

Deactivation of a Zn/TiO₂ Catalyst in the Course of Methanol Steam Reforming in a Microchannel Reactor

A. G. Gribovskii, L. L. Makarshin, D. V. Andreev, S. V. Korotaev,
V. I. Zaikovskii, and V. N. Parmon

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia

e-mail: gribovsk@catalysis.ru

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Abstract—The service life tests of a Zn/TiO₂ catalyst deposited on the microchannel plates of copper foam, nickel foam, and corrugated brass foil in the process of methanol steam reforming demonstrated that the catalyst stability and operation time depend on microchannel plate material. The rate of catalyst deactivation correlated with the thermal conductivity of the microchannel plate material. It was found that catalyst deactivation resulted from the decomposition of zinc titanates, which are active components, and it was accompanied by the appearance of a zinc oxide phase. The best results in the service life tests were obtained with the microchannel plates of copper foam. A microchannel reactor containing 16 copper plates continuously operated at 400°C for 150 h; in this case, the conversion of methanol decreased by 8%. The subsequent microreactor operation for 500 h caused a decrease in the methanol conversion by 26%. It was found that the loss of the catalyst activity was a reversible process, and the activity can be restored by annealing in air.

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INTRODUCTION

The deactivation of copper-containing catalysts in methanol steam reforming was studied by Löffler et al. [1]. This study was performed in a fixed-bed reactor for 1000 h. The Fe₂O₃/Cr₂O₃/CuO/graphite catalyst exhibited the greatest stability at an operation temperature of 400–500°C. It was found that deactivation was caused by catalyst poisoning with reaction products and a decrease in the dispersity of copper metal because of the agglomeration of copper microparticles. It was demonstrated that the agglomeration of copper microparticles occurred at the initial stage of operation and resulted in an insignificant decrease in the catalyst activity (to within a few percents). However, catalyst poisoning with main reaction products or by-products, for example, because of coke formation, was the main cause of catalyst deactivation.

Traditional catalysts for low-temperature methanol steam reforming are the copper–zinc compositions Cu/ZnO and Cu/ZnO/Al₂O₃. Shishido et al. [2] studied these catalysts. The activity of these catalysts decreased by 2–4% after operation for 24 h. It was found that alumina-containing catalysts were more stable. The positive effect of Al₂O₃ on the lifetime of a copper–zinc catalyst was also noted by Breen and Ross [3]. They found that alumina prevents the agglomeration of copper microparticles. Similar results were obtained by Durga Kumari et al. [4] for similar catalysts; the service life tests of the catalysts for 100 h also demonstrated that alumina-containing samples were more stable. With the use of scanning electron microscopy and EDX analysis,

Durga Kumari et al. [4] found that copper metal crystallites sintered in the course of methanol steam reforming. From published data, it follows that, in addition to the above reasons, the stability of catalyst operation also depends on the process conditions of methanol steam reforming: the temperature and the composition of a starting water–methanol mixture.

Pinzari et al. [5] studied a Zn/TiO₂ catalyst, whose activity at 350–450°C was higher than the activity of copper–zinc samples. The aim of this work was to experimentally study the deactivation of the Zn/TiO₂ catalyst in the course of methanol steam reforming. Attention was also focused on procedures for the restoration of catalyst activity and on the effects of various factors on these processes.

EXPERIMENTAL

A stainless steel microreactor of size 30 × 30 × 10 mm was used to test microchannel plates in methanol steam reforming. Figure 1 shows a photograph of this microreactor. A rhombic configuration of the microreactor allowed us to obtain a uniform distribution of flows over the channels of microchannel plates [6]. The microreactor was hermetically sealed using a weld along the perimeter. The microchannel plates of size 20 × 30 mm were made by the cold pressing of metal foam or by the corrugation of brass foil 0.1 mm in thickness. The microchannel plates of copper foam (MCP1) and nickel foam (MCP2) consisted of rectangular channels with a cross section of 0.15 × 5 mm and

a length of 20 mm. The microchannel plate of corrugated brass (MCP3) had channels with a triangular cross section 0.3 mm in height and 0.6 mm in base width, which resulted from alternating corrugated and flat plates. The Zn/TiO₂ composition (Zn/Ti = 0.05) was used as a catalyst. Table 1 summarizes the parameters of three different types of microchannel plates, which were used in the experiments.

