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Deactivation of an industrial iron-molybdate catalyst for methanol oxidation

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ABSTRACT

The oxidation of methanol on iron-molybdenum catalysts was investigated with view of gathering information about catalyst deactivation at temperatures in the catalyst bed lower than 300 °C. A 15 months' industrial experiment was carried out and samples of spent catalyst discharged step by step from the reactors were characterized by Mössbauer spectrometry, XRD, chemical analysis and surface area measuring. Catalytic measurements were also performed using a pseudo-isothermal reactor under conditions close to the industrial experiment. The results obtained demonstrate that, although slower, the process of deactivation of the industrial catalyst takes place even at temperatures lower than 300 °C. We reached the conclusion that the main reason for this is the removal of a part of the MoO_3 and the decreasing of the specific surface. It was established that the formation of $FeMoO_4$ and Fe_2O_3 is negligible and does not represent a dominant factor influencing the catalytic properties of the Fe–Mo catalyst under these conditions of industrial exploitation.

1. Introduction

The most important results from the investigations of oxide catalysts for selective oxidation of methanol, carried out during the last two decades, lead to the conclusion that the system $Fe_2(MoO_4)_3$–MoO_3 has no alternative [1]. The problem with the catalyst's lifetime, however, which stays in the range of 1–2 years depending on the operating conditions, remains open [2]. Resolving the problem requires deep knowledge of the process mechanism and many papers have been devoted to this problem [3–5]. Industrial experiments are needed for the verification of the laboratory results.

It is well known that the main negative process regarding catalyst life is the progressive destruction of the Mo-rich regions, shifting catalyst composition towards pure Fe^{3+} molybdate [6]. Also important are α-Fe_2O_3 formation through the solid-state reaction and the MoO_3 condensation on the surface as a separate phase (in the bed zone below the hot spot). This opinion was confirmed many times for the pseudo-isothermal reactor [2,7,8]. The main reason for the problems, described above is the high temperature (350–370 °C) in the hot spot zone of the catalyst bed. One solution to this problem is the multistage methanol oxidation which leads to a substantial decrease of the temperatures in the catalyst layer [9]. In this manner it is possible to obtain in the beds an optimal reaction temperature between 240 and 320 °C, increasing the capacity and ensuring a long catalyst's life. Unfortunately no data are available for the deactivation phenomena under these conditions of work. Our research aims to shed more light on this problem.

2. Experimental

A 15 months' industrial experiment was carried out. The industrial installation monitored consists of two pseudo-isothermal reactors, each one formed by catalytic tubes with 20 mm inner diameter and 800 mm high catalytic bed. The first reactor (A) was an old one with a bad heat transfer, which led to higher temperature along the catalyst's bed (330–340 °C in the hot spot). The second reactor (B) was a new one with a very good heat transfer and temperatures along the catalyst's bed not exceeding 300 °C. Both reactors were fed with 14,600 Nm^3 of gas mixture ($6.2 \pm 0.2\%$ methanol and $11 \pm 0.5\%$ oxygen) at the start and 12,000 Nm^3 at the end of the experiment. The inlet temperature was 200 ± 5 °C and diathermic fluid (synthetic oil) that laps the tubes externally was maintained at a temperature of 265 °C at the start to 276 °C at the end of the experiment. Inlet and outlet temperature differences of the heat transfer media were nearly the same for both reactors which guarantees a uniform gas distribution. Industrial catalyst prepared by Neochim PLC – Dimitrovgrad, according to BG patent no. 60779 B_1 (1993) [11] with the following main characteristics was used (Table 1).

