

KAUNAS UNIVERSITY OF TECHNOLOGY

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**NANOLAYER COPPER CATALYSTS IN THE
PROCESSES OF METHANOL CONVERSION TO
FORMALDEHYDE**

Summary of the Doctoral Dissertation

Technological Science, Chemical Engineering (05T)

Kaunas, 2005

KAUNO TECHNOLOGIJOS UNIVERSITETAS

Linas Kuzminas

**NANOSLUOKSNIO VARIO KATALIZATORIAI
FORMALDEHIDO GAMYBOS IŠ METANOLIO
PROCESUOSE**

Daktaro disertacijos santrauka

Technologijos mokslai, chemijos inžinerija (05T)

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INTRODUCTION

Relevance of the work. The selective methanol vapor oxidation by air oxygen is used for the large-scale production of formaldehyde. The process is catalytic. At the present time, the most used catalysts for this purpose are made from pure Ag or Ag/support. These catalysts are expensive, because they are prepared by using the pure silver and the special technology of specific surface area formation. In addition, the strict requirements concerning the purity of methanol and stability of technological parameters must be fulfilled. Otherwise, the catalyst deactivation occurs and Ag losses significantly increase.

The catalysts of transition metal oxides ($\text{Fe}_2\text{O}_3 - \text{MoO}_3 - \text{V}_2\text{O}_5$) are also employed in formaldehyde synthesis, however, their use is characterized by high energy expenses.

Copper or its oxides are well known catalysts of organic compounds oxidation. Copper gauzes and tubes were used in early formaldehyde production processes. Later, copper catalyst was replaced with silver. Nevertheless, the potential use of copper and its compounds in formaldehyde synthesis continues to attract attention of many researchers. The metallic copper can promote both selective and total oxidation of organic compounds, depending on the technological conditions. The activity of copper catalyst is influenced by its composition and active copper state on the catalyst surface. The selectivity with respect to desirable product depends also on contact time. In this context, the research on the use of nanolayer Cu/quartz catalysts in methanol oxidation is highly relevant. By using such a catalysts the diffusion limitations in catalyst pores can be avoided. The experimental data concerning the use of such catalysts in organic compounds oxidation are rather scarce.

Recently, the photocatalytic oxidation processes of some organic compounds were investigated. It was established that UV radiation can increase the selectivity of catalysts. Therefore, it is important to study the influence of UV radiation on methanol oxidation in the presence of nanolayer copper catalysts.

Aim of the work. The aim of the present work was to determine operational parameters of methanol conversion to formaldehyde using nanolayer copper catalysts. In order to reach the aim of the work we had to complete these goals:

1. to prepare nanolayer Cu catalysts and to determine their composition, structure and surface parameters;
2. to perform the thermodynamic calculations in order to estimate the stability and possible interactions of methanol oxidation products;
3. to determine operational conditions, methanol conversion degree and selectivity of methanol oxidation by air oxygen to formaldehyde using Cu/quartz catalysts;

4. to determine the possibility to increase the activity of Cu/quartz catalyst using TiO_2 as a modifying additive and UV radiation;
5. to propose the technological peculiarities for the use of synthesized catalysts in the methanol conversion technologies.

Scientific novelty and practical significance. The use of nanolayer Cu/quartz catalysts in methanol oxidation by air oxygen was experimentally and theoretically studied for the first time. An influence of the secondary reactions on the catalyst selectivity was experimentally determined and confirmed by thermodynamics calculations. The technological peculiarities for the use of Cu/quartz catalyst in the methanol conversion process were proposed.

Approval and publication of research results. Results of the research are presented in 10 publications, two of them published in a journal “Chemical technology”, one in journal “The Journal of the University of Chemical Technology and Metallurgy” (Bulgaria) and 2 reported in international conferences.

Structure and contents of the dissertation. Dissertation consists of introduction, literature survey, experimental part, results and discussion, conclusions, list of 202 references, list of 10 publications on dissertation topic and 9 appendixes. The main material is presented in 95 pages, including 31 table and 27 figures.

Statements presented for defense.

1. Using chemical Cu deposition and preparing quartz tubes surface in a special way, the nanolayer Cu/quartz catalyst can be obtained. The active component covers the support in a 60–70 nm layer.
2. The Cu/quartz catalyst is about 250 times more efficient than Cu–pumice–supplement catalysts. Its optimal exploitation temperature is 575 °C. At this temperature the selectivity towards formaldehyde reaches 50.6 % and the methanol conversion is 32 %.
3. During methanol oxidation on the surface of Cu/quartz catalyst, H_2 , CH_4 , CO , CO_2 , H_2O and HCOOH together with formaldehyde are found in postreactive gas. Their formation is related to the thermal destruction and the dehydrogenation of the reagents.
4. The methanol conversion on nanolayer Cu/quartz catalysts slightly increases by modifying them with TiO_2 . An UV radiation enhances methanol dehydrogenation reaction.

EXPERIMENTAL

Catalysts synthesis and activity testing equipment

Nanolayer Cu/quartz catalyst was formed by using quartz glass tubes of 4 mm in diameter and 5 mm in height as a support. For the synthesis of copper catalyst, chemical Cu deposition method has been applied. The following solution was used: CuSO_4 (7 g/l), NiCl_2 (2 g/l), $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (23 g/l), NaOH (5–6 g/l), NaCO_3 (2 g/l) and formaline (26 ml/l). The surface of quartz was prepared by two steps. Sensitizing of the surface has been performed in 5 % SnCl_2 hydrochloric acid solution. The process has been carried out for a few seconds after that quartz tubes were washed with distilled water. Activation was performed in aqueous ammonia solution containing 10 g/l of AgNO_3 . These prepared quartz glass tubes were kept in solution for 1 minute and poured into coppering solution. Compact Cu film has been formed just in 60–70 °C by slowly heating (4–5 °C/min) of cold coppering solution.

Preparing Cu-TiO_2 /quartz catalysts, quartz glass tubes were covered with TiO_2 film (0.75 wt %) and dried before chemical Cu deposition on quartz surface. Cu-TiO_2 /pumice catalyst synthesized similarly. $\text{Cu-pumice-supplement}$ catalysts were prepared by using pumice, clay and CaO , MgO , K_2CO_3 , CaCO_3 as a pore-forming supplements. These catalysts were obtained by mixing wet materials, followed by calcination.

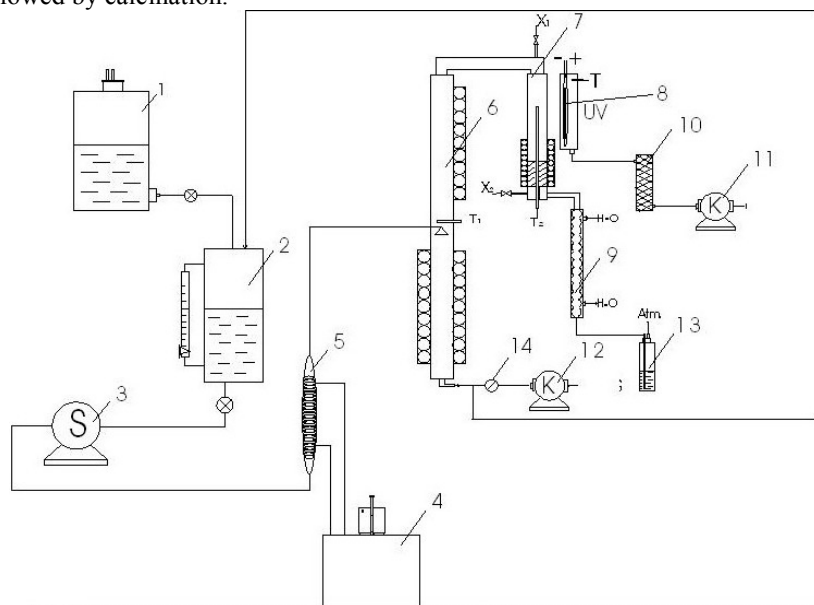


Fig 1. Experimental apparatus scheme: 1 – container with aqueous methanol solution; 2 – vessel, 3 – peristaltic pump, 4 – thermostat, 5 – heater, 6 – evaporator, 7 – reactor, 8 – UV lamp, 9 – cooler, 10 – air purifier, 11, 12 – air blowers, 13 – condensate, 14 – rheostat, X_1, X_2 – sampling; T, T_1, T_2 – thermopiles

Catalyst activity and technological parameters were determined by using experimental apparatus presented in Fig. 1. It consists of such parts: gas feeding, methanol–water mixture dosage, methanol evaporation, methanol conversion, products condensation. During some experimental runs, the quartz glass reactor was irradiated with DRT–240 UV lamp (240–320 nm wavelength, 24.6 W radiant flux).

