



Microchannel reactor for intensifying oxidation of methanol to formaldehyde over Fe-Mo catalyst



A.G. Gribovskii^{a,b,*}, E.V. Ovchinnikova^a, N.V. Vernikovskaya^{a,b}, D.V. Andreev^a, V.A. Chumachenko^a, L.L. Makarshin^a

^a Borekov Institute of Catalysis, Pr. Akad. Lavrentieva, 5, 630090 Novosibirsk, Russia

^b Novosibirsk State University, ul. Pirogova 2, 630090 Novosibirsk, Russia

HIGHLIGHTS

- The rate of formaldehyde formation reached a significant growth in a microchannel reactor.
- Productivity in a micro-channel reactor is 10-fold higher than in a fixed-bed tubular reactor.
- The reaction operated safely within the explosive range of methanol-oxygen mixture.
- The methanol conversion decreased by only 3–12% after operation for 100 h.

ARTICLE INFO

Article history:

Received 15 March 2016

Received in revised form 7 September 2016

Accepted 12 September 2016

Available online 12 September 2016

Keywords:

Catalyst

Catalytic multichannel reactor

Methanol oxidation

Formaldehyde

Process intensification

Fe-Mo catalyst

ABSTRACT

The paper deals with catalytic oxidation of methanol to formaldehyde in a microchannel reactor (MCR) in view of the process intensification. Every channel in the experimental MCR was 1 mm in diameter, 10 mm in height and was filled with an industrial Fe-Mo catalyst ground to a fraction of 0.15–0.25 mm. Methanol concentration in the feed mixture was 6.5 and 12 mol%, oxygen to methanol molar ratio was 1.5, the temperature was in the range 240–360 °C. Safe processing of the reaction in MCR at methanol concentration as high as 12 mol% makes it possible to reach approximately a 10-fold increase in the specific formaldehyde productivity per unit volume of the catalyst even within the explosive range of oxygen-methanol mixtures. Numerical simulation of the process by use of a continuum model revealed its sufficient consistency with the experimental results. It was shown that methanol conversion decreased by ~12% after operation for 100 h at 300 °C and 12 mol% of methanol. In contrast, at the same conditions but at standard 6.5 mol% of methanol, the decrease in the conversion did not exceed 3%. The use of MCR for highly exothermic reactions has high potential due to extremely high rates of heat and mass transfer, provided that the catalyst used has stable activity of fine particles during on-stream operation.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Miniaturization of chemical reactors has become an object of extensive research in the fields of chemistry, biochemistry, science

of nanomaterials, nanotechnology etc.[1]. Recently, microchannel reactors (MCR) that have a large number of parallel sub-millimeter channels, slots or membranes [2] were successfully applied in hydrogen energetics, in autothermal conversion of heavy hydrocarbons [3], in partial oxidation of methane [4], in organic synthesis [5], and in other industrially important processes [6–10].

In conventional reactors, highly exothermic processes are carried out at low concentrations of hydrocarbon feedstock [11], because of restrictions caused by insufficiently effective heat removal and by safety conditions. Such constraints limit the productivity of a catalyst and thus of the entire process. For example, the oxidation of methanol to formaldehyde in multitubular reac-

Abbreviations: LEL, lower explosion level; MCR, microchannel reactor; DME, dimethyl ether; MF, methyl formate; CPSI, channel density (channels per sq. inch); GHSV, gas hourly space velocity (h^{-1}); X, degree of methanol conversion (mol%); S, selectivity toward formaldehyde (mol%); Y, yield of formaldehyde (mol%); C, concentration (mol%); W, reaction rate (s^{-1}); T, temperature (K); U, superficial linear velocity (m/s); τ , residence time (s).

* Corresponding author at: Borekov Institute of Catalysis, Pr. Akad. Lavrentieva, 5, 630090 Novosibirsk, Russia.

E-mail address: gribovsk@catalysis.ru (A.G. Gribovskii).

tors on Fe-Mo oxide catalysts is usually performed below the lower explosion limit (LEL) of the mixture, i.e. at 6.5–7.0 mol% of methanol, which limits the productivity of the catalyst to $0.7 \text{ kg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ of formaldehyde. A use of more active catalysts [12], an increase in the initial concentration of methanol to 9 mol% [11], inserting an adiabatic bed below the main tubular section [13], or an increase in the heat capacity of the mixture [14] do not lead to significant intensification of the process because of a number of technological constraints associated with the kinetic characteristics of the process.

In contrast, catalytic processes in MCR may proceed on fine grains of a catalyst with high specific loading, which provides the rates of mass- and heat transfer that are 1–2 orders of magnitude higher than those in conventional reactors. Consequently, MCR may provide almost isothermal conditions for industrially important reactions with very high thermal effects [15]. On the whole, MCR allows the processes to be intensified by either of the following means: a) by increasing the temperature and pressure; b) by significantly increasing reactant concentrations; c) by implementing the processes within the explosion limits because of the suppression of free radical processes on microchannel walls [16–18]. The best niche for MCR is low capacity unit that produces highly valuable fine chemicals, whereas its application on a larger scale seems questionable. Hydrodynamic flow inside the channels is essentially laminar, which can limit convective mass transfer rate.

The main objective of this work is analysis of methanol to formaldehyde selective oxidation process over commercial Fe-Mo catalyst in MCR, which takes into account specific features of MCR as well as kinetic characteristics of the catalyst. We then discuss a number of factors that lead to the process improvement. This reaction may be considered as a typical example of a highly exothermic reaction performed in MCR.