Four samples of each reactor starting from the top with step of 20 cm were discharged by using glass tube of proper dimensions and vacuum pump. All samples were characterized regarding

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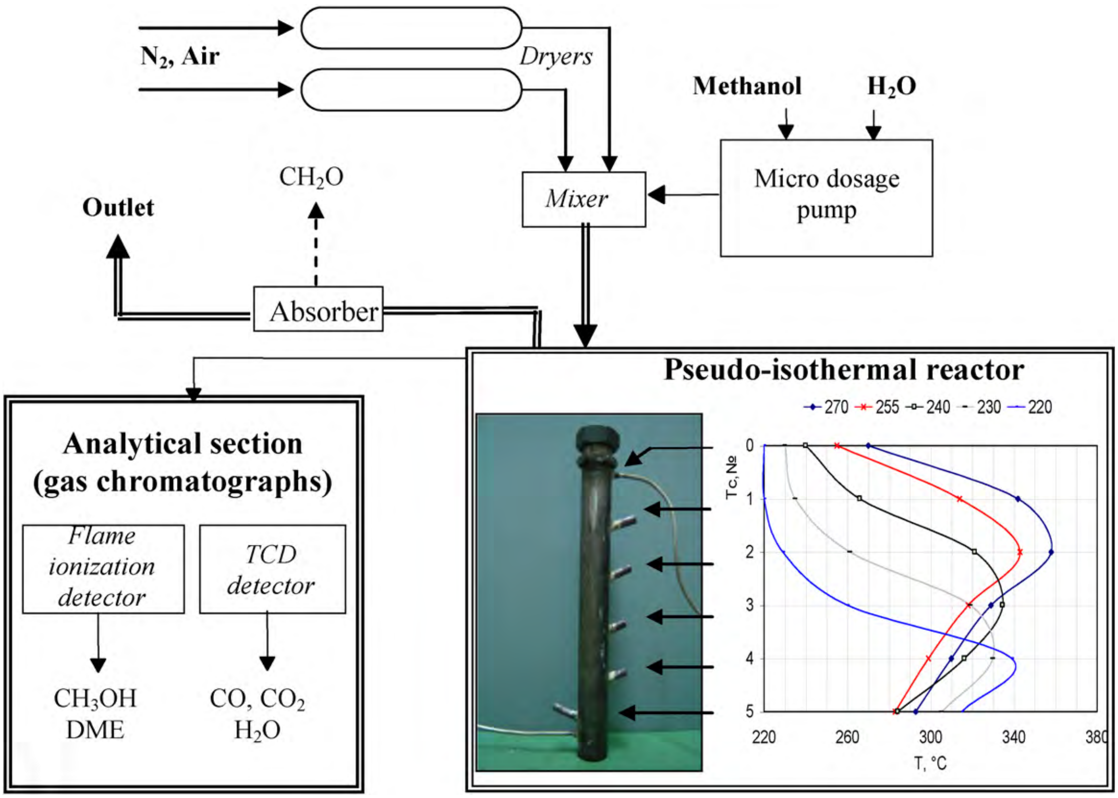

Fig. 1. Apparatus for the estimation of oxide catalysts for methanol oxidation: heat transfer fluid – air; temperature control – six thermocouple; catalyst – maximum 60 cm^3; gas flow – maximum 500 l/h.

phase composition, elemental composition, surface area and catalytic activity. Fresh catalyst was used as reference material.

X-ray diffraction (XRD) patterns were recorded using a TUR M62 apparatus, HZG-4 goniometer with Bregg-Brentano geometry, CoK_α radiation and Fe filter. JCPDF database was used for the phase identification [10]. The transmission Mössbauer spectra were obtained at RT with a Wissel electromechanical Mössbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working at a constant acceleration mode ($^{57}Co/Cr$, 10 mCi, α-Fe standard). Elemental analyses were performed with atomic emission spectroscopy (ICP) after dissolution of the samples in acid solution. The specific surface areas of the samples were measured by BET method.

All catalytic measurements were carried out on a flow apparatus for the estimation of oxide catalysts for methanol oxidation using a stainless steel pseudo-isothermal reactor (50 cm^3 catalyst), located in a precisely controlled thermostat (Fig. 1).

The necessary gases (nitrogen and air), after a passage through a drier for moisture elimination, were led in the mixer. They were dosed through special valves with precision ±1.0 l/h. Liquid methanol and water were injected into the gas flow with a micro-dosage pump with capacity 10–100 g/h and precision ±0.3 g/h, included in the experiment interval. The temperature of the heat transfer fluid was maintained with precision ±0.5 °C. The outlet gas mixture was analyzed by GC using TCD and FID detectors for CO, CO_2, oxygen, methanol and dimethylether (DME) content in the analytical section. The formaldehyde content in the reaction products was determined by the bisulfite method.