Gas analysis

The analysis of the gases was performed on a *Perkin Elmer Clarus 500* GC/MS system (COL-ELITE 5MS capillary column; 30 m 0.25 mm i.d., 0.25 μm film thickness). ‘NIST 95’ database was used for the identification of compounds.

IR spectroscopy has been carried out with the help of spectrometer *Perkin Elmer* FT–IR system Spectrum X. The tablets of specimen have been prepared using 1.2 mg material and 200 mg KBr.

CO_2 , CO, O_2 , H_2 and CH_4 concentrations were measured with gas analyzer *GHL–1*. CO_2 was absorbed by 30–35 % KOH aqueous solution, CO by $[\text{Cu}(\text{NH}_3)_4]\text{Cl}$ ammonium solution, O_2 by pirogalol, and H_2 by 22 % NaCl solution.

In addition, the concentration of methanol and formaldehyde was measured photocolorimetrically using photoelectric colorimeter FEK–56.

Characterization of catalysts

Cu loading in catalyst was determined by *Perkin Elmer AAnalyst 400* atomic absorption spectrometer (AAS).

Differential scanning calorimetry (DSC) was employed for measuring the thermal stability and phase transformation of synthesized products at a heating rate of 15 $^\circ\text{C}/\text{min}$, the temperature ranged from 30 $^\circ\text{C}$ up to 800 $^\circ\text{C}$. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt–Rh were used.

X-ray diffraction (XRD) patterns of the samples have been recorded by a *DRON-6* diffractometer with Ni-filtered CuK_α radiation at 30 kV and 20 mA at 2 $^\circ$ min^{-1} scanning rate.

Scanning electron microscopy (SEM) of samples has been recorded using a *Hitachi S-4000* apparatus.

The specific surface area was measured by a BET surface area analyzer ‘Quantasorb’ (Quantachrome, USA). The surface area, total pore volume and pore size distribution of a sample were determined by employing the techniques of adsorbing the adsorbate gas (N_2) from a flowing mixture of adsorbate and an inert non-adsorbable carrier gas (He) at 77 K. The total pore volume and pore size distribution were calculated according to the corrected Kelvin equation and Orr and Dalla Valle scheme using entire N_2 desorption isotherm at 77 K.

The XPS studies were performed by a *VG Escalab II* electron spectrometer using AlK_α radiation. The residual gas pressure in the analysis chamber was 10 $^{-7}$ Pa. The binding energies (BE) were determined utilizing the C1s line (from an adventitious carbon) as a reference with energy of 285.0 eV. The accuracy of the measured BE was ± 0.2 eV.

RESULTS AND DISCUSSION

Calculated thermodynamic parameters of methanol conversion reactions

Thermodynamic possibility of methanol oxidation, products stability, interaction between components of postreaction mixture was calculated by Hess's, Kirhoff's, heat capacity, entropy and Gibbs energy dependence on temperature equations.

The change in Gibbs energy of reactions was calculated using these equations:

$$\Delta_r G_T^o = \Delta_r H_T^o - T \Delta_r S_T^o,$$

where $\Delta_r H_T^o$ and $\Delta_r S_T^o$ - enthalpy and entropy changes of reactions at temperature T.

Enthalpy change of reactions is defined by the following equations:

$$\Delta_r H_{298}^o = \Sigma(n_i \Delta_f H_{298}^o)_{prod} - \Sigma(n_i \Delta_f H_{298}^o)_{r.m.},$$

$$\Delta_r H_T^o = \Delta_r H_{298}^o + \int_{298}^T \Delta_r C_p dT$$

where $\Delta_r H_{298}^o$ - standard enthalpy change of reactions, kJ/mol;

$\Delta_f H_{298}^o$ - standard enthalpy change of formation of reactants, kJ/mol;

$\Delta_r C_p$ - heat capacity change of reactions, J/mol.K.

The change in reaction heat capacity is defined by the equation:

$$\Delta_r C_p = \Delta_r a + \Delta_r bT + \Delta_r cT^2 + \Delta_r c' \frac{1}{T^2},$$

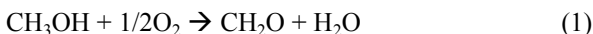
where $\Delta_r a$, $\Delta_r b$, $\Delta_r c$ and $\Delta_r c'$ - constants of heat capacity dependence on temperature.

Entropy change of reactions at temperature T was calculated:

$$\Delta_r S_T^o = \Delta_r S_{298}^o + \int_{298}^T \Delta_r C_p \frac{1}{T} dT,$$

where $\Delta_r S_{298}^o$ - standard reaction entropy.

Methanol conversion to formaldehyde was calculated at first. Under our experimental conditions methanol can be oxidized to formaldehyde by air oxygen or dehydrogenation according to these reactions:



On the basis of calculation results, it was established that the selective methanol oxidation to formaldehyde will dominate in a 548–948 K range (Fig. 2).

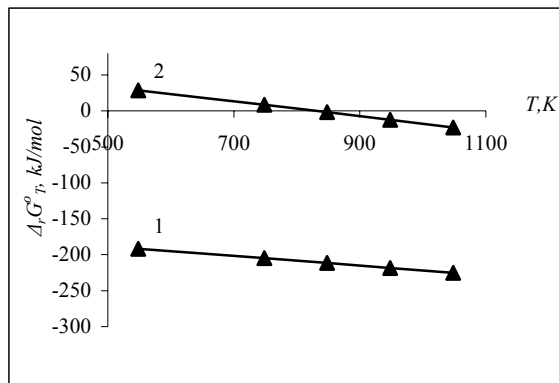
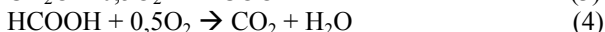


Fig. 2. Gibbs energy ($\Delta_r G^\circ_T$) dependence on temperature of methanol partial oxidation (1) and dehydrogenation (2) reactions

$\Delta_r G^\circ_T$ values of reaction (1) is much more negative than those of methanol dehydrogenation. The latter reaction can cause the formaldehyde formation only at high temperatures. At 548–948 K (2) reaction is even more impossible ($\Delta_r G^\circ_T$ varies between 30.3 and -5.5 kJ/mol). It must be noted that the evaluation based on Gibbs energy is approximate as reactions are recognized to be possible only when $\Delta_r G^\circ_T$ is more negative than -40 kJ/mol.

The thermodynamic possibility of methanol and formaldehyde further oxidation to HCOOH, CO₂ and H₂O was evaluated according to these reactions:



The calculation results (Fig. 3) have showed, that these reactions are thermodynamically possible. The Gibbs energy values are highly negative.

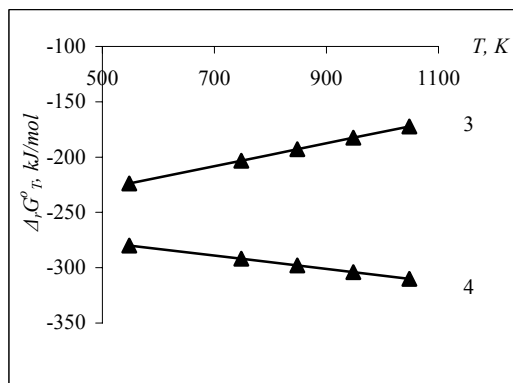


Fig. 3. Gibbs energy ($\Delta_r G^\circ_T$) dependence on temperature of formaldehyde (3) and formic acid (4) oxidation reactions

It can be inferred from the results of thermodynamic calculations that the methanol/oxygen ratio in prereactive gas should not be increased. By increasing O₂ concentration the possibility of methanol and formaldehyde complete oxidation to CO, CO₂ and H₂O increases much (Table 1).