2. Experimental

2.1. Microchannel reactor

Experiments were conducted in a MCR filled with a fixed-bed catalyst. The design of the reactor is described in detail in [19–21]. The reactor (Fig. 1) consisted of a heater, a reagent feeding system, and a microchannel catalytic disc. The heater was designed as two mutually perpendicular slots milled in stainless steel plate to maintain a given temperature of the reaction mixture at the inlet of the reagent feeding system, whereas the reagent feeding system provided uniform distribution of the gas flow through the channels of the disc [21]. The core element of the MCR was the microchannel disc 52 mm in diameter and 10 mm in height made of brass alloy LS59-1V. The central part of the disc had multiple straight-through channels 1 mm in diameter, the distance between the channels' axes being 1.25 mm. The channel density (CPSI) was 227 channels per sq. inch. The channels were filled with the catalyst. Both sides of the microchannel disc were covered with porous stainless steel membranes (1.0 mm thick and with an average pore size of $\sim 30 \mu\text{m}$) to hold the catalyst grains inside the channels.

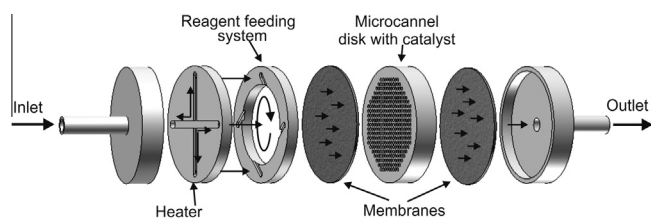


Fig. 1. Configuration of the microchannel reactor.

Industrial iron-molybdenum catalyst KH-26C produced by Perstorp Formox AB (MoO_3 79.95%, Fe_2O_3 20.05%, BET surface $8 \text{ m}^2/\text{g}$) was used in the experiments. Initially, the catalyst was in the form of rings $5 \times 2.5 \times 5 \text{ mm}$ (outer dia., inner dia., height), then the catalyst pellets were crushed and sieved to the fractures $d_p = 0.15\text{--}0.25 \text{ mm}$, bulk density $\gamma = 1.07 \text{ g}/\text{cm}^3$. The ratio of the channel diameter to the average diameter of the catalyst fracture was $ID_c/d_p \approx 5$.

Two MCR with various numbers of channels in the disc were used in the experiments: MCR-1 with 499 channels and catalyst charge 4.2 g was used to study the influence of parameters; MCR-2 with 250 channels and catalyst charge 2.4 g was used to analyze the catalyst's stability. In both cases, the CPSI values were similar. The smaller quantity of channels in MCR-2 allowed saving on consumable materials during long-term testing.

2.2. Experimental setup

A schematic diagram of the experimental setup is shown in Fig. 2. Oxygen from cylinder A1 and nitrogen from cylinder A2 with flow rates of 111–617 mL/min and 957–2400 mL/min respectively were fed by automatic mass flow controllers (RRG-10, Russia), thus maintaining a predetermined ratio $\text{O}_2:\text{N}_2$. Liquid methanol from tank A3 with a flow rate of 0.121–0.672 mL/min at ambient temperature was fed by a plunger pump C5 (Stayer Type2, Russia) into evaporator D6 maintained at $90 \text{ }^\circ\text{C}$. After the evaporator, the methanol vapor was mixed with the gas mixture preheated to $140 \text{ }^\circ\text{C}$ in heater B4, and then the reaction mixture entered the MCR E7 maintained at a desired temperature ($240\text{--}360 \text{ }^\circ\text{C}$) by a tubular electric furnace F8. To prevent water condensation and paraformaldehyde formation at low temperatures, the gas lines were maintained at $140 \text{ }^\circ\text{C}$ at least. The temperature at the edge and in the center at the inlet and outlet of the disc was measured with chromel–alumel thermocouples. The temperatures of the evaporator, preheater, and the temperature in the center of the disc outlet were kept constant within $\pm 0.5 \text{ }^\circ\text{C}$ using a PID temperature controller (THERMODAT, Russia).

By switching a heated 6-way valve H9, the reaction products were directed to GC Crystal-2000 (Russia) equipped with thermal conductivity detector for CO, CO_2 , methanol, and formaldehyde analysis. Formation of minor by-products, such as dimethyl ester, methyl formate, and formic acid, was checked at a separate setup and shown to be negligible on the catalyst used in this study. Analyses were conducted at atmospheric pressure, at $90 \text{ }^\circ\text{C}$, on a 2-m column filled with Porapak T, using helium as a carrier gas; sampling was carried out automatically. Only methanol, formaldehyde, and carbon monoxide were registered, no other reaction products were detected during the experiments.

2.3. Experimental procedure

The reactor was heated to a predetermined temperature in a flow of nitrogen ($50 \text{ mL}/\text{min}$) and then held for 1 h. Thereafter, the reaction mixture containing MeOH, O_2 and N_2 at the oxygen to methanol molar ratio of 1.5 was fed into the reactor with a flow rate of $68\text{--}200 \text{ L}/\text{h}$.

In the first set of experiments (see Section 3.4 below), the influence of parameters on the process productivity was studied in the reactor MCR-1. The temperature varied in the range of $260\text{--}360 \text{ }^\circ\text{C}$, the residence time τ ($\tau = 3600/\text{GHSV}$) varied within $\text{GHSV} = 17,500\text{--}52,500 \text{ h}^{-1}$. Superficial linear gas velocity inside the MCR channels was $0.05\text{--}0.15 \text{ m}/\text{s}$, respectively. To study the influence of the methanol concentration, experiments were carried out at $C_{\text{MeOH}}^0 = 5.8\text{--}6.5 \text{ mol}\%$ and $C_{\text{MeOH}}^0 = 12.0\text{--}12.5 \text{ mol}\%$ in the inlet reaction mixture.

Download English Version:

<https://daneshyari.com/en/article/4763754>

Download Persian Version:

<https://daneshyari.com/article/4763754>

[Daneshyari.com](https://daneshyari.com)