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Research Article

“Sandwich Reactor” for Heterogeneous Catalytic Processes: N₂O Decomposition as a Case Study

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A novel “sandwich” microreactor designed as a thin (~ 300 μm) porous plate of sintered metal fibers (SMF), sandwiched between metallic plates is reported. The SMF surface was coated by Fe-ZSM-5 thin film (< 2 μm) rendering a catalyst highly active in the decomposition of N₂O. The 3D open microstructure of SMF plates presents a low pressure drop during the passage of reacting gases. The high thermoconductivity of metallic SMF improves the heat transfer, avoiding hot-spot formation during exothermic reactions. The temperature measured in the middle and at the outlet of the reactor confirmed the isothermal reactor operation. The sandwich microreactor showed high permeability and a narrow residence time distribution close to an ideal plug-flow reactor. The kinetics of the N₂O decomposition was studied and the reaction was shown not to be limited by mass transfer when conducted in the microreactor.

Keywords: Fe-ZSM-5, Heterogeneous catalysis, Microreactor, Sintered material fiber, Zeolithe coating

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1 Introduction

The manufacture of chemicals in catalytic micro-structured reactors (MSR) has recently become a new branch of chemical reaction engineering focused on process intensification and safety [1–3]. MSR are of high specific surface area in the range of 10000 to 50000 m²/m³ which allows an effective mass and heat transfer if compared to traditional chemical reactors [4]. MSR operated under laminar flow have a heat transfer coefficient for liquids of about 10 kW/(m² K). This is one order of magnitude higher than in the traditional heat exchangers avoiding hot-spot formation, allowing higher reaction temperatures and reducing reaction volumes. This, in turn, improves the energy efficiency and the operational cost. A narrow residence time distribution (RTD) is attained due to small MSR diameters < 500 μm.

One of the main problems in using MSR for heterogeneously catalyzed gas-phase reactions is the introduction of the catalyst in the reaction zone. The straightforward way is to fill the microchannels with catalyst powder [5]. The size of the particles introduced generally ranges between 35 and 75 μm in

diameter, leading to a high pressure drop during the passage of fluid. In addition, each channel must be packed identically to avoid maldistribution, which is known to broaden residence time distribution while diminishing reactor performance [6].

Another approach is MSR with catalytically-active walls [7, 8]. The specific surface area is increased by chemical treatment of the channel walls or by their coating with a porous layer. The porous layer can serve as a catalyst or a support for a catalytic phase. The main limitation of a catalytic-wall MSR is the thickness of the porous layer [9]. Since the majority of MSR are used for fast, highly exothermic reactions, the layer should be < 1–2 μm in order to avoid mass/heat transfer limitations [10]. Therefore, the total mass of the catalyst is too small for achieving high performance preferred for a unit of the reactor volume [11, 12].

We report herein a novel “sandwich microreactor” with a structured catalytic bed of high specific surface area (SSA) consisting of thin (~ 300 μm) porous plates of sintered metal fibers (SMF). SMF plates are sandwiched between regular metallic plates, which provide integrated heat exchange. Each SMF plate possesses a 3-dimensional regular microstructure, resulting in a low pressure drop during the passage of reacting gases.

The SMF porous material serves as a support for the catalytically-active phase, consisting of Fe-ZSM5 film (< 2-μm thickness). The high surface of SMF allows deposition of a considerable quantity of the catalyst without increasing the thickness of the active phase and a low mass-transfer resistance [13–17].

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The Sandwich MSR was characterized for the pressure drop, residence time distribution, and was tested in the N_2O decomposition as a model highly-exothermic reaction [18–21]. The temperature was measured at the reactor outlet confirming the isothermal reactor operation.

2 Reactor Concept

The Sandwich MSR is presented schematically in Fig. 1. The reactor consists of two thick plates with heaters between which sintered metal fiber (SMF) plates ($70\text{ mm} \times 30\text{ mm} \times 0.35\text{ mm}$) were placed (Fig. 2). The reaction mixture enters through an inlet tube in an empty space in front of the SMF, passes through the catalytic bed and is analyzed at the outlet. The inlet and outlet were placed on the same wall of the reactor. A thermocouple was put in the center of the wall, touching the SMF catalyst. Two different configurations were studied. For both, the surface of the catalytic bed is $70\text{ mm} \times 30\text{ mm}$ but they differ in thickness, that is $300\text{ }\mu\text{m}$ for the small MSR (one layer of SMF plate) and $800\text{ }\mu\text{m}$ for the larger MSR (three layers of SMF plate placed as a structured packed bed).

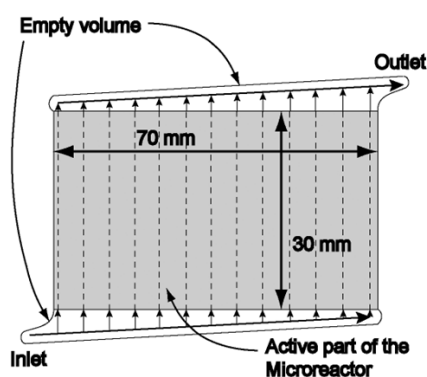


Figure 1. 2D scheme of the sandwich microreactor.