Table 1
Main characteristics of the industrial catalyst.

Chemical composition	81.5% MoO_3–18.5% Fe_2O_3
Shape	Rings: $h = 5$ mm, $R_{in} = 3$ mm, $R_{out} = 5$ mm
BET surface area (m^2/g)	8.0
Porosity (%)	55.3
Particle density (g/cm^3)	1.61
Skeleton density (g/cm^3)	3.59

3. Results and discussion

3.1. Industrial experiment

Part of the results from the industrial experiment is summarized in Table 2.

Table 2
Product distribution, total methanol conversion (X_t) and selectivity (S) versus time of catalyst exploitation.

Days	Reactor	Conversion to, %			X_t, %	S, %
		CO	DME	CH_2O		
2	A	3.2	1.4	94.9	>99.5	95.4
	B	5.2	1.8	92.5	>99.5	93.0
20	A	5.4	2.1	92.0	>99.5	92.5
	B	4.7	2.1	92.7	>99.5	93.2
111	A	5.9	0.8	92.8	>99.5	93.3
	B	3.8	3.1	92.6	>99.5	93.1
184	A	5.4	3.5	90.6	>99.5	91.0
	B	3.3	4.4	91.8	>99.5	92.3
286	A	4.9	1.8	92.7	>99.5	93.2
	B	4.0	3.0	92.5	>99.5	93.0
359	A	5.6	1.3	92.6	>99.5	93.0
	B	2.9	2.5	94.1	>99.5	94.5
432	A	5.6	0.6	93.3	>99.5	93.8
	B	3.0	2.2	94.3	>99.5	94.8
	Average value for the period, reactor "A"					93.8 ± 1.7
	Average value for the period, reactor "B"					93.8 ± 1.8

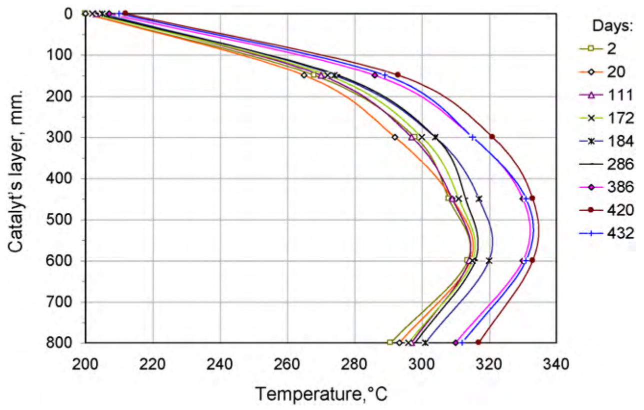

Fig. 2. Influence of the exploitation period on the temperature profile of the catalyst layer in reactor A.

The standard deviation in defining the total degree of methanol conversion and selectivity was calculated by the formula.

$$a=\sqrt{\frac{n\sum x^2-\left(\sum x\right)^2}{n(n-1)}}$$

where a is the standard deviation, x measured value, n is the number of measurements (20).

Methanol conversion to CO, DME and formaldehyde is presented on the basis of the results from the gas-chromatograph's analysis (for CO and DME) and methanol consumption (for the CH_2O). We also detected small amounts of CO_2 (by gas-chromatograph's analysis) and HCOOH (by titration).

The results presented in Table 2 show that the degree of methanol to CO conversion during the entire period of catalyst exploitation is higher in reactor A, while concerning DME we obtained the contrary results. Apparently the reason for this is the higher temperature in the catalyst layer of reactor A, which can be seen clearly from the temperature profiles along the tubes presented in Figs. 2 and 3.

Surprising is the fact that the process selectivity is the same, independently of the different conditions in the two reactors. This is the result of secondary DME oxidation mainly to formaldehyde and compensates for the losses due to the oxidation of methanol to CO. Apparently this process is more strongly expressed in reactor A due to the relatively higher temperatures in the catalyst layer. This confirms the conclusion made earlier [12], namely that DME oxidation under industrial conditions compensates to a considerable degree the losses from the methanol oxidation and the secondary oxidation of formaldehyde to CO.

