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Oxidation of volatile organic compounds in a multifunctional high-temperature and high-pressure cassette microreactor

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1.   Introduction

Microreactors are microstructured devices having internal characteristic dimensions in the submillimeter range [1-5]. Mostly such reactors have multiple parallel channels with diameters between 10 and 1000 micrometers where the chemical reaction proceeds. The main feature of microstructured reactors is their high surface to volume ratio in the range of 10,000-50,000 m^2/m^3 compared to more traditional chemical reactors. The specific surface in conventional laboratory and production vessels is usually 100 m^2/m^3 and seldom exceeds 1000 m^2/m^3. Typical is also high heat transfer capabilities that allows performing highly exothermic or endothermic reactions and avoiding hot-spots formation [6]. Microstructures allow fast heating and cooling of reaction mixtures in the reactor systems [7]. Small diameters of the reactor channels are advantageous for consecutive processes since high selectivity towards a reaction intermediate is achieved. Avoidance of heat and mass transfer limitations is the main advantage of the microreactor systems compared to the conventional apparatus. A review on the microreactors dealing with gas-phase reactions was published by Kolb and Hessel [6].

Two ways of catalytic active phase introduction into the microreactor are possible: a) as a packed bed, and b) as a catalytic wall coating. The use of packed bed is the easiest way, how to fill the channels of the microreactors; also the methodology developed with traditional laboratory reactors can be applied. Typically, the catalyst particles have diameters in the range of 35-75 μm [8] and the catalyst is introduced into a slot of dimension 500 μm or less. Catalytic wall reactors consist of multichannels with catalytic active walls. Typical channel diameter is in the range of 50-1000 μm with a length between 20 and 100 mm. Microchannel reactors usually work under laminar flow conditions.

Cassette microreactor with integrated mixer (microreactor M) was developed by Ehrfeld Mikrotechnik BTS GmbH (Germany) for the Institute of Chemical Process Fundamentals AS CR. This reactor is able to perform chemical processes at high reaction temperature and pressure. Such a system is useful for highly exothermic reactions like total oxidation of volatile organic compounds (VOC) present in air [9].
Functionality of the microreactor M was tested in the presence of catalysts in the form of grains and monolith. The obtained data were compared with those obtained in the glass reactors standardly used in our laboratory.

2.   Experimental
Catalytic measurements

The experiments have been conducted with the Ehrfeld Mikrotechnik BTS High-Temperature Reactor Unit (MCTU 600), which is a high-pressure integrated packed-bed reactor for use within the Modular Microreaction System (MMRS) of the manufacturer. The reactor is designed to carry out gas-phase reactions in a packed catalyst bed at temperatures up to 600°C and pressures up to 100 bars (at <500°C) in a standard laboratory environment. The module is electrically heated (840 W) and features two separate pre-heating lines with

evaporation capability (up to 8 mL/min water in total), a gas mixing stage, the temperature-controlled packed bed and a liquid-cooled cooling unit, all within a compact, thermally insulated housing. The packed bed is implemented in a removable cartridge, which can easily be filled by the user with a powder or granular catalyst (Fig. 1a). Three integrated thermocouples allow a monitoring of the gas temperature at the inlet of the packed-bed cartridge, the product temperature at the outlet of the product cooler and the temperature of the heater jacket.
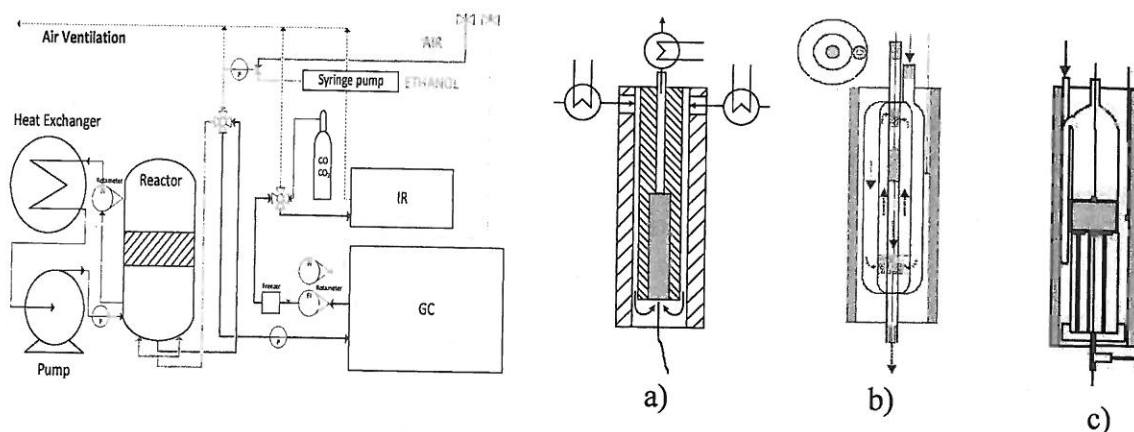