The procedure used for catalyst powder deposition on metal foam was described elsewhere [7]. The deposition of the catalyst on the microchannel plates made of corrugated brass foil 0.1 mm thick was performed in the following manner: Before immobilizing the catalyst, the surface of brass foil was sandblasted followed by thermal annealing at 400–500°C for 10–15 min. Next, a catalyst suspension was prepared. For this purpose, 1 g of the powder of the synthesized Zn/TiO₂ catalyst was dispersed in 10 ml of distilled water for 30 min. Polyethylene oxide (0.1 g) was added to the resulting solution. As a result, a uniform viscous suspension was obtained. To improve catalyst adhesion to metal, 0.5 g of aluminosilicate clay was added to the suspension. The suspension was applied to brass foil with a soft hair brush. The resulting composite layer was dried at 100–150°C for 30 min. Next, the plate with the supported composite layer was annealed at 300°C for 1 h; because of this, the composite lost residual water and polyethylene oxide. After the completion of annealing, the thickness of the supported catalyst layer was ~0.03 mm. Control experiments demonstrated that the microchannel plates without deposited catalyst did not exhibit catalytic activity.

The service life tests of microchannel plates in the reaction of methanol steam reforming were performed using a special system (Fig. 2). A water–methanol mixture with water-to-methanol molar ratio β was supplied with a plunger pump to an evaporator, whose temperature was 200°C, and then to the microreactor. The microreactor and the evaporator were heated using special external electric heater controlled by Miniterm-300 temperature regulators. The microreactor temperature was measured with a Chromel–Alumel thermocouple welded to the body near the microreactor outlet. The reaction products arrived at a separator, where they were cooled to room temperature and unreacted water and methanol vapor were condensed. The space velocity of a dry gas flow was measured using a soap film

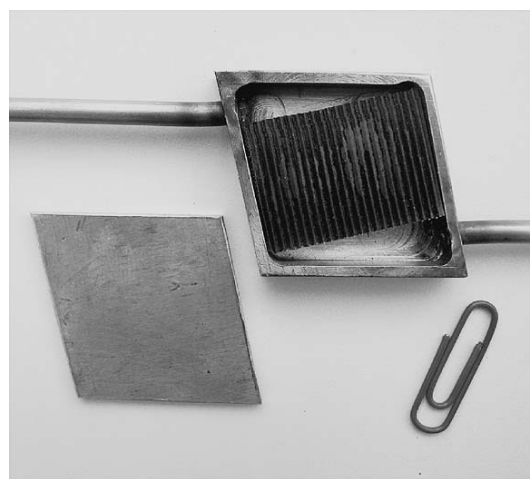


Fig. 1. Microchannel reactor with microchannel plates of corrugated brass.

flow meter at regular intervals. The conversion of methanol was calculated in accordance with a previously published procedure [7, 8].

The high-resolution transmission electron micrographs were obtained on a JEM-2010 electron microscope (JEOL, Japan) with a lattice resolution of 0.14 nm at an accelerating voltage of 200 kV. Local energy dispersive X-ray microanalysis (EDX analysis) was performed on an EDAX spectrometer (EDAX Co.) equipped with a Si(Li) detector with an energy resolution of 130 eV. The test samples were fixed on standard copper gauzes, which were placed in a holder and introduced into the sample chamber of the electron microscope.