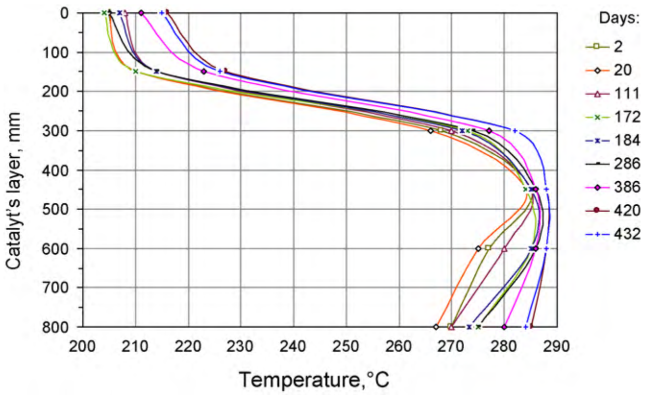

Fig. 3. Influence of the exploitation period on the temperature profile of the catalyst layer in reactor B.

The results presented in Figs. 2 and 3 show considerable differences in the temperature profiles of the catalyst layers in the two reactors. While in reactor A a process of intensive oxidation commences already in the highest 10 cm catalyst layer, in reactor B the upper 15 cm layer practically is not working. However, on the other hand in this reactor the temperature in the layer 20 ± 5 cm sharply rises. This is a sign for the concentration of an intensive oxidation process in this region, after which the increase is insignificant to layer depth of 45 cm. There follows a smooth decrease of temperature, more strongly expressed in the 60–80 cm layer. The maximum temperature in reactor B does not exceed 290 °C during the entire period of catalyst exploitation. This result leads to the important conclusion that full oxidation of methanol under industrial conditions is possible at temperatures lower than 300 °C and confirms the idea of Casale Chem [9] on the improvement of the process parameters by applying temperatures in the range 220–320 °C in a multistage adiabatic reactor. The bad heat transfer in reactor A leads to formation of a huge region in the catalyst layer with temperature 300–335 °C. This fact strongly reflects on the product distribution. Methanol conversion to CO in reactor A is up to 50% higher than that in reactor B. This confirms the rapid increase of the secondary formaldehyde oxidation at the temperatures higher than 300 °C, as concluded above. To the opposite DME concentration in the outlet gas of reactor B is up to 50% higher. Its secondary oxidation is lower at these conditions.

3.2. Catalyst characterization

Fig. 4 presents the appearance of the catalyst discharged from catalyst beds A and B through the above described procedure (typical pellets of each sample have been selected).

Weakly expressed reddish-brown coloration of the upper part of the catalyst discharged from reactor A can be seen. This complies with the formation of Fe_2O_3 during the reoxidation of the $FeMoO_4$ according to the reaction:

$$3FeMoO_4 + (3/4)O_2 \rightarrow Fe_2(MoO_4)_3 + (1/2)Fe_2O_3$$

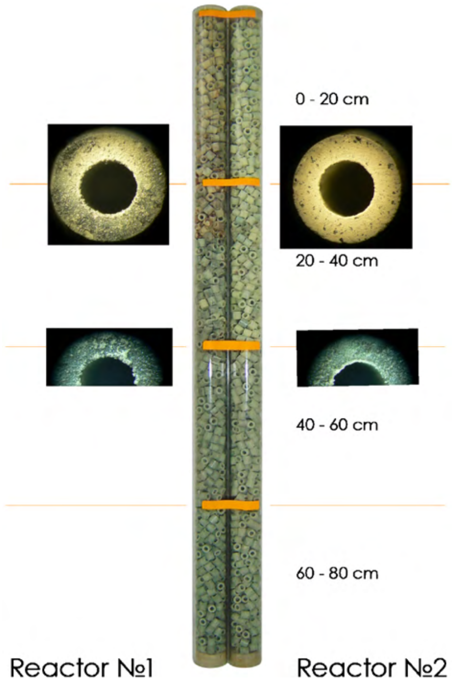

Fig. 4. Typical pellets of catalyst fraction taken at different heights in a tube of industrial reactors A (No. 1) and B (No. 2).