Figure 1 Schema of apparatus and reactors a) microreactor M for testing of the catalyst grains and monolith, b) glass reactor R1 for testing of catalyst grains, c) glass reactor R2 for testing of monolith.

Schema of apparatus (Fig. 1) shows the addition of ethanol into the air stream using syringe pump. After the reaction mixture flow through four-way valve to the reactor. In the reactor, the liquid ethanol in the air passes through the evaporator. Ethanol vapours and air are mixed and resulting mixture enter the catalyst placed in the cartridge. The reaction mixture flows from the cartridge through the internal heat exchanger that is kept at 70°C by the thermo-stating oil bath. Then the reaction mixture with products flows through a four-way valve directly to the gas chromatograph (HP 6890) or flows through the freezer to the NDIR gas analyser (Ultramat 23, Siemens, Germany). Hewlett-Packard 6890 gas chromatograph is equipped with a FID detector and a capillary column (HP-5 19091 J-413, 30 m × 0.32 mm × 0.25 mm with 5% phenylmethyl silicone).

Three kinds of reactors were used for catalytic activity testing: a stainless steel microreactor with inner diameter of reactor bed 4.8 mm, and two laboratory glass reactors, first one with the bed diameter of 5 mm and the second with diameter of 27.6 mm. Schemes of the reactors and their description are shown in Fig. 1 a-c.

The catalytic tests were carried out under unsteady-state conditions with rising reaction temperature from 100 to 400 °C at the constant rate of 2.27 °C min^{-1}. The catalysts were examined at gas hourly space velocity (GHSV) in the range from 20 - 80 m^3 kg^{-1} h^{-1}, unless it is mentioned otherwise. The inlet concentration of VOC (ethanol was chosen as a model compound) in the air was 1.5 g m^{-3}, i.e. 772 vpm. The temperatures at which 50% and 90% conversion of ethanol was observed (T_{50} and T_{90}) were chosen as measures of the catalyst activity.

Selectivity of the catalysts in ethanol conversion was evaluated as the concentration of reaction by-products (in vpm) corresponding to maximum GC peak area of by-products observed during oxidation of ethanol. The accuracy of the conversion and selectivity determination was ± 5 %.

Catalysts

Two kinds of industrially manufactured catalysts were used in the experiments:

a) Transition metal Co-Mn-Al mixed oxide catalyst (AST 2-100, manufactured by ASTIN s.r.o., Litvinov, Czech Republic) in the form of pellets 5x5 mm. Catalyst pellets were crushed and sieved to obtain grains of sizes 0.16 - 0.315 mm that were used for catalyst activity tests. The AST 2-100 catalyst contained Co, Mn, Al metals in molar ratio Co : Mn : Al = 4 : 0.66 : 0.74. Specific surface area was 93 m^2/g.

b) A Pd, Pt monolithic ceramic catalyst with cpsi = 400 taken from a car exhaust system after the end of its lifetime. Two smaller elements were cut off from original monolith of diameter 10 cm. The diameter of the first one was 4.3 mm and length 38 mm, diameter of the second one was 27.5 mm and length 20 mm. Chemical analysis of the monolith showed following data: 1.33 wt. % Pd, <0.1 wt. % Pt and 0.07 wt. % Ce. Surface area of the monolith was 0.6 m^2/g.

All samples were calcined 4 h in a pot furnace at 500 °C in the atmosphere of air before catalyst activity testing.

3.   Results and discussion

Catalyst activity

The grains of mixed oxide catalyst were tested in the microreactor and compared with the data from laboratory glass reactor R1. Light-off curves of ethanol conversion over the AST2-100 catalyst are shown in Fig. 2. The curves obtained in both reactors are very close but those from microreactor were observed at slightly lower temperatures. Similar course of light-off curves were obtained for the second catalyst (monolith from a car) tested in both forms monolith grains and proper monolith. From the light-off curves, the temperatures necessary for achieving 50 and 90 % conversion of ethanol ($T_{50}Et$, $T_{90}Et$) and of all organic compounds ($T_{50}VOC$, $T_{90}VOC$) were determined. Ethanol conversion 50 % was found to be at 100 °C with AST 2-100 catalyst, while the same conversion was met at 200 °C with the monolith.