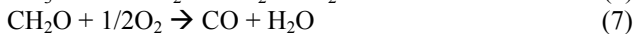
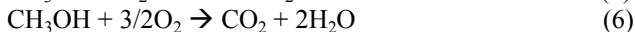


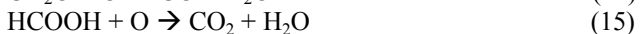
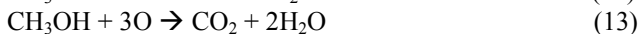
Table 1. Methanol (5, 6) and formaldehyde (7, 8) complete oxidation reactions parameters enthalpy ($\Delta_r H^\circ_T$), entropy ($\Delta_r S^\circ_T$) and Gibbs energy ($\Delta_r G^\circ_T$) in 548–1048 K range

Reactions	T, K	548	748	848	948	1048
5	$\Delta_r H^\circ_T$, kJ/mol	-391.49	-393.92	-396.38	-399.67	-403.79
	$\Delta_r S^\circ_T$, J/molK	134.73	131.08	127.99	124.34	120.21
	$\Delta_r G^\circ_T$, kJ/mol	-462.79	-491.24	-506.71	-523.02	-540.15
6	$\Delta_r H^\circ_T$, kJ/mol	-674.15	-676.17	-678.37	-681.37	-685.17
	$\Delta_r S^\circ_T$, J/molK	49.28	46.28	43.53	40.19	36.39
	$\Delta_r G^\circ_T$, kJ/mol	-698.19	-708.97	-715.56	-722.94	-731.13
7	$\Delta_r H^\circ_T$, kJ/mol	-235.23	-236.33	-237.55	-239.23	-241.36
	$\Delta_r S^\circ_T$, J/molK	68.02	66.39	64.86	62.99	60.86
	$\Delta_r G^\circ_T$, kJ/mol	-270.744	-284.80	-292.51	-300.67	-309.27
8	$\Delta_r H^\circ_T$, kJ/mol	-517.89	-518.57	-519.54	-520.93	-522.73
	$\Delta_r S^\circ_T$, J/molK	-17.42	-18.40	-19.61	-21.15	-22.96
	$\Delta_r G^\circ_T$, kJ/mol	-506.14	-502.53	-501.35	-500.59	-500.25

Oxygen amount should not exceed reaction's (1) stoichiometric amount. By increasing O₂/CH₃OH ratio to 1, $\Delta_r G^\circ_T$ at 1048 K is -529,06 kJ/mol. It means that the reaction (5) possibility is increased more than 2 times. By increasing molar O₂/CH₃OH ratio to 1.5, $\Delta_r G^\circ_T$ is -719.21 kJ/mol.

The thermodynamic data of methanol oxidation justifies the molar O₂/CH₃OH ratio 0.26–0.27. In this case the O₂ has been dosed less than (1) reaction stoichiometry needs in purpose to avoid further oxidation of formaldehyde to HCOOH. Experimental results show that this reaction could not be totally avoided: FT–IR analysis confirmed the presence of HCOOH.

The methanol oxidation reaction proceeds on the surface of Cu catalyst. It is known that various oxoradicals are present at high temperature on a surface of Cu catalyst. Highly reactive O atoms can participate in methanol oxidation. Participating hypothetic reactions can be written as follows:



Gibbs energy of these reactions acquire a highly negative values that overcomes the Gibbs energy of oxidation with participating molecular oxygen. Thus, it is expected that these reactions will dominate in the methanol oxidation processes (Table 2).

Table 2. Gibbs energy ($\Delta_r G^\circ_T$) of methanol conversion reactions (9–15) in 548–1048 K range

Reaction	$\Delta_r G^\circ_T$ (kJ/mol) at temperature T, K				
	548	748	848	948	1048
$\text{CH}_3\text{OH} + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$ (9)	-410.28	-413.79	-416.08	-418.74	-421.76
$\text{CH}_2\text{O} + \text{O} \rightarrow \text{HCOOH}$ (10)	-439.59	-410.39	-394.97	-379.01	-362.50
$\text{HCOOH} + \text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ (11)	-503.02	-506.83	-510.13	-514.36	-519.51
$\text{CH}_3\text{OH} + 2\text{O} \rightarrow \text{CO} + 2\text{H}_2\text{O}$ (12)	-899.26	-905.93	-910.46	-915.79	-921.92
$\text{CH}_3\text{OH} + 3\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ (13)	-1352.89	-1331.01	-1321.18	-1312.11	-1303.78
$\text{CH}_2\text{O} + \text{O} \rightarrow \text{CO} + \text{H}_2\text{O}$ (14)	-488.98	-492.15	-494.38	-497.05	-500.16
$\text{CH}_2\text{O} + 2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ (15)	-942.62	-917.22	-905.09	-893.37	-882.02

The presence of H_2 and CH_4 in postreactive gas confirms that together with methanol and intermediate compounds oxidation, a lot of other reactions can occur. H_2 can form in a process of methanol, formaldehyde or HCOOH thermal destruction at high temperature:



Methane can be formed during methanation reactions:



Carbon can be formed in Boudouard reaction:



This process is possible in the absence of oxidant. During the above mentioned reactions, when O_2 and H_2O vapors are present in postreactive mixture, other reactions are possible as well:



The thermodynamic calculations of mentioned reactions show that the increasing temperature in process an influence of secondary reactions would change (Fig. 4).

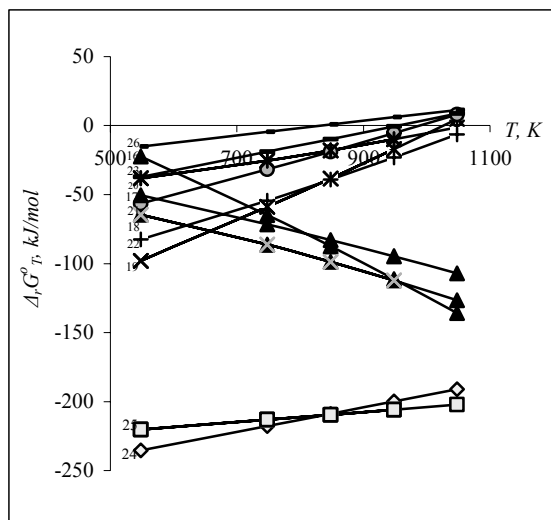


Fig. 4. Gibbs energy ($\Delta_r G^\circ_T$) of mentioned (16–24) reactions at 548–1048 K

The thermodynamic possibility of CH_3OH , CH_2O and HCOOH thermal destruction to CO and H_2 increases with the increase of temperature. The thermodynamic possibility of exothermic (19–22) reactions increases by decreasing temperature. The possibility of Boudouard reaction (23) by forming elemental carbon is the highest at low temperatures. However, the rate of carbon formation will be low. From thermodynamic point of view, this process should be accompanied by two fast H_2 and CO oxidation reactions (24) and (25). If the concentration of oxygen in postreactive gas would be sufficient, the unreacted CO and H_2 should not remain. However, the presence of CO , H_2 and O_2 have been confirmed experimentally. This shows that the final concentrations of CO and H_2 depend on a short contact time of the used catalysts, and the fast gas cooling in the equipment. On the other hand, the results of thermodynamic calculations of secondary reactions explain the optimum contact time and catalyst load. When the optimal τ_K is exceeded, amounts of formaldehyde, H_2 and CO decrease. On the basis of thermodynamic calculations it can be concluded that CH_2O forms on the Cu catalyst surface because of the dominating oxidation reactions. The presence of H_2 and CO in postreactive gas is caused by thermal destruction of methanol, formaldehyde, formic acid and not by methanol dehydrogenation. Amount of methane is caused by CO and CO_2 methanation reactions. An influence of the carbon methanation has been valued as not important if the optimal 848 K temperature in reactor is kept. To the CO and CO_2 proportion in the postreactive gas the reaction can have an influence, and in a higher temperature region, $\Delta_r G^\circ_T$ of the reaction (26) is positive and the reaction is valued as thermodynamically not possible.