This process is clearly demonstrated in many papers [1,7]. Our results for the catalyst, discharged from reactor A are very close to the results, described in scientific literature – surface area decrease and loss of Mo as well as formation of inactive Fe_2O_3 [8]. We will not discuss them but will focus mainly on the catalyst, discharged from reactor B.

No visual differences are found between the sample of "fresh" catalyst and the samples discharged from reactor B. So we can suggest that at temperatures below 300 °C the formation of $FeMoO_4$ and the subsequent reoxidation of $Fe_2(MoO_4)_3$ is very weakly expressed.

Grains of catalyst from the "hot spot" and the lower part of the layer are carefully examined by a microscope and deposits of small crystals are observed on the inner and outer walls. Apparently we observe MoO_3 transfer from the intensive process zone to the lower part of the catalyst layer.

To determine the reasons for catalyst deactivation at temperatures of the catalyst layer lower than 300 °C we examined the change in its physical properties and chemical composition along the catalyst bed.

XRD analysis and Mössbauer spectrometry are used to check the changes in the phase composition of the catalyst. Two types of samples are analyzed – "medium samples", obtained by grinding and homogenization of the whole pellets and "surface samples", obtained by scraping of the pellets surface layer. No differences in chemical composition and crystalline structure of the "medium samples" are determined by XRD analysis.

Fig. 5 presents the X-ray diagrams of a "fresh" catalyst and of samples from the surface layer of the catalyst grains discharged from reactor B.

In both the "fresh" and the "spent" samples the X-ray diffraction patterns (Fig. 5) registered two main crystalline phases – $Fe_2(MoO_4)_3$ (monoclinic structure) and MoO_3 (orthorhombic structure) with additional carbon phase used as a solid lubricant. The results presented do not show a change in the phase content of the samples. Low intensity reflection from MoO_3 of the sample from the hot spot zone (20–40 cm) can be seen. Considerably more intense reflection is observed with the sample under the hot spot zone (40–60 cm), while the reflection in the lower part of the catalyst bed (60–80 cm) is commensurable with the reflection of the fresh catalyst. This is due to the MoO_3 sublimation from the intensive process zone and its depositing as well-shaped crystals in the lower layers.

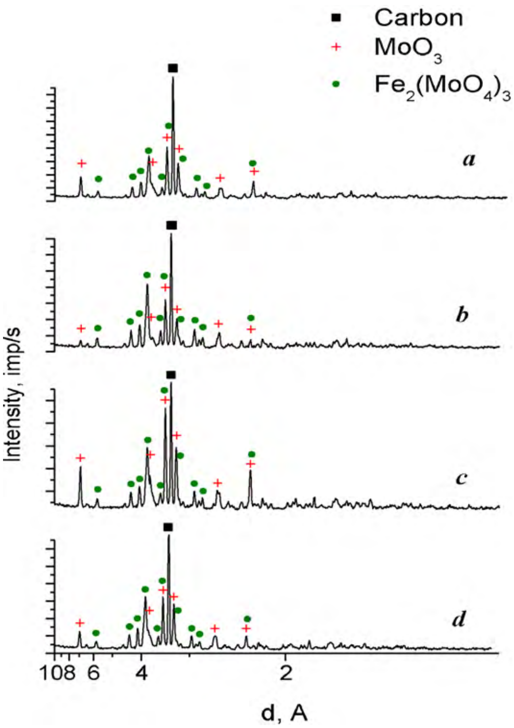

Fig. 5. Powder XRD patterns of selected samples: (a) fresh; (b) 20–40 cm; (c) 40–60 cm; (d) 60–80 cm.