RESULTS

Figure 3 shows the experimental dependences of the conversion of methanol on the value of W/F , which is the reciprocal of the specific flow rate of methanol to the reactor on a catalyst weight basis. Here, W is the weight of the catalyst deposited on the microchannel plate, and F is the molar flow rate of methanol. The main activity characteristics of the test microchannel plates can be calculated using previously derived relationships [7]. Table 2 summarizes the hydrogen capacities of the microreactor with the test samples. It can be

Table 1. Parameters of the microchannel plates used in the experiment

Microchannel plate characteristic	Copper foam (MCP1)	Nickel foam (MCP2)	Brass foil (MCP3)
Catalyst composition	Zn/TiO ₂	Zn/TiO ₂	Zn/TiO ₂ : clay 2 : 1 (wt %)
Catalyst weight, g _{Cat}	1.5	3.1	0.7
Plate thickness, mm	0.38	0.5	0.85
Number of microchannel plates in the microchannel microreactor	16	12	7
Total channel volume in the microchannel plate, cm ³	0.96	0.72	1.75

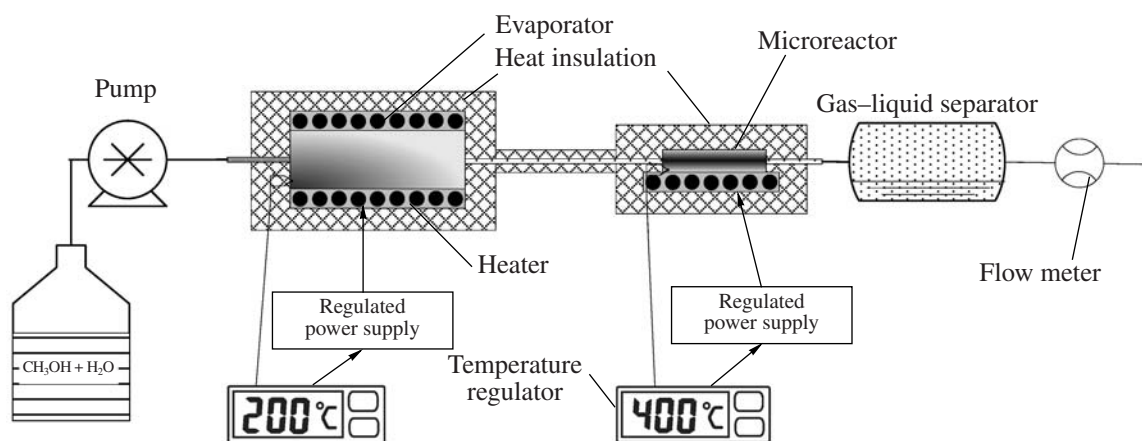


Fig. 2. Experimental setup for the service life tests of the catalyst.

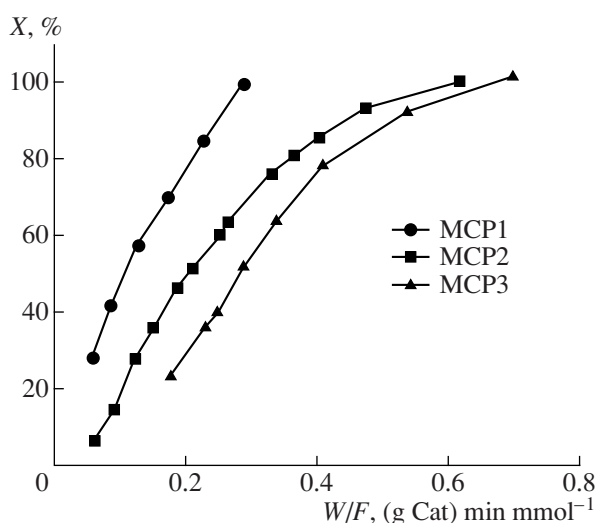


Fig. 3. Dependence of methanol conversion on the value of W/F for the test microchannel plates.