Methanol oxidation using Cu–pumice–supplements catalysts

These catalysts were prepared by the procedure presented in experimental part. Catalysts have a small specific surface area $S_{\text{BET}} = 0.06\text{--}0.58 \text{ m}^2/\text{g}$. The smaller S_{BET} has been obtained for catalysts calcined in an air atmosphere. S_{BET} increased to $0.43\text{--}0.58 \text{ m}^2/\text{g}$ when calcination was performed in N_2 atmosphere. The pores with 3–8 nm radius are prevailing in these catalysts.

Table 3. Composition of Cu catalysts

Catalyst No.	Components of catalyst, wt %							The specific surface area S_{BET} , m^2/g	Average radius of pores r_p , nm	Condition of synthesis
	Cu	Pumice	Expanded clay	Calcinating supplement	CaO	MgO	K_2O			
I	0.5	63.5	9.1	0.4	9.0	15.51	1.99	0.39	3.19	Prepared in air atmosphere
II	0.5	63.7	9.1	0.4	10.7	15.60	-	0.06	8.07	
III	0.5	63.5	9.1	0.4	9.0	15.51	1.99	0.43	5.24	Prepared in N_2 atmosphere
IV	0.5	63.7	9.1	0.4	10.7	15.60	-	0.58	4.38	

The experimental data of catalyst activity showed that supplying the mixture of air and methanol vapor with 42 % of methanol into reactor at $300 \text{ }^\circ\text{C}$, the temperature of all loads autothermally increases to $573\text{--}617 \text{ }^\circ\text{C}$.

The data shows rather low activity of Cu catalysts (methanol conversion degree $\eta = 21.0\text{--}36.15 \%$). A large amount of the unreacted methanol is present in post reactive gas. There is the unreacted O_2 ($1.92\text{--}4.92 \%$) as well. The concentration of formaldehyde does not exceed 5.69% . The catalysts are not enough selective, the direct methanol oxidation reactions to formaldehyde influences selectivity from 14.26 to 66.06% . H_2 and methane were detected in post reactive gases. These materials could form because of thermal fission of methanol. It has been established that activity of all catalysts increases by increasing reactor temperature above $617 \text{ }^\circ\text{C}$ (Table 4).

Table 4. Product yields, conversion and selectivity of 100 % methanol oxidation on Cu catalysts at $615\text{--}675 \text{ }^\circ\text{C}$ and molar $\text{O}_2/\text{CH}_3\text{OH}$ ratio $0.26\text{--}0.27$

Catalyst No. Table 3	Temperature in reactor, $^\circ\text{C}$	Concentrations of components in postreactive gas, % (volume)								Selectivity S, %	Conversion degree η , %
		CH_3OH	CH_2O	CO_2	O_2	CO	H_2	CH_4	H_2O		
I	647	23.87	5.69	1.84	3.42	0.07	12.44	4.21	11.06	48.18	33.10
II	645	8.17	2.31	0.56	2.14	0.05	12.35	6.20	51.10	25.34	52.73
III	615	13.51	0.86	3.54	4.89	0.08	28.07	8.18	7.29	6.79	48.38
IV	675	0.07	1.0	1.89	4.94	0.21	35.08	16.59	0.98	5.08	99.65

* – remaining amount is inert gas

When the temperature is $675 \text{ }^\circ\text{C}$, η reaches 99.65% (Table 4) for the catalyst of the IV sample (Table 3). η varies between $33.10\text{--}48.38 \%$ for the catalysts with a K_2O supplement. The concentration of formaldehyde and selectivity of the catalyst decreases in postreactive gas.

When the molar $\text{O}_2/\text{CH}_3\text{OH}$ ratio is $0.26\text{--}0.27$, there is not enough of oxygen for total oxidation reactions, thus, the amount of unreacted oxygen is remained practically unchanged at $573\text{--}617 \text{ }^\circ\text{C}$ and $645\text{--}675 \text{ }^\circ\text{C}$. The concentration

of CO₂ in post reactive gases did not change as well. H₂ and CH₄ concentrations significantly change in gases after the use of catalyst at higher temperature. It shows that during temperature increase of the used catalyst, the thermal methanol dissociation proceeds faster than its oxidation by oxygen. That is the reason to not increase the temperature above 675 °C for the used catalysts.

More active catalysts are Cu without K₂O supplements, especially if they are calcined in the N₂ atmosphere. A larger specific surface area S_{BET} influences higher activity. It can be concluded that increasing O₂ concentration to the needed one according to methanol reaction stoichiometry, temperature of the catalyst autothermally would exceed 675 °C, and methanol conversion degree would reach 100 %, however, the catalyst becomes less selective with respect to formaldehyde.

One can conclude that used catalysts containing 0.5 wt % of Cu are not enough selective towards formaldehyde and they promote total oxidation and thermal destruction of methanol.

In order to increase the activity of Cu/pumice catalysts, the TiO₂ supplement has been used. When the temperature of the load autothermally increases to 575 °C, methanol conversion degree η is not high and reaches 27.02 %. Concentration of formaldehyde in postreactive gas is higher than in the case of previous tested catalysts and reaches 7.81 % (S = 69.08 %), and concentrations of H₂ and CH₄ are lower. When reagent mixture is illuminated by UV radiation, CO₂ and H₂O concentrations in postreactive gas increases from 1.26 to 1.82 % and from 34.54 to 41.21 %, respectively. Methanol conversion degree η reaches 35.59 %. TiO₂ (3.61 wt %) supplement increases selectivity of Cu catalysts, however, methanol conversion degree remains not high.

It is known that the surface area S_{BET} of the best methanol oxidation catalysts is rather small at high temperatures. By increasing contact time of the reagents on the surface of the catalyst, concentrations of by-products increases. Thus, it is advantageous to use non porous material (such as quartz glass tubes) as the catalyst support. Quartz glass is thermally stable up to 1500–1670 °C. It is possible to form a thermally stable, having a good adhesion, layer of Cu or the other active component on a surface of quartz tubes.

Synthesis and properties of Cu/quartz catalysts

Cu/quartz catalyst was synthesized by the method described in experimental part. The results of experiments have showed that the structure of copper films on the surface of quartz tubes depends on synthesis temperature. Coppering solution is not thermally stable. If the temperature quickly reaches 80 °C, the solution starts to boil and brown deposits of copper are formed. Under these conditions copper film on quartz surface were not succeeded as Cu layer can be easily washed by water. Cu film on the surface of support was not succeeded at a lower than 60 °C because of a slow CuSO₄ reduction to metallic copper.

Compact Cu film has been formed only at 60–70 °C by slowly heating (4–5 °C/min) of cold coppering solution.

The best catalyst sample contain 0.125 wt % of Cu, as measured by AAS method. The data of X-ray diffraction analysis have showed (Fig. 5) that metallic copper prevails on a surface of quartz and there are traces of Cu₂O as well.

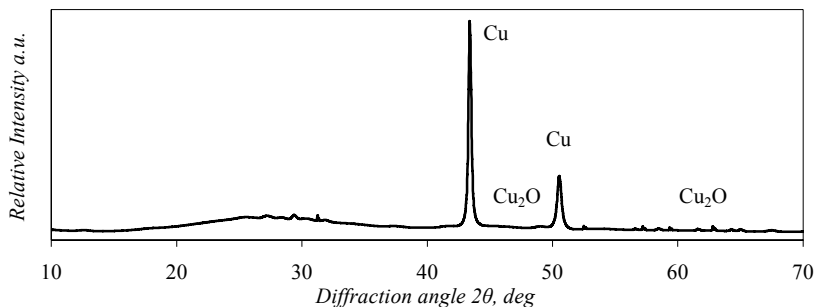


Fig. 5. X-ray diffraction patterns of Cu/quartz catalyst's Cu layer

Scanning electronic microscopy (SEM) analysis showed the dispersion of copper particles on the surface of quartz. It was estimated that the thickness of copper film is 50–100 nm (calculated thickness 68.71 nm).

The stability of Cu film in the studied reaction medium was evaluated on the basis of thermodynamic parameters of possible copper oxidation–reduction.