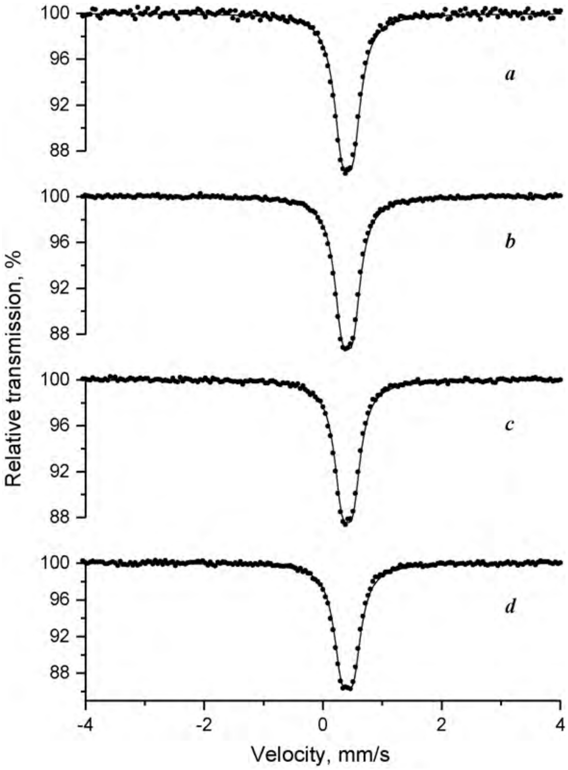

Fig. 6. Mössbauer spectra of selected samples: (a) fresh; (b) 20–40 cm; (c) 40–60 cm; (d) 60–80 cm.

Fig. 6 and Table 3 present the results from "medium samples" of catalyst discharged from reactor B examined by means of Mössbauer spectrometry.

The obtained experimental Mössbauer spectra consist of a single wide line summing two lines of a quadruple doublet. The mathematical processing was done using the same model-two lines with the same intensity included as components of a quadruple doublet. The obtained Mössbauer parameters are presented in Table 3.

The computed IS values for all samples do not differ significantly and is typical for Fe^{3+} ions. No lines of partially or completely reduced iron ions were registered. Most probably Fe^{3+} are located in polyhedrons with octahedral symmetry, i.e. they are octahedrally coordinated and in all cases are highly spin. The latter indicates low degree of doubling of $3d^5Fe^{3+}$-ions valent electrons. No lines of partially or completely reduced iron ions were registered.

Table 3
Isomeric shift IS, quadruple splitting (QS), line width (FWHM) and relative mass of the partial components (*G*) of "fresh" catalyst and samples discharged from reactor B.

Sample	Compound	IS, mm/s	QS, mm/s	FWHM, mm/s	*G*
"Fresh"	$Fe_2(MoO_4)_3$	0.41	0.19	0.33	100
$B_{20–40}$	$Fe_2(MoO_4)_3$	0.41	0.18	0.32	100
$B_{40–60}$	$Fe_2(MoO_4)_3$	0.41	0.19	0.30	100
$B_{60–80}$	$Fe_2(MoO_4)_3$	0.41	0.20	0.32	100

Table 4
Isomeric shift IS, quadruple splitting (QS), line width (FWHM) and relative mass of the partial components (*G*) of sample from the surface layer of the catalyst grains of samples B.

Sample	Compound	IS, mm/s	QS, mm/s	FWHM, mm/s	*G*, %
B_{0-20}	$Fe_2(MoO_4)_3$	0.41	0.18	0.32	100
B_{20-40}	$Fe_2(MoO_4)_3$	0.41	0.18	0.31	100

The determined QS values are also similar or virtually coincide. They are characteristic for the relatively well-shaped structure of iron-molybdate consisting of slightly deformed iron octahedrons and molybdenum tetrahedrons linked by a common oxygen bridge. The width of the lines fall within 0.30–0.32 mm/s and the negligible difference may be due to dimension effect of the articles, a small difference in the degree of crystallinity, surface and volume heterogeneity. The results presented in Fig. 6 and Table 3 show that all samples include only one iron containing phase-$Fe_2(MoO4)_3$. The calculated parameters correspond to a crystal substance with a relatively good degree of crystallization. The presented results show that the phase content is maintained under the conditions of the catalytic reaction. There are no data that any reduction or chemical deactivation took place, which could lead to a significant change of the composition and structure of the catalysts. The presence of free MoO_3 is not reflected as it does not include active Mössbauer nucleus.

Table 4 and Fig. 7 present the results from the Mössbauer analysis of the surface layer of the samples, discharged from reactor B.