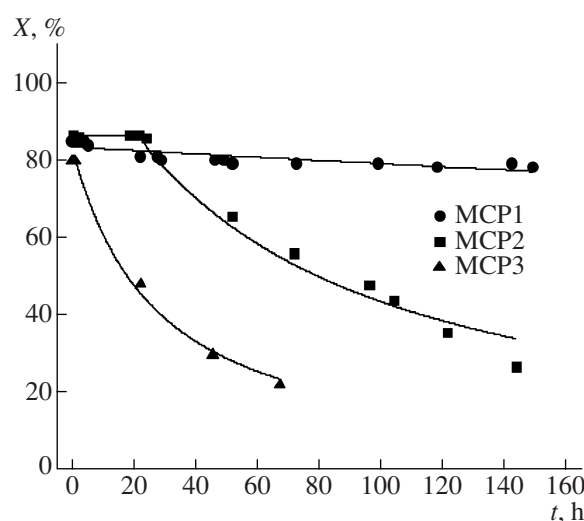


Fig. 4. Dependence of methanol conversion on the operation time of microchannel plates ($\beta = 1.1$). Solid lines show approximations of the experimental data by Eq. (1).

seen that the microchannel plates made of metal foam exhibited the highest activity.

Figure 4 shows the dependence of the conversion of methanol on the time of continuous operation for the test microchannel plates. The molar flow rate of methanol F for the water–methanol mixture with $\beta = 1.1$ was maintained constant during the entire experiment. In the testing of MCP1 and MCP2, it was 8.78 mmol/min CH_3OH , whereas it was 1.77 mmol/min CH_3OH for MCP3. The inlet flows were chosen based on the catalyst activity at which the conversion of methanol was $\sim 80\%$. In all cases, the microreactor temperature was maintained at 400°C . Figure 4 indicates that plate MCP1 exhibited the best results in the service life tests. The conversion of methanol on these plates decreased by 8% after continuous operation for 150 h. At the same time, the conversion of methanol on MCP2 after operation for 140 h decreased by 67%. The greatest catalyst

deactivation was observed in MCP3. Here, the conversion of methanol decreased by 75% after 70-h operation.

Additional experiments were performed in order to determine reasons for catalyst deactivation in the course of methanol steam reforming procedures for the restoration of catalyst activity. Among them were the annealing of spent microchannel plates in an atmosphere of oxygen, a change in the water/methanol ratio, and an increase in the concentration of dissolved oxygen in the inlet water–methanol mixture.

The catalyst activity was restored by annealing spent microchannel plates in an atmosphere of oxygen. The experiment was performed with MCP2 after continuous operation for 140 h. After that, the conversion of methanol after this lapse of time decreased by 68% and was 27%. The annealing of MCP2 was performed

Table 2. Hydrogen production capacity of microchannel plates in the microreactor at a methanol conversion of 80%

Process characteristics	MCP1	MCP2	MCP3
W/F at a 80% conversion, g _{Cat} min mmol ⁻¹	0.21	0.36	0.42
Inlet CH ₃ OH flow rate, mmol/min	7.14	8.61	1.66
Residence time of reactants in the microreactor, s	0.17	0.11	1.3
Hydrogen production capacity U_{H_2} , l/h	25.47	30.5	5.9
Specific hydrogen production capacity on a catalyst weight basis $U_{H_2}(W)$, l g _{Cat} ⁻¹ h ⁻¹	16.87	9.84	8.43
Specific hydrogen production capacity on a volume basis $U_{H_2}(V)$, l cm ⁻³ h ⁻¹	7.08	8.47	1.64
Outlet concentration of CO, vol %	0.6	0.7	1.2

at 400°C immediately in the microreactor with continuously purging air (60 cm³/min) for 2 h. As a result of this procedure, the catalyst activity on MCP2 was completely restored; that is, the conversion of methanol (which was 86% at the onset of operation and decreased to 27% after service life tests) was restored to 86.7% after annealing in an atmosphere of oxygen.