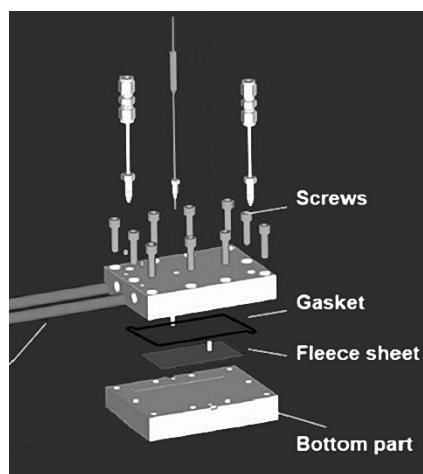


Figure 2. 3D scheme of the sandwich microreactor, a small arrangement with 1 fleece of SMF and a larger one with 3 fleeces of MSF inside the MSR.

3 Experiments

3.1 Materials

Sintered metal fibers (SMF) (Southwest Screens & Filters SA, Belgium) made of FeCrAlloy (Cr 20%; Al 4.75%; Y 0.27%; other elements 1–2%; Fe balance) in the form of a uniform pore panel (0.29 mm thick, 71% porosity, 675 g/m^2) were used as supports for zeolite coating. The panels were cut to fit the Sandwich reactor dimensions ($70\text{ mm} \times 30\text{ mm}$). Chemicals (Fluka, Aldrich, > 98%) and gases (Carbagas, > 99.99%) were used as received.

3.2 Catalyst Preparation

Prior to the catalyst preparation, the SMF plates were boiled twice in toluene for 0.5 h, calcined in air at 874 K to remove contamination and to form an oxide layer. The SMF plates were then treated in a 0.5-% aqueous solution of poly(dimethylamine-co-epichlorohydrine) for 0.5 h, rinsed in a 0.1-M ammonia solution, and air dried. The colloidal solution of seed crystals (silicalite-1) was prepared from a mixture containing tetrapropylammonium hydroxide (TPAOH, Fluka, 20% in water), tetraethoxysilane (TEOS, Fluka, 98%), water and ethanol in the molar ratio TPAOH:TEOS:H₂O:C₂H₅OH = 9:25:480:100 [22, 23]. The mixture was treated hydrothermally with reflux at 374 K for 48 h. The silicalite-1 solution obtained was purified four times by centrifugation and redispersion in water. The final pH, 10, was obtained by the addition of aqueous ammonia. The polyelectrolyte modified SMF plates were immersed in the silicate-1 solution for 0.5 h. After adsorption of the seeds, the filters were rinsed in a 0.1-M NH₃ solution with sonication (four times), dried in air at 824 K for 4 h. In order to form a zeolite film on the metal surface, the seeded filters were placed in a synthesis gel and hydrothermally treated in a 200-ml autoclave at 449 K for 24 h [24]. Tetraethylorthosilicate (TEOS, Fluka, 98%) was added to an aqueous solution of tetrapropylammonium hydroxide (TPAOH, Fluka, 20% in water) used as a template, NaAlO₂ (Riedel-de Haën, Na₂O, 40–45%; Al₂O₃, 50–56%), and Fe(NO₃)₃·9H₂O (Fluka, 98%). The molar ratios between components were TEOS:TPAOH:H₂O = 40:10:20,000 and Si:Al:Fe = 50:1:0.025. To increase the zeolite film thickness, the hydrothermal treatment can be repeated.

The zeolite/SMF samples obtained and powder zeolite were calcined in air at 824 K for 24 h to burn the organic template and converted into the H-form by ion exchange with a 1-M NH₄NO₃ aqueous solution (24 h, 298 K) followed by calcination at 824 K for 4 h. Finally, the FeZSM-5/filters catalyst was activated by steaming (H₂O partial pressure of 0.3 bar, He flow, 2.0 l/min) at 824 K for 4 h [13].

3.3 Catalyst Characterization

The specific surface area (SSA) of the catalysts was measured using N₂ adsorption-desorption at 77 K with a Sorptomatic 1990 (Carlo Erba) after catalyst pre-treatment in vacuum at 523 K for 2 h, and calculated employing the BET method.

Due to the presence of Fe in the filters, the element analysis of powder zeolites collected from the bottom of the autoclave was performed. The chemical composition (concentration of Fe and the ratio of Si/Al) of the powder zeolites were determined by atomic absorption spectroscopy (AAS) via a Shimadzu AA-6650 spectrometer with a N₂O-acetylene and air-acetylene flame after dissolving the powder zeolite in aqueous HF and HNO₃.

Catalyst morphology was studied by scanning electron microscopy (SEM) using a Philips XL 30 SFEG.

3.4 Reactor Characterization

The pressure drop in the sandwich reactor was measured with a N₂ gas flow in the empty reactor, and reactor + SMF with different zeolite loadings (0 wt %, 4 wt %, and 6.5 wt %). The pressure drop was measured by a manometer for several flow rates.

