
573	2.035	0.292	3.159	1.568	1.276	4.912
623	5.700	0.019	2.515	1.741	1.410	2.108
673	9.425	3.175	2.205	1.514	1.105	3.236
723	304.500	8.943	1.028	4.083	1.499	5.874
773	125.173	18.463	2.650	7.571	1.080	9.049

might be due to the changed catalyst structure in the latter case, which changed the catalyst activity.

Comparison between experimental data and the values predicted by the 1D heterogeneous model is illustrated in Fig. 2–4. Generally, good agreement was achieved. As shown in Fig. 3, dimensionless concentration of unreacted NO at the reactor exit decreases with temperature increase. In other words, the reaction rate increases with temperature. Similar results are reported for the powder catalyst^{18,24}. An apparent activation energy of eq. (4) was determined from the Arrhenius plot (Fig. 5). It was found to be 28.88 kJ mol⁻¹ for the monolith catalyst and 102.81 kJ mol⁻¹ for the powder catalyst. Different values of activation energy might be due to different structure of the catalysts as well as to the influence of the intraphase diffusion on the overall reaction rate.

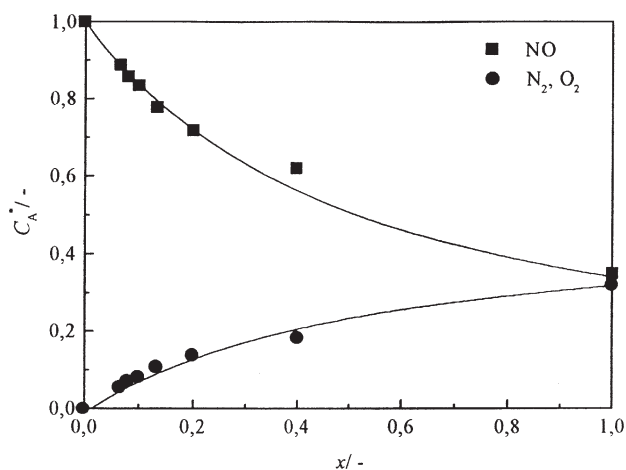


Fig. 2 – Comparison between experimental data (points) and the values predicted by the model, eq. 9–11 (lines) at 723 K

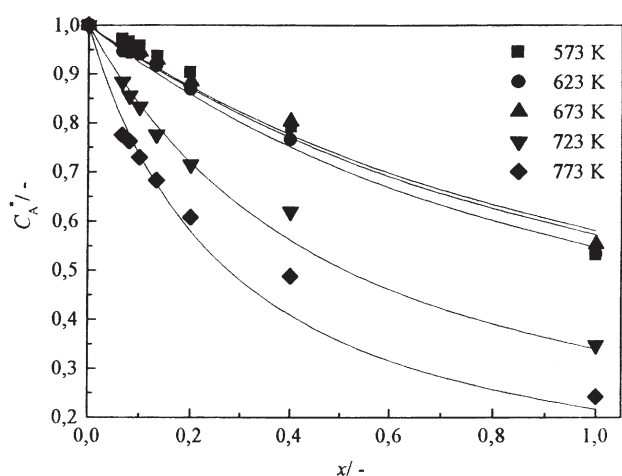


Fig. 3 – Comparison between experimental data (points) and the values predicted by the model, eq. 9–11 (lines) at different temperatures. Kinetic quantities are in Table 3

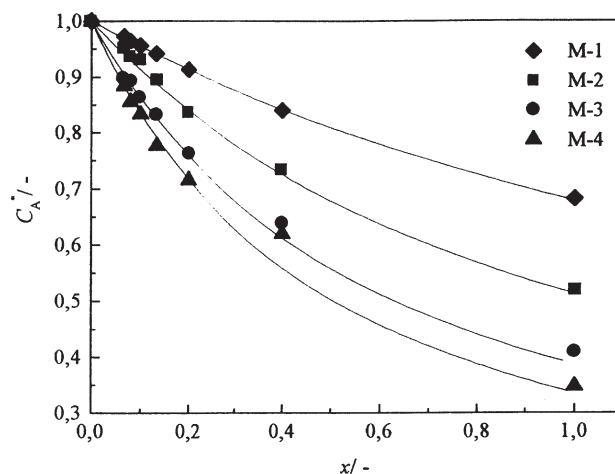


Fig. 4 – Comparison between experimental data (points) and the values predicted by the model, eq. 9–11 (lines) for various monolith samples at 773 K. Kinetic quantities are given in Table 4