The obtained results show that the surface layer of the spent catalysts, discharged from reactor B does not contain other iron containing phase except $Fe_2(MoO_4)_3$ in a quantity exceeding the detectability limit of the method.

The data in Fig. 8 show the change in the catalyst chemical composition along the catalyst bed.

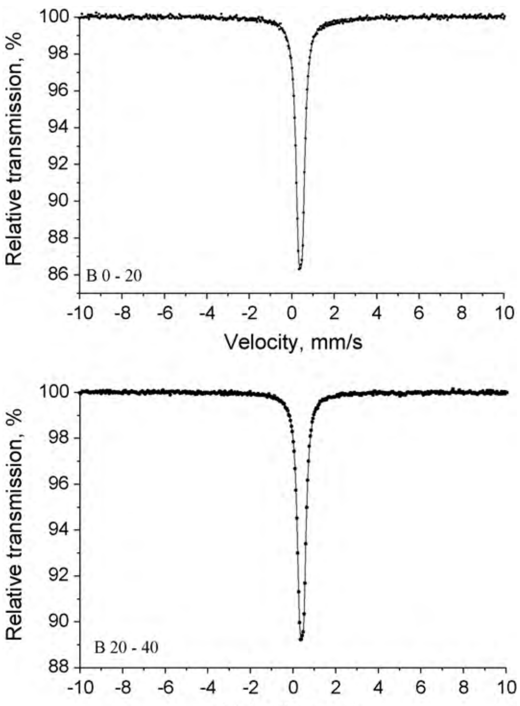

Fig. 7. Mössbauer spectra of a “fresh” catalyst and of samples from the surface layer of the catalyst grains of reactor B.

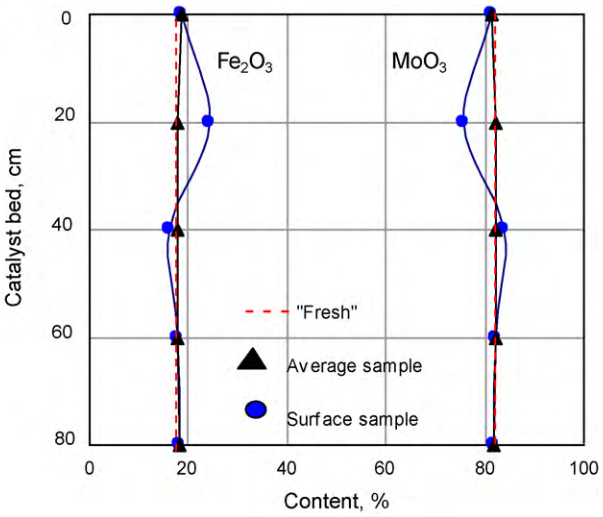

Fig. 8. Catalyst composition along the catalyst’s bed.

Medium samples and surface composition of all catalyst fractions discharged from reactor B were analyzed. A mixture of H_2SO_4 and H_3PO_4 is used for catalyst dissolving and the quantitative determination is made by means of ICP spectrometer of the company “Spectro” – Germany. The results of the “fresh” industrial catalyst analysis are shown by a dotted line.

Fig. 8 shows that the results of the average composition of all samples practically coincide with those of the fresh sample. However the difference in the composition of catalyst grain surface from the upper part of the catalyst layer is significant. MoO_3 content decreases significantly contrary to the content of F_2O_3. This shows that during operation of the catalyst Mo species migrate along the catalyst bed. This is related to a decrease of the specific catalyst surface in this region by about 25%. Taking into account that the temperature in the catalyst bed is less than 300 °C the main reason for Mo sublimation from the catalyst is the interaction of MoO_3 with methanol producing gaseous methoxy species. The presented results show that the change in the catalyst phase composition during the work process affects only the surface layer of catalyst grains in the intensive process zone.

The catalytic activity of the samples, discharged from reactor B is studied under the conditions described in Table 5.

The results from the reactive products distribution, the total degree of conversion and process selectivity, depending on the catalyst position in the reactor, are shown in Table 6 and in Fig. 9.