Residence time distribution (RTD) was characterized by a step method, measuring the break-through curves using He and N₂. First, gas (He) is injected uninterruptedly and a second gas (N₂) replaces it quickly. Various flow rates were used between 6 and 100 ml/min. The measurements were performed in a Micromeritics AutoChem 2910 analyzer at atmospheric pressure and room temperature (298 K).

3.5 Model Exothermic Reaction

The N₂O decomposition [25] was used as a model exothermic reaction to characterize the sandwich MSR. The reaction mixture contained 10 vol.-% N₂O and 90 vol.-% He, and was analyzed by online GC (Perkin-Elmer Autosystem XL). The gases (N₂, O₂, and N₂O) were separated in a Carboxen-1010 capillary column and detected by TCD. The reaction temperature was monitored by a thermocouple placed in the center of the catalytic filters (Fig. 2). A second thermocouple was placed at the outlet.

The catalyst was pre-treated at 774 K in He (2.0 L/min) for 1 h before the N₂O decomposition, in order to remove the water adsorbed. The reaction temperature was increased stepwise every 324 K from 300 to 874 K. The N₂O, N₂, and O₂ concentrations were monitored. The conversion was calculated from the difference between inlet and outlet concentrations of N₂O (see Eq. (1)).

$$X = \frac{C_{in} - C_{out}}{C_{in}} \quad (1)$$

4 Results and Discussion

4.1 Catalysts Characterization

The morphology of the zeolite layer on SMF was studied by SEM and the results are presented in Figs. 3a–b). The homogeneity of the ZSM deposition can be observed and the thickness of the deposited layer of zeolite can be estimated. SEM images

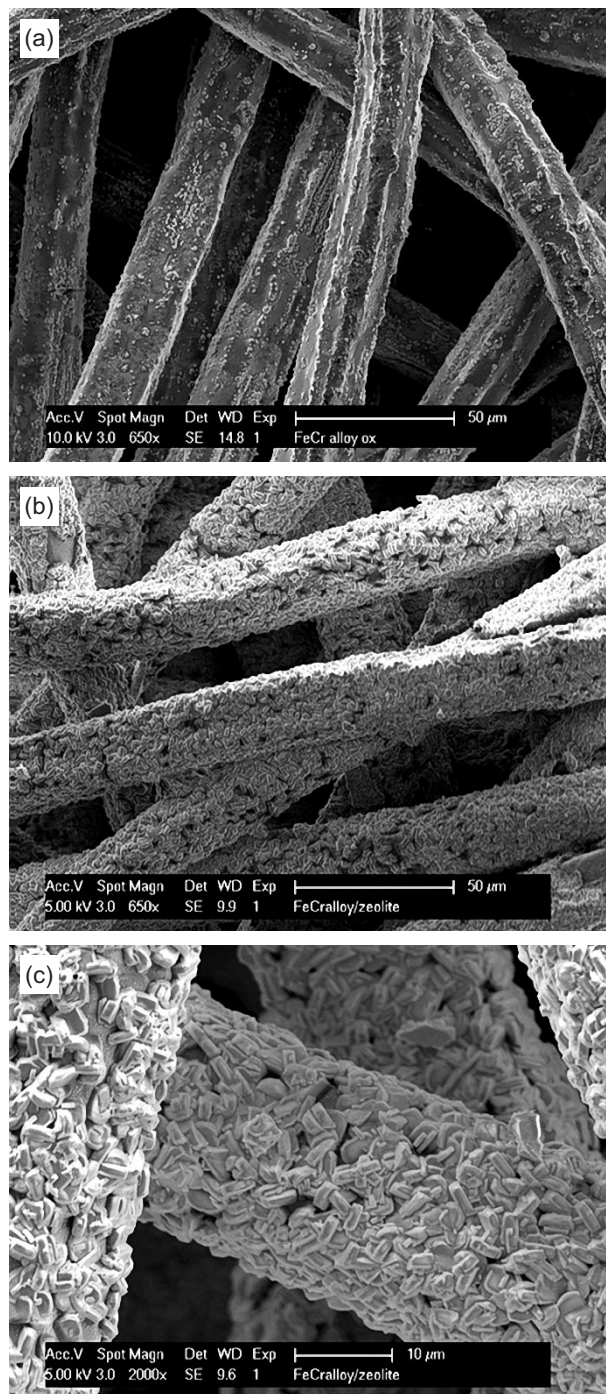


Figure 3. SEM pictures of the SMF before (a) and after (b, c) coating by ZSM-5 (loading 5 wt %).

before and after the deposition reveal the absence of agglomerates between the fibers. Moreover, the thickness of the coated fibers is constant, confirming the deposition homogeneity. The thickness for a loading of 5 wt % estimated by the comparisons between the images, with and without deposition, was ~ 2 μm. The specific surface area (SSA) of this sample was found to be 300–320 m²/g.

The results of the chemical analysis shows a ratio of Si/Al = 85 and the concentration of Fe = 6540 ppm.