Detailed analysis of the results which consisted in comparison of all characteristic temperatures obtained in glass reactor R1 and R2 versus those obtained in the microreactor M led to the temperature differences given in Table 1. Subsequent conclusions can be done: Temperatures $T_{50}Et$ and $T_{50}VOC$ of AST2-100 from glass reactor R1 are nearly identical with those from microreactor M, whereas the temperatures $T_{90}Et$ and $T_{90}VOC$ observed in the glass reactor R1 are lower by ca. 11 °C. The reason can consist in overheating of the catalyst surface during high ethanol conversion.

Characteristic temperatures observed for monolith grains in glass reactor R1 were in all cases somewhat higher (by 7 °C) than those observed in the microreactor M. Because of lower oxidation activity of the catalyst (necessary temperature region in which ethanol conversion proceeds is substantially higher) different heat flow from the catalyst layer to its vicinity in both reactors proceeds, very probably, better in the case of microreactor M.

Table 1
Temperature differences in $T_{50}Et$, $T_{90}Et$, $T_{50}VOC$, $T_{90}VOC$ resulting from comparison of data obtained in glass reactors R1 and R2 versus those from microreactor M.

Catalyst	$\Delta T_{50}Et$	$\Delta T_{50}VOC$	$\Delta T_{90}Et$	$\Delta T_{90}VOC$
AST2-100 grains	4	0	-10	-12
Monolith-grains	7	7	7	7
Monolith	-25	-25	-25	-25

In case of proper monolith catalyst testing, all characteristic temperatures determined in glass reactor R2 are lower by 25 °C. Evidently, the external mass and heat transfer in the glass reactor R2 is more substantial than in the microreactor M.

Selectivity

Depending on surface properties of the heterogeneous catalyst, oxidation of ethanol towards CO_2 can proceed, in general, via various reaction intermediates, like acetaldehyde, ethyl acetate, acetone, acidic acid, and carbon monoxide, according to following reaction scheme:

$$C_2H_5OH \rightarrow CH_3CHO \rightarrow (CH_3COOH, CH_3COOC_2H_5, CH_3COCH_3, CO) \rightarrow CO_2$$
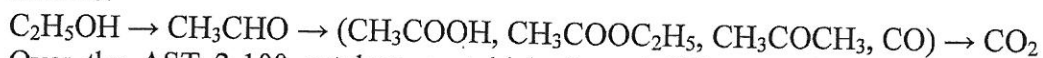
Over the AST 2-100 catalyst, acetaldehyde and CO were the only intermediate products during ethanol oxidation towards CO_2; acetaldehyde being the major intermediate product. The absence of ethyl acetate in the products indicates that acetate species are not formed on the catalyst surface and therefore, they cannot react with adsorbed ethanol via an esterification reaction. The major path appears to be the direct oxidation of acetaldehyde to CO_2, while its oxidation via the acetic acid should be a minor path, because neither acetic acid, nor ethyl acetate is detected in the products. Moreover, acetic acid is oxidized at higher temperatures than ethanol [10, 11] and if it is produced in the course of ethanol oxidation, it should certainly appear in the reaction products.

Fig. 3 presents the concentration of acetaldehyde found in the reaction mixtures obtained with this catalyst at space velocities 20; 40; and 80 m^3 kg^{-1} h^{-1}. Higher space velocity led to a shift of the maximum of acetaldehyde concentration to higher temperatures what corresponds to lower ethanol conversions due to shorter residence time. Differences in the data obtained for the catalyst grains from the microreactor and the glass reactor R1 seems to be relatively small with exception of CO concentration in the reaction mixture.
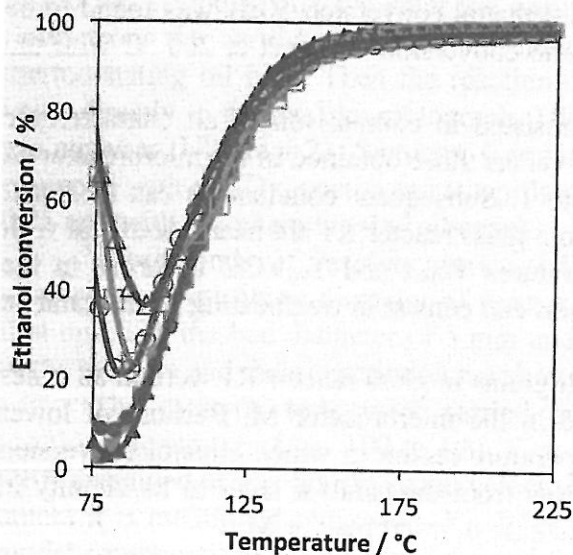