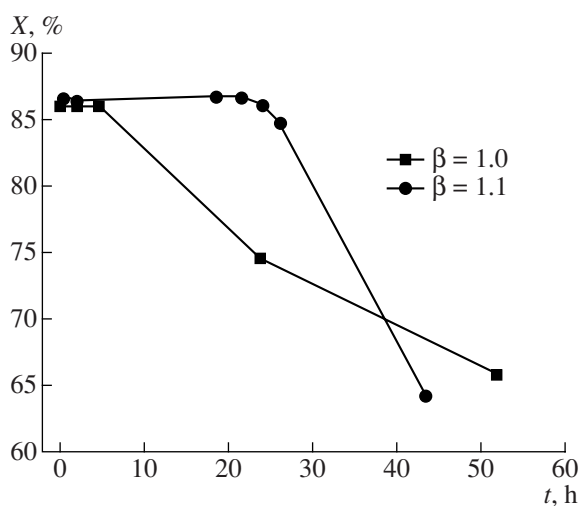
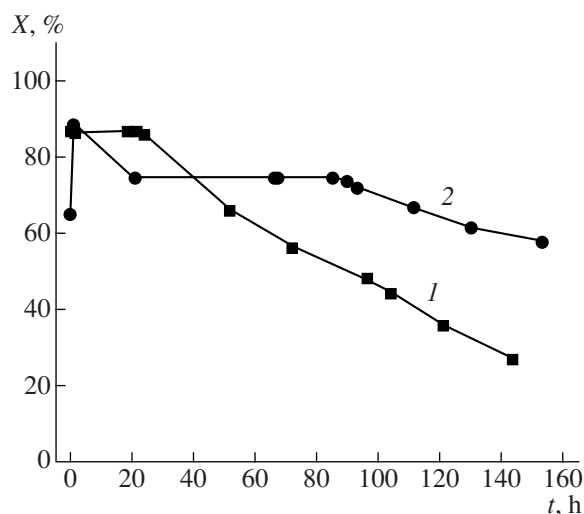
The effect of the water/methanol ratio in the feed mixture (β) on catalyst deactivation was studied on MCP2 plates. Figure 5 shows the dependence of the conversion of methanol at $\beta = 1.0$ and 1.1. It can be seen that even a small increase in the concentration of water in the inlet mixture over a stoichiometric value for the methanol steam reforming reaction resulted in a stabilization of catalyst operation: the conversion of methanol remained almost unchanged over 25 h. Thereafter, a decrease in the conversion of methanol at approximately the same rate as in the case of a mixture containing equal amounts of water and methanol ($\beta = 1$) was observed.

Figure 6 shows the results of a study of the effect of oxygen present in a water–methanol mixture on

changes in the catalyst activity with time. The tests were performed on plates MCP2 pretreated with a flow of a water–methanol mixture with $\beta = 1.1$ for 45 h. In this case, the conversion of methanol decreased from 86 to 65%. Next, of air was blown through a flask with the water–methanol mixture at a rate of 1 l/min at room temperature to enrich the mixture with oxygen. In Fig. 6, it can be seen that the conversion of methanol sharply increased (for 1 h) to the initial value of 86% since the onset of blowing. Thereafter, the conversion of methanol began to decrease even though blowing was continued. However, the rate of decrease was almost three times lower than that in the reference experiment, in which the water–methanol mixture was not enriched with oxygen.

DATA PROCESSING AND DISCUSSION

The formation of surface condensed carbon compounds (coke), which block active sites, and the modification of catalytically active catalyst microparticles are the main causes of catalyst deactivation in the

**Fig. 5.** Dependence of methanol conversion on the operation time of plates MCP2 at different compositions of the water–methanol mixture.**Fig. 6.** Effect of the saturation of the water–methanol mixture with oxygen on the rate of deactivation for MCP2: (1) with no oxygen saturation and (2) with oxygen saturation.