4.2 Pressure Drop

Two different arrangements of the sandwich MSR were tested: (1) containing only one SMF with a loading of 0, 5.4, and 8.9 wt %; (2) containing 3 plates of SMF with the same loading. The pressure drop was measured in the laminar flow regime and the results are presented in Fig. 4. Linear dependence on the flow rate for both arrangements has been found.

Darcy's law (Eq. (2)) for the pressure drop (ΔP^D) in a laminar flow was fitted to the experimental data by a least-squares method, minimizing the sum of the squared residuals (SSR):

$$\frac{\Delta P}{\Delta h} = \frac{\mu Q}{kA} \left[\frac{Pa}{m} \right] \quad (2)$$

with the surface, $A = 3 \cdot 10^{-4} \text{ m} \times 7 \cdot 10^{-2} \text{ m}$, the length of the reactor, $\Delta h = 3 \cdot 10^{-2} \text{ m}$, the dynamic viscosity, $\mu_{N_2} = 0.01691 \text{ mPa s}$ (NTP), and the flux, Q (units of volume per time, m^3/s). The permeability factor, k (units of area, m^2), was calculated for different loadings of zeolite and is plotted in Fig. 5. The zeolite coating decreases permeability and leads to a higher pressure drop.

The pressure drop over a fixed bed of 1- μm spherical particles (same order of magnitude as the individual crystals in the coating on the SMF) was estimated with the Ergun equation, porosity = 0.4. The comparison was performed with the same flow rate and the same catalyst mass. The pressure drop over the fixed bed would be three orders of magnitude higher compared with the structure bed in the sandwich reactor.

4.3 Residence Time of Distribution

The RTD was obtained from measured response curves to the step change in the reactor inlet from flow of He to N_2 . The responses were first obtained for the installation only (without reactor). Then the measurements were carried out for the empty reactor without SMF. Finally, MSR + SMF coated by FeZSM-5 (6.9%) was characterized. The $F[-]$ function was obtained after a normalization of the concentration response. These three functions, $F[-]$, are shown in Fig. 6.

The axial dispersion in MSR is however more visible when the function, $F[-]$, is transformed into a function, $E(t)$, as presented in Fig. 7.

The $E(t)$ curve was calculated from the following equation:

$$E(t) = \frac{dF}{dt} \approx \frac{\Delta F}{\Delta t} \quad (3)$$

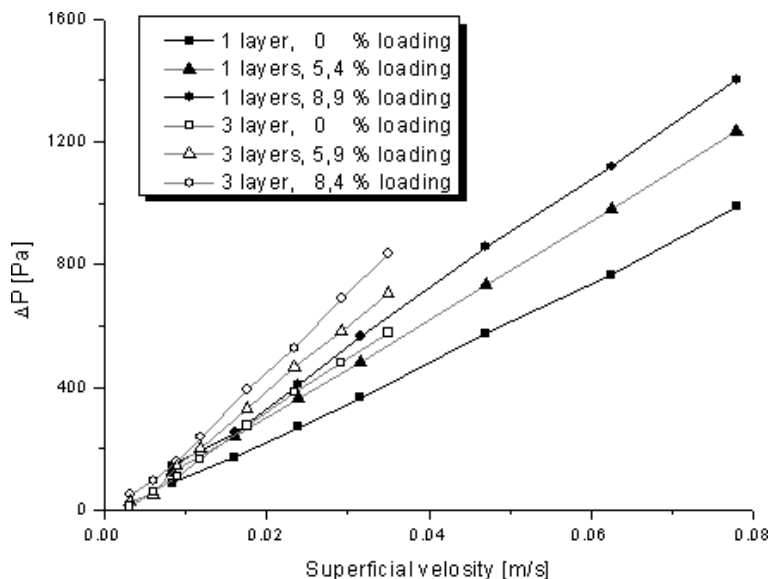


Figure 4. Pressure drop in the compact “sandwich reactor” with and without ZSM-5 coated SMF.

The mean residence time, \bar{t}_R , was calculated as the difference in residence time of the installation with the reactor, \bar{t}_{I+R} , and without the reactor \bar{t}_I :

$$\bar{t}_R = \bar{t}_{I+R} - \bar{t}_I \quad (4)$$

The RTD obtained for the sandwich reactor with or without filter is the result of the distribution of the installation without reactor and the RTD of the reactor itself.

$$F(t)_{I+R} = F(t)_I - F(t)_R \quad (5)$$

A numeric simulation with the software, Berkeley MadonnaTM [26], using the relation in Eq. (5) was conducted to get the RTD within the reactor without influence of the installation.