Table 5. Gibbs energy of oxidation–reduction reactions at 25–800 °C

No	Reaction	$\Delta_r G_r^0$ (kJ/mol) at temperature t , °C				
		25	200	400	600	800
1	$\text{Cu} + 0,5\text{O}_2 \rightarrow \text{CuO}$	-134.26	-113.87	-94.26	-73.44	-52.09
2	$\text{CuO} + \text{CH}_3\text{OH} \rightarrow \text{Cu} + \text{CH}_2\text{O} + \text{H}_2\text{O}$	-41.91	-73.72	-105.3	-139.3	-174.4
3	$\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$	-94.35	-77.49	-74.18	-73.11	-72.65
4	$2\text{CuO} + \text{CH}_3\text{OH} \rightarrow 2\text{Cu} + \text{CO} + 2\text{H}_2\text{O}$	-81.74	-113.04	-144.50	-178.41	-213.53
5	$3\text{CuO} + \text{CH}_3\text{OH} \rightarrow 3\text{Cu} + \text{CO}_2 + 2\text{H}_2\text{O}$	-95.48	-116.79	-139.01	-162.79	-187.41
6	$\text{CuO} + \text{CO} \rightarrow \text{Cu} + \text{CO}_2$	-122.96	-124.28	-128.04	-131.55	-135.17

The results of thermodynamic calculations (Table 5) confirmed the results of investigation.

Cu oxidation reaction with pure oxygen is possible even at low temperature, however, the rate is slow. Oxidation rate will increase, if the temperature and the partial oxygen pressure p_{O_2} increases. During methanol oxidation, the catalyst works in a gas mixture containing a large amount of reductants: CH₃OH, CH₂O, H₂, CO. The Gibbs energy $\Delta_r G_r^0$ of CuO reduction reactions with these materials is significantly lower than $\Delta_r G_r^0$ of oxidation reactions. It shows that CuO reduction reactions will prevail in 575–675 °C range.

Under these conditions the thin layer of metallic Cu should remain stable on the surface of catalyst, if the molar O₂/CH₃OH ratio is 0.26–0.27. CuO is not desirable because of his property to catalyze the non-selective oxidation of methanol to CO₂ and H₂O.

Activity of Cu/quartz catalyst

Cu/quartz catalyst was put into reactor within the 1.5 cm layer of catalyst. Feeding the prereactive O_2 -CH₃OH gas mixture by the flow of 5.22 l/min, the degree of methanol conversion reaches 35.9 % when molar O_2 /CH₃OH ratio is 0.26 at 675 °C. Unreacted methanol, hydrogen, methan and formaldehyde vapor were found in postreactive mixture (Table 6).

Table 6. Product yields, conversion and selectivity of 100 % methanol oxidation on Cu/quartz catalyst at 675 °C and molar O_2 /CH₃OH ratio 0.26

Concentrations of components in postreactive gas*, % (volume)								Selectivity S, %	Conversion degree η , %
CH ₃ OH	CH ₂ O	CO ₂	O ₂	CO	H ₂	CH ₄	H ₂ O		
21.25	4.96	0.65	4.43	0.52	9.32	5.80	16.07	41.55	35.97

* – remaining amount is inert gas

CO₂ and CO concentrations are low, they reach 0.65 % and 0.52 %, respectively. Catalysts selectivity towards formaldehyde is 41.55 %. The unreacted O₂ is also present. That shows a short gas contact time (τ_K). τ_K , for the used catalyst, which has been calculated according to the filling geometrical volume of the load in the reactor, is 0.026 s.

The methanol conversion degree η increases using 75 % methanol aqueous solution. It was found that the methanol conversion degree η increases by increasing the catalysts temperature at the molar O_2 /CH₃OH ratio 0.27. η exceeds 50 % when the temperature reaches 675 °C. The catalyst selectivity decreases quickly above 575 °C. The obtained data show that when the temperature is higher than 575 °C, concentrations of H₂ and CH₄ start to increase in postreactive gas, due to the methanol thermal destruction and CO, CO₂ methanation reactions (Table 7).

It was determined that changing the methanol load from 36.87 to 55.29 g/(cm²h), the methanol conversion degree η practically does not change, and the selectivity towards formaldehyde decreases from 57.94 to 50.82 %. Concentrations of H₂ and CH₄ increases by increasing a load.

Table 7. Product yields, conversion and selectivity of 75 % aqueous solution of methanol oxidation on Cu/quartz catalyst as a function of temperature at molar O_2 /CH₃OH ratio 0.27

Concentrations of components in postreactive gas*, % (volume)								Selectivity S, %	Conversion degree η , %
CH ₃ OH	CH ₂ O	CO ₂	O ₂	CO	H ₂	CH ₄	H ₂ O		
21.25	4.96	0.65	4.43	0.52	9.32	5.80	16.07	41.55	35.97

* – remaining amount is inert gas

The highest Cu/quartz selectivity towards formaldehyde has been obtained when the temperature was 575 °C and the height of catalysts bed in reactor was 1,5 cm (Table 8). This corresponds to the contact time of gas flow $\tau_K = 0.017$ s.

Table 8. Product yields, conversion and selectivity of 75 % aqueous solution of methanol oxidation on Cu/quartz catalysts as a function of catalysts layer height at 575 °C and molar O₂/CH₃OH ratio 0.27

The height of catalysts bed H, cm	Concentrations of components in postreactive gas*, % (volume)								Selectivity S, %	Conversion degree η, %
	CH ₃ OH	CH ₂ O	CO ₂	O ₂	CO	H ₂	CH ₄	H ₂ O		
0.75	30.64	5.18	0.53	4.50	0.05	2.97	7.38	28.62	39.44	29.41
1.5	29.80	7.18	0.63	3.50	0.04	2.24	6.28	31.86	50.82	32.16
3.0	21.48	6.02	1.35	3.68	0.05	2.16	7.13	29.13	41.35	40.40

* – remaining amount is inert gas

Increasing the height of catalysts bed from 1.5 to 3.0 cm and τ_K , the selectivity of catalyst towards formaldehyde decrease from 50.82 % to 41.35 %, while methanol conversion degree have increased. The data showed that it is not useful to increase τ_K above 0.017 s.

Comparing activity of Cu/quartz and Cu–pumice–supplements, Cu–TiO₂/pumice catalysts, it has been found that Cu/quartz catalyst functions at a lower τ_K and related load for the surface area unit of catalyst. It has been determined that the used Cu/quartz catalyst is more efficient than the catalysts having a pumice as a support, after calculating the methanol conversion degree per surface area unit of catalyst.

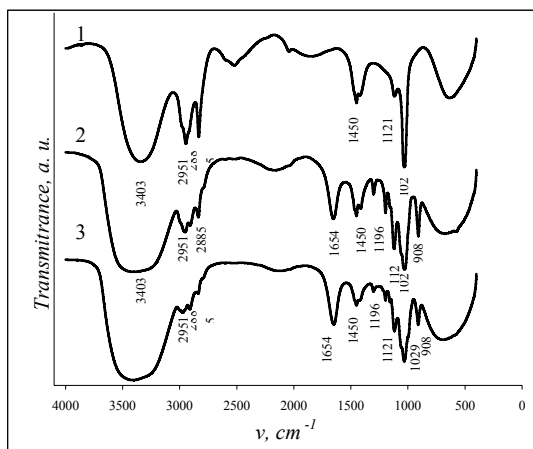


Fig. 6. FT-IR spectrograms of methanol conversion products: 1 – pure methanol, 2 – condensate of postreactive gas (–60 °C), 3 – condensate of postreactive gas (20 °C)

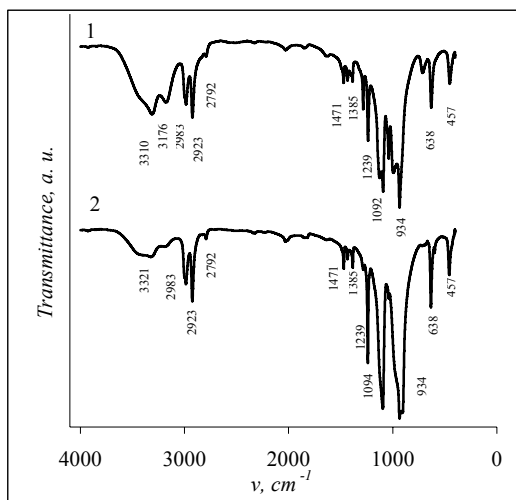
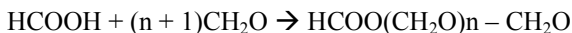


Fig. 7. FT-IR spectrograms: 1 – pure paraformaldehyde, 2 – paraformaldehyde obtained during experiment

Methanol oxidation products were extra analyzed by IR spectrometry method. For this purpose, the hot postreactive gases were cooled at 20 °C and -60 °C. The obtained data is presented in Fig. 6. The absorption bands at 3600–3200, 2951, 2885, 1450 and 1029 cm^{-1} frequencies range could be ascribed to methanol. The characteristic bands of $=\text{CH}_2$ bonds (aliphatic aldehydes) are near 1654 and 908 cm^{-1} and can be related to formaldehyde. The band near 1121 cm^{-1} could be ascribed to carboxylated acids (formic acid).