Fig. 2 Ethanol conversion over AST2-100 catalyst grains obtained in the microreactor M (open symbols) and the glass reactor R1 (filled symbols) in dependence on reaction temperature for various space velocities (■, □ - 80, ●, ○ - 40, ▲, △ - 20 m^3 kg^{-1} h^{-1}.
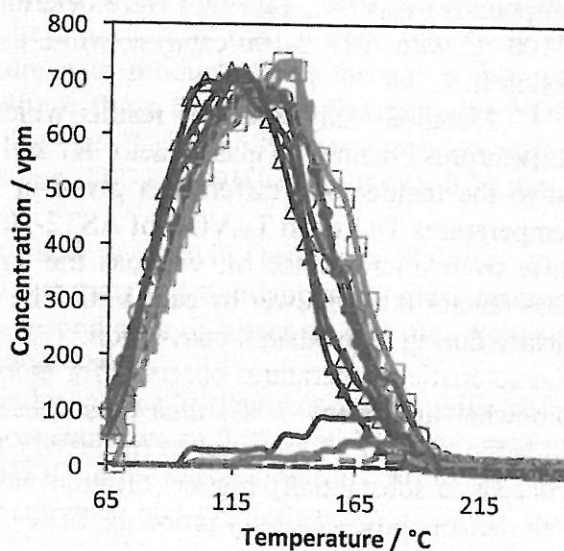
Fig. 3 Concentration of acetaldehyde and CO formed during oxidation of ethanol over the AST2-100 catalyst grains at various space velocities (■,□ - 80, ●,○ 40, ▲,△ 20 m^3 kg^{-1} h^{-1}) in the microreactor M (open symbols) and the glass reactor R1 (filled symbols). Solid lines without points – CO concentration glass reactor R1, dashed lines – CO concentrations in microreactor M.

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In the glass reactor R1, CO appeared already at very low temperature, about 90 °C, what indicates that such low temperature is not sufficiently high for complete oxidation of CO to CO_2 as temperature higher than 200 °C is necessary. In the microreactor M, CO either appeared at temperature above 150 °C (at space velocity 80 m^3 kg^{-1} h^{-1}) or did not appear at all (at space velocities 20 and 40 m^3 kg^{-1} h^{-1}).

The second catalyst tested (Pd, Pt catalyst supported over monolith) did not show identical selectivity as the AST 2-100 catalyst. Again, the main reaction intermediate was acetaldehyde, but the minor part of intermediates varied: in contrast to the metal oxides catalyst which showed distinct amount of CO in the reaction mixture, the Pd, Pt monolithic catalyst exhibited small quantity of acetic acid. The results obtained with monolith grains in both reactors, M and R1, can be seen in Figures 4a, b. Figure 4a shows concentrations of reaction component, reaction intermediates and reaction product (CO_2) obtained in the microreactor M and Fig. 4b shows concentrations of the same components obtained in the glass reactor R1. It can be seen that the main difference is in concentration of acetaldehyde whose appearance starts in the glass reactor at lower temperature than in the microreactor M. In the microreactor M, concentration of acetaldehyde in dependence on reaction temperature is symmetric, in contrast to that obtained from glass reactor R1. The finding indicates the influence of external mass and heat transfer in the glass reactor R1.