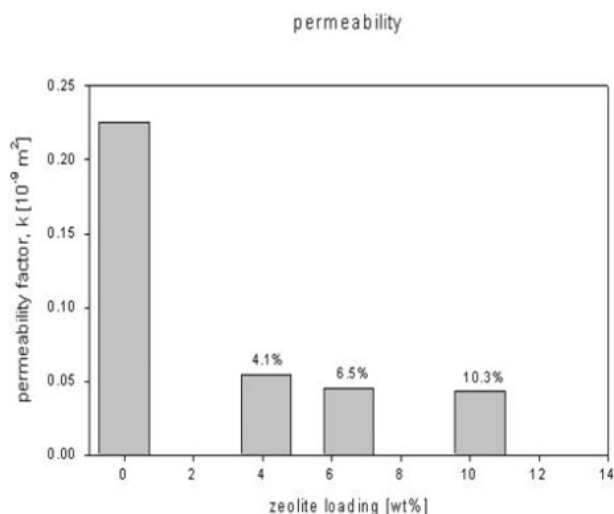


Figure 5. Permeability of the reactor containing one layer of SFM with different loadings of ZSM-5.

1) List of symbols at the end of the paper.

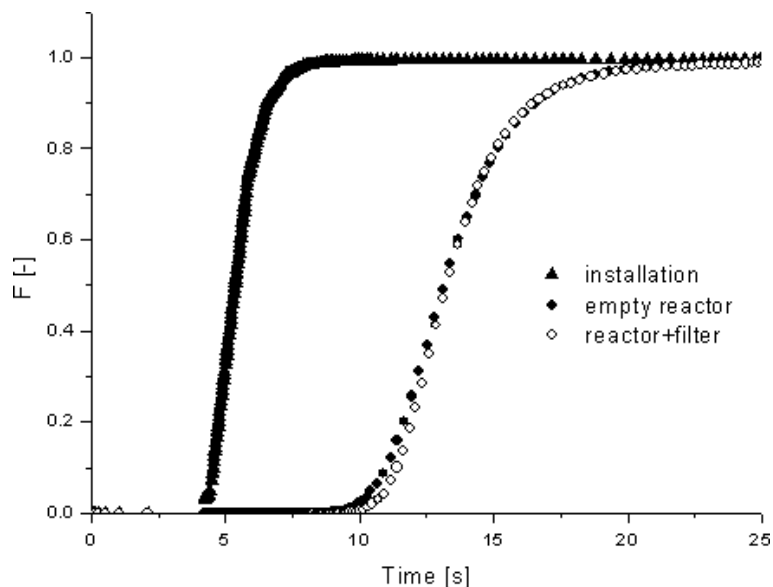


Figure 6. Break-through curve, He→N₂ at flow rate 20 mL/min, T = 298 K.

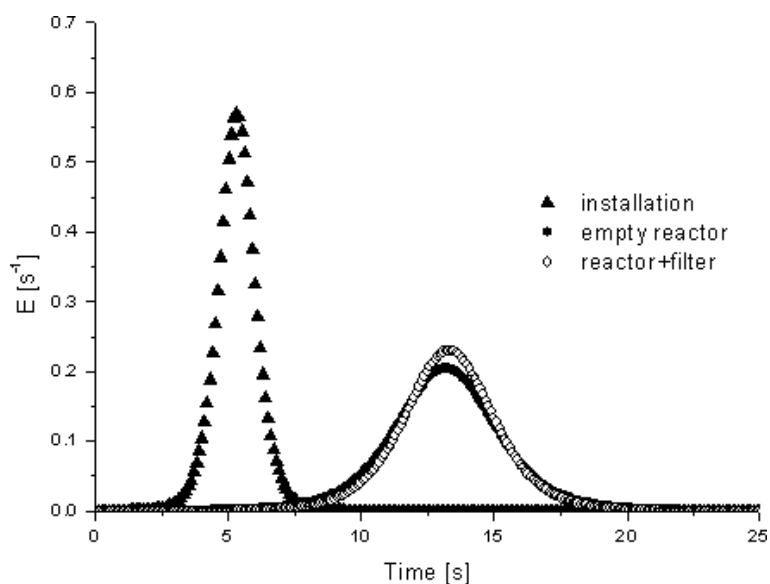


Figure 7. $E(t)$ curve, He→N₂ at flow rate 20 mL/min, T = 298 K.

Table 1. Characterization of RTD.

Flow rate (mL/min)	Reactor with 1 layer		Flow rate (mL/min)	Reactor with 3 layers	
	Bo (empty reactor)	Bo (reactor + filter)		Bo (empty reactor)	Bo (reactor + filter)
6	11	22	9	8	15
10	15	38	15	11	18
20	42	59	30	23	44
30	73	86	45	21	40
40	75	89	60	22	44

Comparison of the RTD of the sandwich reactor with and without the catalytic filter is shown in Fig. 8. The addition of the filter improves the RTD under all conditions applied.

Different flow rates were applied to obtain the RTD curves. Fig. 9 shows the RTD with SMF filter placed in the reactor as one layer and Fig. 10 is for the reactor with three layers of SMF.

The flow rates during the measurements were adjusted to have the same residence time (τ) for three layers as for the single-layer reactor configuration. Although the dimensions of the SMF layer correspond to nearly three times less the dimensions of three layers, it was calculated that the total volume of the sandwich reactor increased only 1.5 times because of the impact of the empty volume (see Fig. 1). The volumes before and after the SMF plate were taken into account. Tab. 1 presents the results obtained.