It has been determined that the aerosol has appeared in postreactive gas in all the experiments on Cu/quartz surface at temperature above 260 °C. This aerosol has been separated by filtering postreactive mixture. The FT-IR spectrum suggests (Fig. 7) the formation of paraformaldehyde.

It is possible to form the paraformaldehyde at a high temperature there is when a short gas mixture contact time τ_K on the surface of catalyst and a fast cooling of post reactive gases in laboratory equipment. Paraformaldehyde can form after the use of copper catalysts and because of the formaldehyde oxidation by-product – formic acid – reaction with formaldehyde. This effect has not been observed in the case of Cu/pumice catalysts.



The possibility of HCOOH formation on Cu/quartz catalyst surface was proved by thermodynamic calculations and experimentally. Despite that using Cu/quartz catalyst and cooling postreactive gas in a fast way, paraformaldehyde was gotten and indicated with FT-IR and MS analytic methods in a high quality. The paraformaldehyde has been formed only in the case of Cu/quartz catalyst. The paraformaldehyde was not formed using Cu-support catalysts.

In our opinion, the formation of paraformaldehyde has been caused by HCOOH presence in a process of methanol oxidation and by a short gas material contact time with the catalyst.

The results of mass spectrometric analysis of postreactive gases confirm the results of FT-IR analysis (Fig. 8).

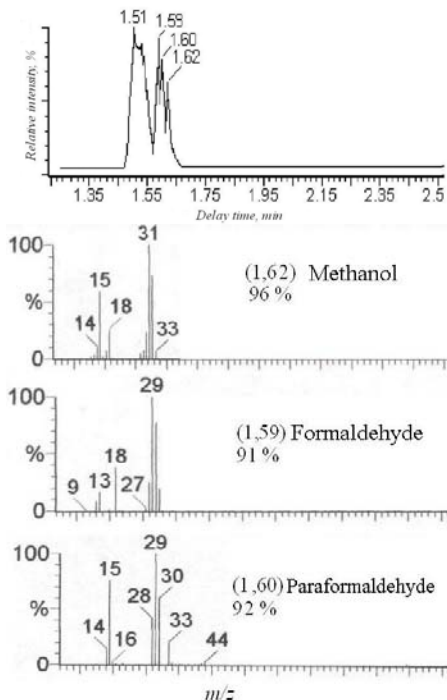


Fig. 8. Characteristic chromatograms and mass spectrums of product gas mixtures during selective methanol oxidation over Cu/quartz at 575 °C using molar O₂/CH₃OH ratio – 0.27

Properties and activity of Cu-TiO₂/quartz catalyst

Cu-TiO₂/quartz catalyst was synthesized by the method presented in experimental part. Amount of TiO₂ in catalyst was 0.75 wt %. It is determined that amount of Cu in the Cu-TiO₂/quartz catalyst is 3.6 times higher than in Cu/quartz catalyst and it is 0.45 wt %. The XRD analysis results show (Fig. 9), that TiO₂ modification is anatase and rutile and copper is metallic.

The obtained results showed that methanol conversion degree η reaches 30.1 % when temperature is 575 °C and it is similar to the conversion degree using Cu/quartz catalyst. The selectivity toward formaldehyde of modified catalyst increases to 62.03 %.

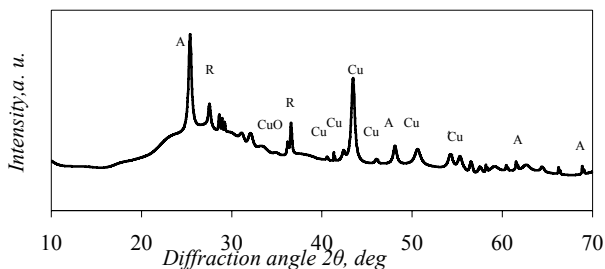


Fig. 9. X-ray diffraction pattern of Cu-TiO₂/quartz catalyst's Cu-TiO₂ layer; (A) – anatase, (R) – rutile

The highest Cu-TiO₂/quartz selectivity was obtained at molar O₂/CH₃OH ratio 0.28 (Fig. 10).

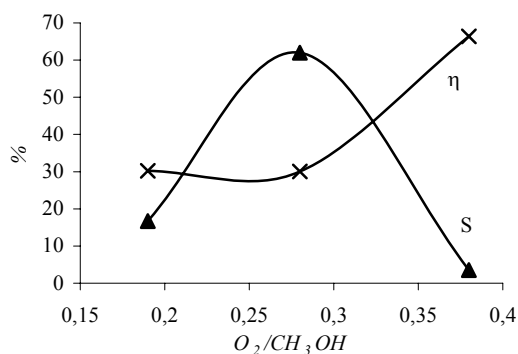


Fig. 10. Influence of molar O₂/CH₃OH ratio on conversion (η) and selectivity (S) of 75 % aqueous solution of methanol using Cu-TiO₂/quartz at 575 °C

The methanol conversion degree increases to 54 % when 75 % methanol aqueous solution was used (Table 9).

Table 9. Product yields, conversion and selectivity of 75 % aqueous solution of methanol oxidation on Cu-TiO₂/quartz catalyst as a function of temperature at molar O₂/CH₃OH ratio 0.27

Temperature in reactor, °C	Concentrations of components in postreactive gas*, % (volume)								Selectivity S, %	Conversion degree η, %
	CH ₃ OH	CH ₂ O	CO ₂	O ₂	CO	H ₂	CH ₄	H ₂ O		
450	31.25	2.74	0.75	8.46	0.06	0.23	2.43	16.15	41.45	17.46
575	16.50	9.09	1.49	3.42	1.01	3.71	3.80	38.59	46.95	53.99
675	6.01	6.66	2.14	3.41	0.07	11.77	6.82	27.96	34.70	76.15

* – remaining amount is inert gas

The results in Table 9 show that unreacted CH₃OH and O₂, H₂, CH₄, CH₂O are present in postreacted gas. Amounts of the other compounds are small. Concentrations of H₂ and CH₄ increase markedly when the temperature of reaction increases.

Catalyst support TiO₂/quartz is not absolutely indifferent to the studied process. At 575 °C the obtained methanol conversion degree is 38.38 % and selectivity towards formaldehyde is 46.63 %.

Trying to activate Cu/quartz catalyst with TiO₂ supplement, big differences were not noticed except the paraformaldehyde formation, but methanol conversion

degree have increased. Taking into account the results of thermodynamic calculations, the influence of TiO₂ can be explained as increasing influence of CH₃OH reactions with atomic O. This is in accord with the known fact: oxygen radical O[•] concentrates on TiO₂ surface in the oxygen environment and high temperature and increases activity.

Influence of UV radiation on the activity of Cu/quartz and Cu–TiO₂/quartz catalysts

DRT–240 lamp was used as a source of UV radiation. It radiates 24.6 W radiant flux. The UV radiation spectrum covers the 240–320 nm wavelength range. The reactor radiation flux to the area unit of the prereactive zone was 0.27 W/cm². Using Cu/quartz catalyst which contains 0.125 wt % of Cu and in a 1.5 cm load high has been found that the anhydrous methanol vapor conversion degree and the selectivity of the process, comparing to parameters of the process without UV radiation, changes not much. In both cases η varies between 30–36 % and selectivity S changes from 41.6 % to 45.4 % at 675 °C.

An influence of UV radiation is more noticeable using 75 % methanol aqueous solution, when the molar O₂/CH₃OH ratio is 0.27.