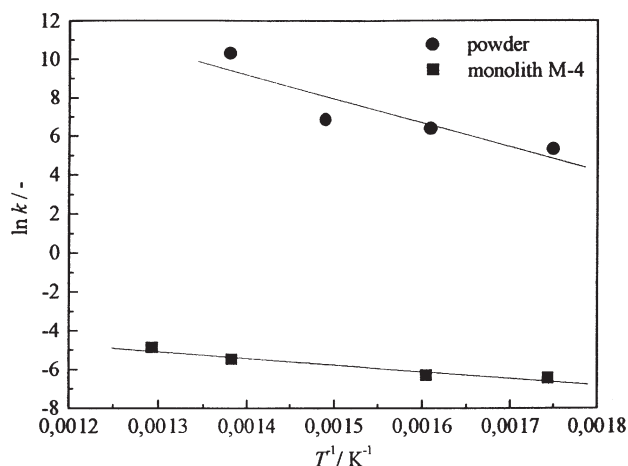


Fig. 5 – Arrhenius plot for determination of activation energy

Comparison of the rate constant values for the monolith catalyst at various thickness of the washcoat, shows that they increase with the increased thickness of the catalytic washcoat (Table 4, Fig. 4). These results reveal porosity of the catalytic layer and indicate that the reaction took place,

Table 4 – Estimated values of rate coefficients for different monolith samples at 773 K

Monolith sample*	$\frac{k \cdot 10^3}{\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\text{SD} \cdot 10^3$
M-1 (0.3)	0.570	0.756
M-2 (0.02)	0.884	1.641
M-3 (0.3)	5.455	3.717
M-4 (0.5)	7.571	9.049

* numbers in parentheses indicate washcoat thickness in mm

both, on the surface and within the catalytic layer. Taking into account that 1D model is based on the assumption that the reaction occurs on the surface of the catalytic washcoat, it appears that it is not suitable for describing NO decomposition over the monolith catalyst under conditions employed in this study.

Conclusion

Aluminum nitrate has shown its suitability for coating of the catalytic layer on the monolith surface. Irrespective of the changed structure, compared to the powder catalyst, activity of the obtained catalyst was satisfactory.

Generally, the monolith reactor can be well approximated by one-dimensional heterogeneous model. However, since rate constant increases with the increase of the thickness of the catalytic layer, the reaction occurs within the layer, rather than solely on its surface. In other words, two-dimensional heterogeneous model, which takes into account intraphase diffusion, will be more suitable for describing the above process.

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Nomenclature

A – cross-sectional area of the channel, m^2
 a_v – geometric surface area ($a_v = 4/d_h$) $m^2 m^{-3}$
 c_A, c_{As}, c_{A0} – concentration of NO in bulk, surface concentration, initial concentration, $mol dm^{-3}$
 C_A^*, C_{As}^* – concentration of NO in bulk, surface concentration, dimensionless
 $D_{NO,He}$ – molecular diffusion coefficient, $m^2 s^{-1}$
 d_h – hydraulic diameter of the monolith channel ($d_h = 4 A/W_p$), m
 K – adsorption equilibrium constant, $m^3 mol^{-1}$
 k – rate coefficient, $m^3 mol^{-1} s^{-1}$
 k_g – external mass transfer coefficient, $m s^{-1}$
 l – monolith length, m
 M_{NO}, M_{He} – molar mass of NO and He, $g mol^{-1}$
 p_t – total pressure, Pa
 r_A – reaction rate, $mol m^3 s^{-1}$
 SD – mean square deviation, dimensionless
 T – temperature, K
 u – superficial gas velocity, $m^3 m^{-2} s^{-1}$

m – mass of the active phase, g
 W_p – wetted wall perimeter, m
 x – axial coordinate, dimensionless
 z – axial coordinate, m
 w – mass fraction, %

Greek symbols

ν – kinematic viscosity of gas, $m^2 s^{-1}$
 ρ – gas density, $kg m^{-3}$
 $\sigma_{NO,He}$ – force constant in the Lennard-Jones potential function, Å
 τ – reactor space time, s
 $\Omega_{NO,He}$ – diffusion collision integral, dimensionless

Dimensionless numbers

Re – Reynolds number ($d_h u/\nu$)
 Sc – Schmidt number ($\nu/D_{NO,He}$)
 Sh – Sherwood number ($d_h k_g/D_{NO,He}$)

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