The RTD was characterized by the Bodenstein number calculating as the following:

$$Bo = \frac{t_{\text{disp}}}{\tau} = \frac{u L}{D_{\text{ax}}} \quad (6)$$

where t_{disp} is dispersion time, τ [s] – residence time, u [m/s] – linear velocity, L [m] – length of the reactor, and D_{ax} [m²/s] – axial dispersion coefficient of the gas. The beneficial influence of the metal fiber plate on the RTD was observed in all cases. The reactor with one layer presents a Bodenstein number much higher than the reactor with three layers. At relatively high flow rate (> 20 mL/min), the sandwich reactor with one SMF layer demonstrated a flow pattern close to an ideal plug-flow tubular reactor ($Bo > 100$). These results indicate that for 3-layer MSR configuration, a longer bed is needed to obtain narrow RTD with higher Bo numbers (narrow RTD).

4.4 N₂O Decomposition

N₂O decomposition was used as a model reaction to test the performance of the sandwich micro-structured reactor. The decomposition of N₂O into N₂ and O₂ catalyzed by Fe-ZSM-5 is known to be

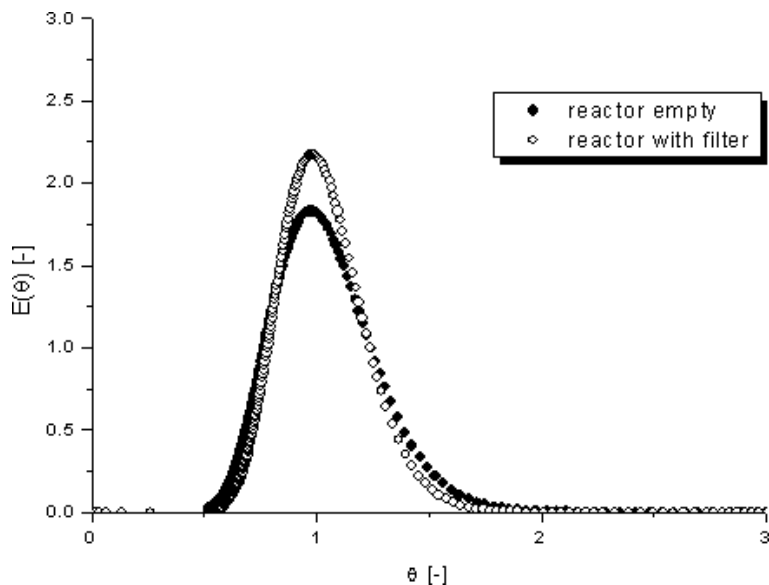


Figure 8. $E(\theta)$ curve, $\text{He} \rightarrow \text{N}_2$ at flow rate 20 mL/min, $T = 298$ K, numerical simulation.

highly exothermic; $\Delta H = -88$ kJ/mol at 673 K. The reaction starts at temperatures higher than 574–674 K. The synthesized structure of Fe-ZSM-5/SMF with zeolite loading of 5.0 wt % was placed in the MSR and tested in N_2O decomposition. Three SMF samples with equivalent amounts of zeolite were prepared to compare the conversion in two reactor configurations. The total mass of the FeZSM-5 coating was 0.08 g for the sandwich reactor with one layer and 0.24 g for three layers. The mass of the catalyst per unit volume is the same for these two reactors (the difference < 5 %). A series of measurements were conducted to compare the influence of different para-

meters on the decomposition. Two space times through the catalytic bed were applied, $\tau = 1.2$ and 3.9 seconds. For each space time, the conversion was measured at different temperatures between 578 K and 878 K. The results obtained are presented in Fig. 11. As is seen, the reaction starts at a temperature higher than 578 K, but the difference in conversion becomes noticeable only above 800 K.

The catalyst activity for both reaction configurations was found to be identical. The increase by 3-fold the residence time with a 3-fold decrease of the internal volume gives the same conversion (for the configuration 1-layer with $\tau = 3.9$ s and the 3 layers with $\tau = 1.2$ s). During these measurements, no hot-spot formation was observed even at conversion up to 90 %.

The N_2O decomposition is known to have 1st order kinetics toward N_2O . So the conversion could be related to the residence time supposing plug flow behavior:

$$X = 1 - \exp(-k\tau) \quad (7)$$

where k is the reaction rate constant according to the Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

Therefore, from Eqs. (7) and (8), we obtain:

$$X = 1 - \exp\left(-k_0\tau \exp\left(-\frac{E_a}{RT}\right)\right) \quad (9)$$

Eq. (9) was applied for two different flow rates as shown in Fig. 12 and was used to estimate the apparent activation energy (E_a).