Table 10. Product yields, conversion and selectivity of 75 % aqueous solution of methanol oxidation on Cu/quartz catalyst under UV radiation as a function of temperature at molar O₂/CH₃OH ratio 0.27

Temperature in reactor, °C	Concentrations of components in postreactive gas*, % (volume)								Selectivity S, %	Conversion degree η , %
	CH ₃ OH	CH ₂ O	CO ₂	O ₂	CO	H ₂	CH ₄	H ₂ O		
275	38.69	1.08	0.05	9.55	0.05	1.40	0.19	25.80	79.44	3.39
375	31.25	3.30	0.23	6.71	0.05	2.79	2.42	29.84	55.04	16.10
475	27.45	7.84	0.42	5.33	0.05	5.33	3.02	30.38	69.21	29.21
575	26.85	10.41	0.50	1.92	0.05	9.39	3.48	30.14	72.10	34.97
675	14.23	5.48	0.99	1.17	0.06	8.53	9.39	27.29	34.42	52.80

* – remaining amount is inert gas

At optimal 575 °C temperature under the influence of UV radiation, the selectivity of 72.1 % towards the reaction to CH₂O was reached. UV radiation does not much change methanol conversion degree η . η mostly depends on the process temperature and not on the UV radiation. η increases by increasing temperature (Table 10).

Changing Cu/quartz catalyst load towards methanol, higher selectivity of 72.1 % could not be reached (Table 11).

Table 11. Product yields, conversion and selectivity of 75 % aqueous solution of methanol oxidation on Cu/quartz catalyst under UV radiation as a function of load at 575 °C and molar O₂/CH₃OH ratio 0.27

Load, g/(cm ² h)	Concentrations of components in postreactive gas*, % (volume)								Selectivity S, %	Conversion degree η , %
	CH ₃ OH	CH ₂ O	CO ₂	O ₂	CO	H ₂	CH ₄	H ₂ O		
36.87	23.35	7.59	0.95	3.48	0.04	1.76	6.63	40.63	49.92	39.44
46.08	25.54	9.23	0.77	3.45	0.05	3.74	4.6	30.31	63.01	36.45
55.29	26.85	10.41	0.5	1.92	0.05	9.39	3.48	30.14	72.10	34.97

* – remaining amount is inert gas

The highest selectivity of the catalyst towards formaldehyde under our experimental conditions corresponds to 1.5 cm catalyst bed. Increasing or decreasing the bed height, the selectivity of the catalyst towards formaldehyde decreases.

Using Cu–TiO₂/quartz catalyst has been established that selectivity of the catalysts under UV radiation increases too, however, the methanol conversion degree η changes not much (Table 12).

Table 12. Product yields, conversion and selectivity of 75 % aqueous solution of methanol oxidation on Cu–TiO₂/quartz catalyst as a function of temperature at molar O₂/CH₃OH ratio 0.27 and under UV radiation

Temperature in reactor, °C	Concentrations of components in postreactive gas*, % (volume)								Selectivity S, %	Conversion degree η , %
	CH ₃ OH	CH ₂ O	CO ₂	O ₂	CO	H ₂	CH ₄	H ₂ O		
575	17.59	9.84	1.71	2.18	0.81	7.87	1.47	37.88	60.55	48.02
675	8.23	9.75	2.11	2.69	1.05	11.88	2.17	32.63	55.22	68.21

* – remaining amount is inert gas

The obtained experimental data show that using UV radiation in analogous technological conditions (temperature, catalysts load, high of layer and etc.) H₂ concentration increases in postreactive gas. Amounts of the other methanol conversion products changes: unreacted CH₃OH and O₂, CH₄, H₂O vapor, CO₂ concentrations decreases not much in postreactive gas. At 575 °C the amount of unreacted O₂ decreases from 3.5 % to 1.92 %, the amount of the formed CH₄ decreases from 6.28 % to 3.48 %, CO₂ – from 0.63 % to 0.5 %, H₂O vapor amount decreases about 2 % under UV radiation. CH₂O and CO concentrations increase only slightly: formaldehyde from 7.18 % to 10.41 %, CO – from 0.04 % to 0.05 %. H₂ concentration in postreactive gas increases markedly using Cu–TiO₂/quartz catalyst as well. The results show that UV radiation promotes the methanol dehydrogenation. UV radiation ($\lambda = 240\text{--}320$ nm) should increase the possibility of these reactions more, because it stimulates methanol destruction. The energy of used UV radiation is sufficient to induce the dissociation of CH₃O–H, CH₃–OH and HCO–H bonds.

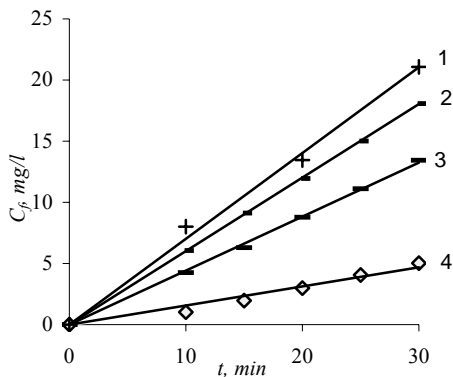


Fig. 11. 100 % methanol conversion to formaldehyde under UV radiation kinetic dependences: 2, 3, 4 – reactions in 30, 40, 50 °C; 1 – reaction in 30 °C and nitrogen atmosphere

Methanol dehydrogenation is influenced by temperature of the process, Cu catalysts and UV radiation. To order to evaluate an influence of UV radiation to the methanol stability, additional experimental runs have been done by studying reactions in the fluid phase. The closed experimental equipment was used.

The results of experiments show that the process depends on temperature. The rate constant of the synthesized formaldehyde in the photochemical process decreases 4 times, when reaction mixtures temperature increases from 30 °C to 50 °C.

In the photochemical experiments with methanol where oxygen was eliminated and not (before the process methanol was purged with nitrogen in reactor), it was found that under the same conditions the formed formaldehyde concentration in methanol without oxygen is higher than in methanol with not eliminated oxygen (Fig. 11). That lets us to think that formaldehyde forms straight in the process of methanol dehydrogenation and the decreased formaldehyde concentration, when the reactive mixture consists with oxygen as well, shows that further the formaldehyde can be oxidized to CO or CO₂. Analysis of the formed gas above reactive mixture analysis showed the following composition: C_{CO2} = 1 % (volume), C_{O2} = 20.5 %, C_{CO} = 0.2 %, C_{H2} = 3.1 %.

Under UV radiation, the concentration of H₂ increased in postreactive gas using all the investigated catalysts. In our opinion, UV radiation under experimental conditions does not promote the selective methanol oxidation to formaldehyde. On the contrary, UV radiation initiates methanol dehydrogenation and thermal destruction processes. This suggestion has been experimentally confirmed by studying methanol reactions in fluid phase under UV radiation in oxygen free (N₂) and air environments.

TECHNOLOGICAL PECULIARITIES OF NANOLAYER COPPER CATALYSTS USE

The determined efficiency of Cu/quartz catalyst in methanol oxidation process is 276.6 g/min·m². The corresponding efficiency of catalysts synthesized with pumice as support varies between 0.06 and 1.08 g/(min·m²) (Table 13).

The research results show that the efficiency of nanolayer Cu/quartz catalyst per surface area unit is approximately 250 times more higher than that of porous Cu catalysts used for comparison. The highest selectivity of catalyst is 72 % when contact time is equal 0.017 s. The selectivity decrease by increasing contact time. However, the decrease in contact time results in the decrease of methanol conversion degree.

Table 13. Catalysts efficiency and the load with respect to CH₃OH in 573–675 °C range and molar O₂/CH₃OH ratio 0.26

Catalyst	Specific surface area, m ² /g	Surface area of used catalyst, m ²	Reacted CH ₃ OH amount on catalyst, g/min	Efficiency of catalyst, g/min m ²
Cu/quartz	0.00118	0.00568	1.571	276.6
Cu–pumice–supplements				
I	0.39	2.91	0.89	0.31
II	0.09	0.67	0.73	1.08
III	0.43	3.21	1.26	0.39
IV	0.58	4.33	3.18	0.73
Cu–TiO ₂ /pumice	5.42	15.52	0.87	0.06

Parameters of catalyst stabilize during the first hour of process and later remain constant.