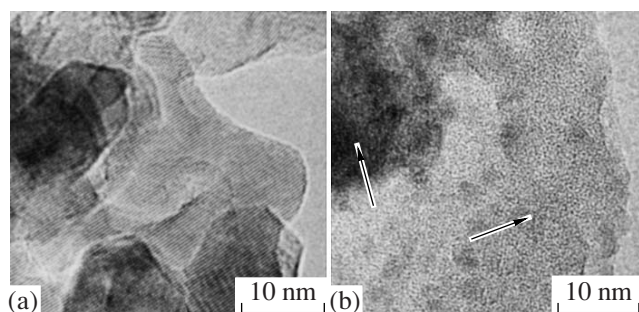


Fig. 7. Micrographs of Zn/TiO₂ catalyst surfaces: (a) the initial catalyst and (b) the catalyst after 140-h operation in the process of methanol steam reforming. Arrows indicate the formation of a ZnO phase.

course of methanol steam reforming. To determine the cause of the deactivation of the Zn/TiO₂ catalyst, plate MCP3 was chosen; this plate exhibited the greatest loss of catalyst activity. Figures 7a and 7b show the HRTEM images of the catalyst surface before and after 70-h operation in the process of methanol steam reforming, respectively. According to HRTEM data, trace carbon compounds (coke) were absent from the catalyst surface; that is, deactivation was not due to the blocking of active sites. The micrograph of the initial catalyst exhibited the crystallites of TiO₂ (anatase) of size ~20 nm. In this case, zinc-containing phases were not detected on the surface. According to published data [9], zinc oxide and titanium dioxide form zinc titanates upon calcination; the composition of these titanates (Zn₂TiO₄, ZnTiO₃, or Zn₂Ti₃O₈) depends on the ratio between the starting oxides, the temperature of calcination, etc. It is likely that, in our case, the crystallites of zinc titanate (active component of the catalyst) were very small or poorly crystallized, and they cannot be detected by crystallographic analysis. It can be seen that a new crystalline phase with microparticle sizes of about 1 nm appeared on the surface of anatase after 70 h of catalyst operation (Fig. 7b). Crystallographic analysis demonstrated that this phase corresponds to the compound ZnO in terms of lattice parameters. Moretti et al. [10] noted that Ti⁴⁺ cations can be converted into Ti³⁺ cations in a reducing atmosphere. It is likely that, in this case, the structure of zinc titanate degraded, as found by Lew et al. [11], to form the particles of TiO₂ and ZnO phases, which are inactive in the process of methanol steam reforming.

The results of experiments on the restoration of catalyst activity upon annealing in an atmosphere of oxygen and on a decrease in the rate of catalyst deactivation by increasing the concentration of water or dissolved oxygen in the inlet water–methanol mixture can be indirect evidence for the above mechanism of deactivation. It is likely that the annealing of the catalyst in an oxidizing atmosphere results in the repeated formation of zinc titanates, which facilitate an increase in the catalyst activity. The addition of water or oxygen to the

inlet mixture in the course of methanol steam reforming decreases the rate of decomposition of zinc titanates [11] and, consequently, the rate of formation of the ZnO phase. The effects of reducing and oxidizing atmospheres on the ZnO–TiO₂ system will be the subject matter of further investigation.

Catalytic processes in the microchannel reactor are adequately described by the model of a plug-flow reactor. Using previously published results [12], we write an expression to relate the conversion of methanol with initial experimental data and reaction rate parameters:

$$\frac{W}{F} = \frac{1}{k_e \Phi_N(t) 0.5^\alpha} \int_0^x \left(\frac{1+z}{1-z} \right)^\alpha dz, \quad (1)$$