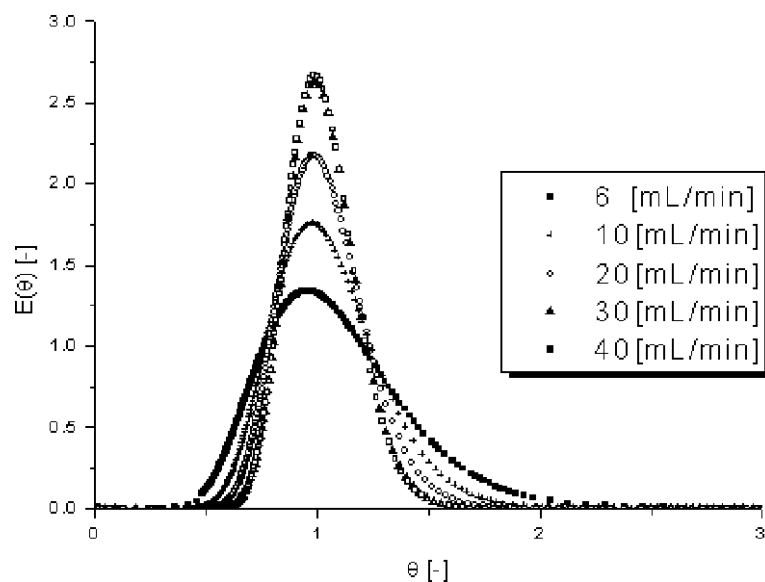


Figure 9. RTD curve in the sandwich reactor characterized by the $E(\tau)$ function obtain at different flow rates, one SMF layer.

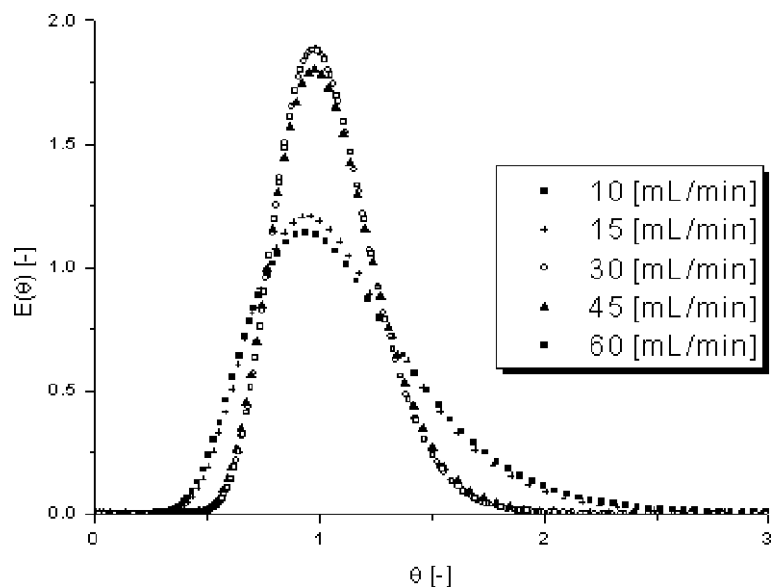


Figure 10. RTD curve in the sandwich reactor characterized by the $E(\tau)$ function obtain at different flow rates, three SMF layers.

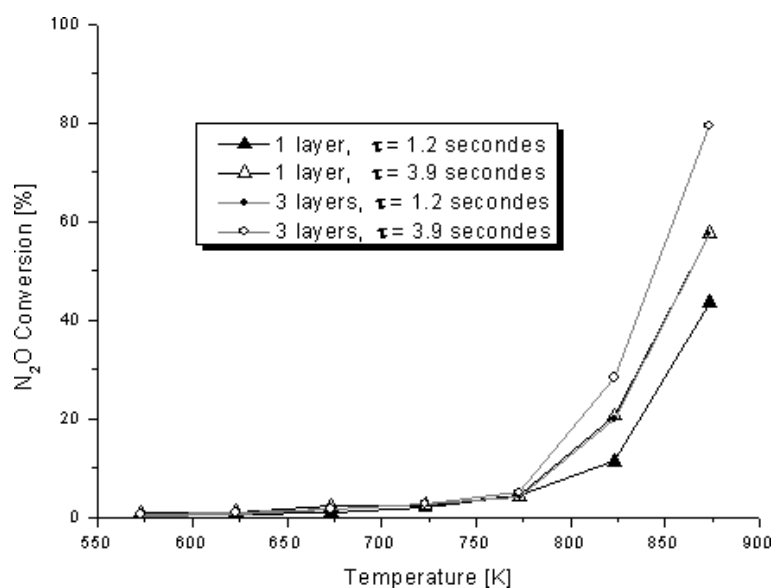


Figure 11. Conversion for 2 different space times (reaction mixture: 10 vol.-% of N_2O , 90 vol.-% of He, zeolite 0.08 g (one layer) and 0.24 g (three layer)).

The high energy of activation found ($E_a = 79$ kJ/mol) indicates that the reaction is not limited by diffusion.