Ethanol oxidation towards CO_2 over supported monolithic Pd, Pt catalyst, in contrast to ethanol oxidation over AST 2-100 catalyst, proceeds through intermediate formation of both acetaldehyde and acetic acid, concentration of CO being very low (Figure 5a, b). Similar products were identified in the reaction mixture of ethanol oxidation over Pt/Al_2O_3 catalysts [12, 13].
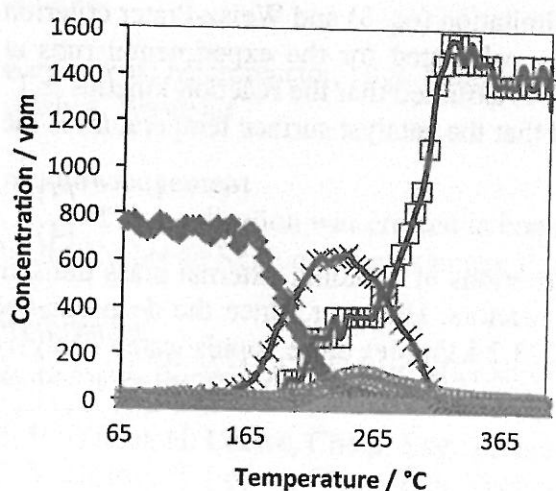
Figure 4a
Concentrations of ethanol (♦), acetaldehyde (x), CO (Δ), acidic acid (O) and CO_2 (□) observed in the microreactor M during oxidation of ethanol over the monolith grains at space velocity 80 m^3 kg^{-1} h^{-1}.
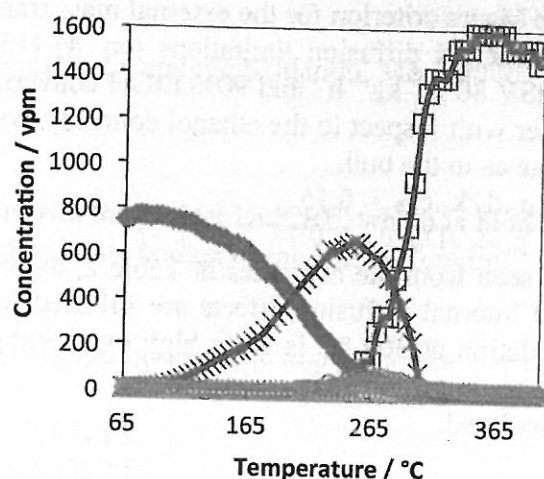
Figure 4b
Concentrations of ethanol (♦), acetaldehyde (x), CO (Δ), acidic acid (O) and CO_2 (□) observed in the glass reactor R2 during oxidation of ethanol over the monolith grains at space velocity 80 m^3 kg^{-1} h^{-1}.

Influence of macrokinetic effects is supposed to be more pronounced in the glass reactor R2 used for examination of the large monolithic catalyst samples. Following test was performed to prove experimentally the mentioned idea: oxidation of ethanol was carried out first with increasing temperature of the catalyst layer and immediately after achieving the maximum temperature (400 °C) the catalyst was cooled down with the same rate to 50 °C. Distinct differences in the course of both dependencies were detected (temperature hysteresis

of $\Delta T_{50}Et$ is nearly 45 °C), temperatures observed during cooling of the catalyst monolith being always lower. The phenomenon is evolved by overheating of the catalyst surface caused by reaction heat in preceding catalytic test.

As the microreactor M is made of stainless steel (Alloy 600), it was necessary to prove, whether the reactor construction material is not catalytically active. It was found out that the construction material of the microreactor exhibits some catalytic activity when the reaction mixture entered the empty reactor. Starting at ca. 170 °C formation of acetaldehyde appeared reaching the maximum 420 ppm at ca. 320 °C. Conversion of ethanol at 400 °C met the value of ca. 30 %, concentration of acetaldehyde was 200 ppm and the other by-product, CO, met the value of 150 vpm. Fortunately, the results of the AST 2-100 testing are not affected by this fact, as formation of acetaldehyde was finished at ca. 170 °C. In case of the monolith testing, the situation is more complicated as acetaldehyde started forming at about 170 °C and therefore, both catalytic actions are coinciding. For that reason, it is necessary to secure minimal influence of the microreactor construction material on data of catalyst testing.

Analysis of mass and heat transfer in the reactors used

The reactors M, and R1 used for testing of catalyst grains were analysed from the mass and heat transfer point of view. Analysis concerns of the plug flow, axial dispersion, external heat and diffusion limitations. With the packed bed, plug flow and rectangular velocity profile can be considered [14, 15] for ratio $D_t/d_p > 10 - 15$. (1)

From Table 2 it can be seen that this condition for both packed bed reactors is roughly fulfilled except the testing of the monolith in the reactor R1.

Axial dispersion is negligible when $L_b/d_p > (a/Pe_p) \ln (1/(1-X_A))$, where a= 8 or 20. (2)

The condition is fulfilled for both packed bed reactors and the reactors for monolith testing.