The results obtained showed drastic difference in the catalytic activity of the “spent” catalyst, located at different levels of the catalytic layer. The samples of the intensive process zone (to 40 cm) show very low activity. The results obtained demonstrate that the process of deactivation of the industrial catalyst is slower but takes place even at temperatures below 300 °C. For that reason at the end of the exploitation period a significant part of the process is shifted to the lower part of the catalyst layer, which is confirmed by the temperature profiles, presented in Figs. 2 and 3. The absence

Table 5
Conditions of the experiment.

Index	Value
Temperature of the heat transfer media	220 °C
Gas composition	7.0% CH_3OH, 10.0% O_2, 3.3% H_2O, N_2 to 100%
Space velocity	4800 h^{-1}
Catalyst	50 ml

Table 6
Reactive products distribution, total degree of conversion (X_t) and process selectivity (S) depending on the catalyst position in reactor B.

No.	Catalyst	Conversion to, %			X_t, %	S, %
		CH_2O	CO	DME		
1	B_{0-20}	31.3	0.0	1.8	33.0	94.6
2	B_{20-40}	92.7	5.3	1.6	99.7	93.0
3	B_{40-60}	91.6	7.7	0.5	>99.5	91.8
4	B_{60-80}	90.4	8.3	1.1	>99.5	90.6
5	"Fresh"	92.1	6.1	1.8	>99.5	92.1

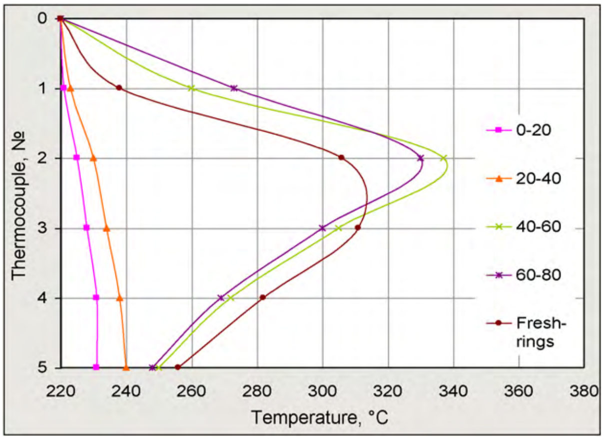

Fig. 9. Temperature profile of the catalysts taken from reactor B. Temperature of the heat transfer media 220 °C.

of reddish-brown coloration due to the formation of Fe_2O_3 by oxidation of $FeMoO_4$ ($2FeMoO_4 + (1/2)O_2 = Fe_2O_3 + 2MoO_3$) shows that the following reactions are the main reason for MoO_3 sublimation and deactivation of the industrial catalyst at low temperatures:

$$MoO_4^{2-} + 2H_2O \leftrightarrow MoO_2(OH)_2 + 2OH^-$$

$$MoO_2(OH)_2 \leftrightarrow MoO_3 + H_2O$$

It seems that at temperatures below 300 °C the formation of $FeMoO_4$ and Fe_2O_3 is negligible and does not represent a dominant factor influencing the catalytic properties of the Fe–Mo catalyst under these conditions of industrial exploitation.

The samples of the catalyst located in the layer from 40 to 80 cm show activity which is commensurable to and even higher that the activity of the "fresh" catalyst.

4. Conclusions

The results obtained from the study of spent catalysts from the formalin producing industrial plant show that:

1. No visible changes in iron-molybdate catalyst appearance and phase composition are observed at temperatures of the catalyst layer lower than 300 °C. Its specific surface area and MoO_3 content in the intensive process zone decrease while the Fe_2O_3 content increases.
2. The catalytic properties of the catalyst located in the intensive process zone significantly deteriorate during the exploitation in spite of the low temperature in the catalyst layer. The catalyst, located in the lower part of the layer (40–80 cm) completely maintains its properties during the whole period of exploitation.
3. The main reason for catalyst deactivation in the intensive process zone is the change in its surface layer composition due to sublimation of part of MoO_3 and decrease of its specific surface. At temperatures lower than 300 °C the formation of $FeMoO_4$ and Fe_2O_3 is insignificant and is not a dominant factor, affecting the catalytic properties of iron-molybdate catalyst during its industrial exploitation.

Acknowledgement

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