5 Conclusion

- A new compact catalytic “sandwich” microreactor with a structured catalytic bed is developed using sintered metal fiber (SMF) coated homogeneously by a thin (2 μ m) layer of FeZSM-5.
- The sandwich reactor was characterized by permeability, pressure drop (ΔP), and the residence time distribution

(RTD). The introduction of the SMF bed inside the microreactor increases ΔP , decreasing the permeability. The RTD was characterized by Bodenstein numbers, and the value ~ 90 indicates a flow pattern close to that of an ideal plug-flow reactor.

- The sandwich MSR was tested in exothermic decomposition of N_2O at temperatures 574–874 K, varying residence time between 1.2 and 3.9 s. Under the conditions applied, no hot-spots formation has been observed and the reaction kinetics was not influenced by diffusion.

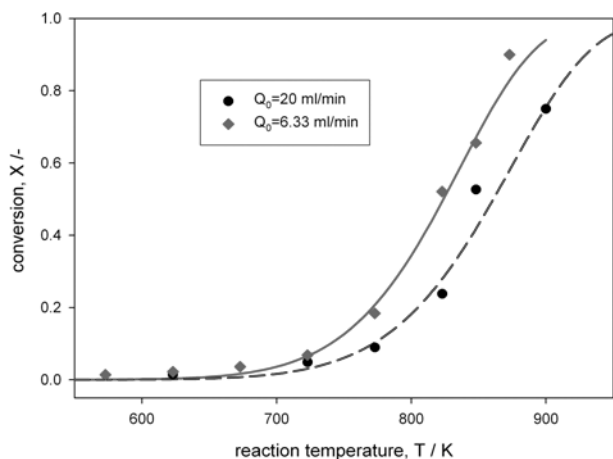


Figure 12. N_2O decomposition conducted in the sandwich reactor, one layer for two different space times, zeolite 0.08 g.

Acknowledgements

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References

- [1] G. Kolb, V. Hessel, *Chem. Eng. J.* **2004**, *98*, 1.
- [2] K. F. Jensen, *Chem. Eng. Sci.* **2001**, *56*, 293.
- [3] K. Schubert et al., *Microscale Thermophys. Eng.* **2001**, *5*, 17.
- [4] L. Kiwi-Minsker, A. Renken, *Catal. Today* **2005**, *110*, 2.
- [5] S. K. Ajmera, C. Delattre, M. A. Schmidt, K. F. Jensen, *J. Catal.* **2002**, *209*, 401.
- [6] O. Wolfarth, L. Kiwi-Minsker, A. Renken, in *Microreaction Technology* (Eds: M. Matlosz, W. Ehrfeld, J. P. Baselt), **2001**, 192.
- [7] A. Rouge, *Chem. Eng. Sci.* **2001**, *56*, 1419.
- [8] C. Horny, L. Kiwi-Minsker, A. Renken, *Chem. Eng. J.* **2004**, *101*, 3.
- [9] M. J. Stutz, N. Hotz, D. Poulidakos, *Chem. Eng. Sci.* **2006**, *61*, 4027.
- [10] S. Walter, S. Malmberg, B. Schmidt, M. A. Liauw, *Catal. Today* **2005**, *110*, 15.
- [11] H. L. V. Hessel, *Chem. Eng. Technol.* **2003**, *26*, 391.
- [12] G. Vesper, J. Frauhammer, *Chem. Eng. Sci.* **2000**, *55*, 2271.
- [13] I. Yuranov, A. Renken, L. Kiwi-Minsker, *Appl. Catal., A.* **2005**, *281*, 55.
- [14] I. Yuranov, L. Kiwi-Minsker, A. Renken, *Appl. Catal., B.* **2003**, *43*, 217.
- [15] C. J. Marrion, D. R. Cahela, S. Ahn, B. J. Tatarchuk, *J. Power Sources* **1994**, *47*, 297.
- [16] I. Cerri, M. Pavese, G. Saracco, V. Specchia, *Catal. Today* **2003**, *83*, 19.
- [17] Y. Wang et al., *J. Mater. Sci. Lett.* **2001**, *20*, 2091.
- [18] D. A. Bulushev, L. Kiwi-Minsker, A. Renken, *J. Catal.* **2004**, *222*, 389.
- [19] A. Heyden, B. Peters, A. T. Bell, F. J. Keil, *J. Phys. Chem. B.* **2005**, *109*, 1857.
- [20] F. Kapteijn, J. Rodriguez-Mirasol, J. A. Moulijn, *Appl. Catal., B.* **1996**, *9*, 25.
- [21] J. Perez-Ramirez, F. Kapteijn, A. Bruckner, *J. Catal.* **2003**, *218*, 234.
- [22] S. Mintova et al., *Microporous Mat.* **1997**, *11*, 149.
- [23] A. E. Persson, B. J. Schoeman, J. Sterte, J. E. Otterstedt, *Zeolites* **1994**, *14*, 557.
- [24] J. Sterte et al., *Catal. Today* **2001**, *69*, 323.
- [25] L. Kiwi-Minsker, D. A. Bulushev, A. Renken, *Catal. Today* **2005**, *110*, 191.
- [26] R. Macey, G. Oster, *Madonna 7.0*, University of California, **1999**.