where k_e is the effective rate constant of reaction (1); α is the order of reaction with respect to methanol; $\Phi_N(t) = (N_0 - N)/N_0$ is the catalyst deactivation function, which depends on catalyst operation time; N_0 and N are the numbers of initial and deactivated active sites, respectively; and z is the integration variable. According to the accepted model of deactivation, the decomposition of zinc titanates results in a decrease in the active catalyst surface. Consequently, the catalyst deactivation function can be written in the form $\Phi_N(t) = S(t)/S_0$, where S_0 is the catalytically active surface area of the initial catalyst, and $S(t)$ characterizes the change of this surface area in the course of operation. An analytic expression for this function was proposed by Löfller et al. [1], who considered a similar model:

$$\Phi_N(t) = \gamma + (1 - \gamma) \exp(-k_s t), \quad (2)$$

where $\gamma = S_s/S_0$, S_s is the catalytically active surface area remained after catalyst operation for time $t \rightarrow \infty$; and k_s is the rate constant of catalyst deactivation. Substituting the previously found order of reaction with respect to methanol $\alpha = 0.5$, the effective rate constant $k_e = 0.07 \text{ mol bar}^{-0.5} (\text{kg Cat})^{-1} \text{ s}^{-1}$ [12], and the expression for deactivation function (2) into Eq. (1), we approximate experimental points shown in Fig. 4 using the MathCAD software to obtain the values of γ and k_s for the test microchannel plates. Table 3 summarizes the parameters γ and k_s thus obtained. It can be seen that the catalyst deposited on a microchannel plate of copper foam was most stable, and its rate constant of deactivation k_s reached a minimum value of 0.0069 h^{-1} . On the assumption that the catalyst deactivation mechanism remains unchanged during operation, the catalyst activity will decrease by 20% at $\gamma = 0.79$ after a sufficiently long operation time. In the course of an experiment with the operation of MCP1 for 500 h, the catalyst activity decreased by 26%. Catalyst deactivation occurred more rapidly on the other microchannel plates. Thus, the activity of the catalyst on MCP2 decreased by 75% after 150-h-long operation, whereas that on MCP3 decreased by 85% after 70-h operation. It is likely that the difference in the rates of catalyst deactivation was due to a temperature gradient across

Table 3. Calculated values of γ and k_s for the test microchannel plates

Microchannel plate type	k_s, h^{-1}	$\gamma, \text{mol bar}^{-0.5} (\text{kg Cat})^{-1} \text{s}^{-1}$
MCP1	0.0069	0.078
MCP2	0.017	0.260
MCP3	0.037	0.150

the microchannel plate. This gradient appears because of a finite thermal conductivity of the microchannel plate material, and it can increase the rate of decomposition of zinc titanates in higher temperature regions. In this case, plates with the lowest thermal conductivity exhibit the highest temperature gradients. Indeed, deactivation on MCP1 of copper foam with a higher thermal conductivity (the thermal conductivity coefficient is $373 \text{ W m}^{-1} \text{ K}^{-1}$ at 300°C) occurred more slowly than that on MCP2 of nickel foam (the thermal conductivity coefficient is $68 \text{ W m}^{-1} \text{ K}^{-1}$ [13]). The catalyst deactivation process on MCP3 of brass foil occurred most rapidly; it is likely that this process depends on the procedure used for catalyst deposition on this microchannel plate. The substrate material can also exert an additional effect on the catalyst deactivation process. Thus, Durga Kumari et al. [4] found that the diffusion of ions from the substrate material affects the activity of an deposited catalyst.

CONCLUSIONS

The service life tests of the Zn/TiO₂ catalyst deposited on various microchannel plates in the process of methanol steam reforming demonstrated that the catalyst stability and lifetime depend on the microchannel plate material. The decomposition of zinc titanate microparticles, which are responsible for the activity of the catalyst, is the main reason of catalyst deactivation. The best results were obtained in the service life tests of MCP1 made of copper foam.

The rate of catalyst deactivation correlates with the thermal conductivity of the microchannel plate material. We found that catalyst deactivation is a reversible process and the activity of the catalyst can be restored by annealing in an atmosphere of air. An increase in the concentrations of water and oxygen in the inlet mixture

improve catalyst operation and decrease the deactivation process.

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