The Maers criterion for the external mass transfer limitation (eq. 3) and Weisz-Prater criterion for internal diffusion limitations (eq. 4) [15] were calculated for the experimental runs at GHSV 80 m^3 kg^{-1} h^{-1} and 90% EtOH conversion. It is assumed that the reaction kinetics is 1st order with respect to the ethanol concentration and that the catalyst surface temperature is the same as in the bulk.

$-r_A.\rho_c.d_p/k_c.c_{Ab} < 0.15$ (3)

$-r_A. \rho_c.d_p^2/D_{eff}.c_{As} > 0.15$ (4)

As seen from the estimates in Table 2, the both criterions of avoiding external mass transfer and internal diffusion effects are fulfilled for all reactors. However, since the deep ethanol oxidation at 300 °C is quite high exothermic (-1273.2 kJ/mole) more sophisticated analysis has to be performed to confirm the validity of assumptions taken and hence criterion values calculated.

Conclusion

Analysis of the total oxidation of ethanol including reaction intermediates data obtained in the examined reactors on the temperature showed that different material applied in the construction of reactors and their arrangement give slightly different results of catalyst testing, the ones obtained from microreactor being more precise. More precise control of reaction temperature due to higher heat transfer capabilities and limited backmixing of reaction mixture in a packed bed microreactor is advantageous and leads to the more accurate results of oxidation catalysts testing. However, it is necessary to ensure in order the material used for the reactor construction did not affect the catalytic reaction.

The results accomplished confirm that microreactors are not only suitable for performing of catalytic reactions in a laboratory scale but also promising way for creation of new, safer and cleaner production processes.

Table 2

Description of the experimental reactors M, R1 and R2.

Catalyst	AST 2-100	AST 2-100	Monolith	Monolith	Monolith	Monolith
Catalyst form	Grains	Grains	Grains	Grains	Monolith[a]	Monolith[a]
Reactor	M	R1	M	R1	M	R2
D_t (mm)	4.8	5	4.8	5	4.8	27.6
Catalyst weight (g)	0.100	0.100	0.100	0.100	0.228	5.8368
Catalyst size (mm)	0.315	0.315	0.315	0.315	4.3x38	27.5x20
Number of channels	-	-	-	-	5	306
d_p (mm)[b]	0.315	0.315	0.315	0.315	d_H=1.17	d_H=1.17
Bed density (g/ml)	1.3158	1.3158	0.918	0.918	0.400	0.400
Length of bed L_b (mm)	4.2	3.9	4.2	3.9	38	20
Porosity of particle (%)	35	35			35	35
D_t/d_p[b]	15.2	15.9			4.1	23.6
L_b/d_p[b,c]	14	12	13	12	33	17
GHSV (m^3/kg/h)	80	80	80	80	73	80
Maers (eq. 3)	0,0017	0,0019	-	-	0,0001	0,0001
Weisz-Prater (eq. 4)	1.33	1,15	-	-	33,20	9,19

[a]cpsi (number of channels per square inch) = 400, characteristic dimension [16]: cell density 62 cell/cm^2; wall thickness 0.16 mm; geometrical surface area 25700 m^2/m^3; void fraction 0.35; dimension of channels = 1.0369 mm

[b]The biggest particles are considered for verification of plug flow. In the case of monolith, hydraulic diameter of channels d_h was taken into account;

[c]Calculated for 90 % C_2H_5OH conversion and Pe_p=0.5 valid for low Re [15]. Required minimal value is 15-38.

Key words: Microreactor, High-temperature application, Catalytic oxidation, Monolithic catalyst, Waste air

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List of symbols

Abbreviation	Description
c_{Ab}	Concentration of A in bulk of gas (mol m^{-3})
c_{As}	Concentration of A on the catalyst surface (mol m^{-3})
d_p	Catalyst particle diameter (m)
d_h	Channel hydraulic diameter (m)
D_t	Reactor tube diameter (m)
D_{eff}	Effective diffusion coefficient (m^2/s)
k_c	Mass transfer coefficient (m s^{-1})
L_b	Length of catalyst bed (m)
$-r_A$	Reaction rate of component A (mol s^{-1} g^{-1}) at 90 % conversion
Pe_p	Peclet number
Re	Reynolds number
X_A	Conversion of component A

Greek letters

ρ_c	Bulk density of catalyst (kg m^{-3})

Subscripts

A	Component A = Ethanol
b	Catalyst bed
c	Catalyst
p	Particle