The obtained results show that Cu/quartz selectivity towards formaldehyde in methanol oxidation reactions is less than that of industrial Ag catalyst. The industrial reactors produce 10000–25000 t/year of formalin. Cu/quartz catalysts are not used in industrial formaldehyde synthesis. However, they can be used in a combinative technological schemes, where formaldehyde and especially paraformaldehyde is a secondary product.

In order to use Cu/quartz catalyst in the best way, the following optimal parameters must be kept: temperature of methanol–water vapor–air mixture 570–580 °C, load towards methanol 55.29 g/(cm²·h), contact time $\tau_k = 0.017$ s and molar O₂/CH₃OH ratio 0.27. Assuming 0.5 t/h periodic production of 37 % formalin, 0.375 t/h of liquid or 262.5 Nm³/h of gaseous methanol, 0.125 t/h of water and 338 Nm³/h of air would be needed. Under our experimental conditions, the used gas flow volume rate is 64·10³ h⁻¹, so the process needs 0.0118–0.012 m³ of Cu/quartz or Cu–TiO₂/quartz catalyst. It is recommended that catalyst bed in reactor would be 0.29–0.3 m in diameter and 0.17–0.18 m height. The process technological scheme could be analogical to that used in industrial Formox process.

CONCLUSIONS

- Using chemical Cu deposition method, the nanolayer Cu/quartz catalyst containing 0.125 wt % of Cu has been prepared. The surface of support is covered by 60–70 nm copper layer. The active catalyst component is metallic Cu.
- The optimal temperature of methanol oxidation to formaldehyde is 570–580 °C, the molar O₂/CH₃OH ratio being 0.27. Under these conditions, the methanol conversion degree is 32 %, and the selectivity towards formaldehyde exceeds 50 %. By increasing temperature to 675 °C, the selectivity decreases to 27 % and methanol conversion degree increases to 50 %.
- In the process of selective methanol oxidation to formaldehyde, H₂, CH₄, CO, CO₂, H₂O and HCOOH products in postreactive gas have been detected together with formaldehyde and unreacted methanol. Besides methanol oxidation reaction, methanol and reaction products dehydrogenation and thermal destruction processes

occur on the surface of Cu/quartz catalyst. These experimental results are confirmed by calculated thermodynamic parameters of reactions. Using Cu/quartz catalyst at 570–580 °C and short contact time of gas mixture on catalyst surface (0.017 s), the formation of paraformaldehyde aerosol is observed.

4. The nanolayer Cu/quartz catalyst containing 0.125 wt % of copper is approximately 250 times more efficient than Cu–pumice–supplements catalysts used for comparison. Under experimental condition, the specific efficiency of Cu/quartz catalyst is determined to be 276.6 g/(min m²).

5. The methanol conversion degree under optimal technological conditions increases from 32 % to 54 %, when TiO₂ (0.75 wt %) is added to the Cu/quartz catalyst.

6. Under 240–320 nm UV radiation, the process of methanol and reaction products dehydrogenation on the surface of nanolayer Cu/quartz and Cu–TiO₂/quartz catalysts is enhanced, thus, H₂ concentration in postreactive gas is increased.

7. Nanolayer Cu/quartz and Cu–TiO₂/quartz catalysts are less selective than pure Ag and Ag/support catalysts used in industry. However, they can be used in a combinative methanol conversion technological schemes, where formaldehyde and especially paraformaldehyde is a secondary product. In a periodic reactor with 400–500 t/year capacity, the Cu/quartz catalyst can be used as a bed of 0.29–0.3 m in diameter and 0.17–0.18 m in height.

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NANOSLUOKSNIO VARIO KATALIZATORIAI FORMALDEHIDO GAMYBOS IŠ METANOLIO PROCESUOSE

Reziumė

Metanolio garų atrankusis oksidavimas oro deguonimi naudojamas pramonėje gaminant formaldehidą. Procesas katalizinis. Pramonėje daugiausiai naudojami kristalinio sidabro, sidabro tinklelių ir Ag/nešiklis katalizatoriai. Šie katalizatoriai yra brangūs, kadangi ruošiami naudojant gryną sidabrą ir specialią savitojo paviršiaus formavimo technologiją. Naudojant šiuos katalizatorius keliami griežti reikalavimai naudojamos žaliavos – metanolio – kokybei ir technologinio proceso parametru palaikymui. Esant nekokybiškai žaliai ir technologinio proceso sutrikimams (molinio O_2/CH_3OH santykio ir temperatūros padidėjimas) katalizatorius dezaktyvuojasi. Todėl svarbūs sidabro katalizatorių aktyvios būsenos išsaugojimo ir sidabro nuostolių mažinimo klausimai.

Formaldehido gamyboje taikomi ir metalų oksidų ($Fe_2O_3-MoO_3-V_2O_5$) katalizatoriai. Jų panaudojimas susijęs su ženkliais energetinėmis sąnaudomis.

Varis ir jo oksidai žinomi kaip organinių junginių oksidavimo katalizatoriai. Be to, pirmosios formaldehido sintezės, atliktos naudojant katalizatoriumi vario tinklelius, vamzdelius. Vėliau sidabro katalizatoriai išstūmė vario katalizatorius, bet tyrėjų susidomėjimas vario ir jo junginių panaudojimu katalizatoriumi metanolio atrankiam oksidavimui iki formaldehido išliko. Metalinis varis, priklausomai nuo technologinių sąlygų, gali skatinti tiek atrankaus, tiek ir visiško oksidavimo reakcijas. Vario veiklumas kataliziniuose procesuose priklauso nuo katalizatoriaus sudėties ir nuo aktyvios vario būsenos katalizatoriaus paviršiuje. Atrankumas tikslinio produkto atžvilgiu priklauso ir nuo kontaktavimo su katalizatoriumi laiko. Šiuo požiūriu turėtų būti aktualūs nanosluoksnių Cu/kvarcas katalizatorių panaudojimo metanolio oksidavimui tyrimai. Naudojant tokius katalizatorius išvengiama difuzinių apribojimų katalizatoriaus porose. Duomenų literatūroje apie tokių katalizatorių panaudojimą organinių junginių oksidavimui nėra daug, o konkrečiai metanolii – nėra.

Pastaruoju metu literatūroje nagrinėjami fotokataliziniai kai kurių organinių junginių oksidavimo aspektai. Nustatyta, kad tam tikrose sąlygose UV spinduliuotės panaudojimas padidina katalizatoriaus atrankumą. UV spinduliuotės poveikio įvertinimas kataliziniam metanolio oksidavimui naudojant vario katalizatorius yra aktualus.

Darbo tikslas buvo nustatyti metanolio konversijos taikant nanosluoksnius Cu/kvarcas katalizatorius darbo rodiklius. Buvo eksperimentiškai pagamintas Cu/kvarcas katalizatorius. Nustatyta jo sudėtis, aktyviųjų komponentų struktūra, paviršiaus parametrai ir palygintas jo aktyvumas su Cu–porėtas nešiklis katalizatorių aktyvumu. Nustatytas katalizatorių aktyvumas atrankaus metanolio oksidavimo oro deguonimi reakcijose priklausomai nuo proceso technologinių parametru. Ištirtos Cu/kvarcas aktyvumo didinimo galimybės naudojant TiO_2

modifikuojantį priedą ir UV spinduliuotę. Taip pat buvo apskaičiuoti reakcijų termodinaminiai parametrai ir nustatytas metanolio oksidavimo mechanizmas. Pagal gautus rezultatus pateiktos technologinės prielaidos šių katalizatorių panaudojimui.

Remiantis tyrimų duomenimis padarytos šios išvados:

1. Naudojant cheminių vario nusodinimo metodą pagamintas nanosluoksniu Cu katalizatorius, turintis 0,125 % vario, dengiančio nešiklio kvarco paviršių 60–70 nm storio sluoksniu. Aktyvusis katalizatoriaus komponentas yra metalinis Cu.
2. Metanolio oksidavimo iki formaldehido naudojant nanosluoksniu Cu katalizatorių optimali temperatūra yra 570–580 °C, esant moliniam santykiui $O_2/CH_3OH = 0,27$. Šiomis sąlygomis metanolio konversijos laipsnis 32 %, esant atrankumui formaldehido atžvilgiu virš 50 %. Didinant temperatūrą iki 675 °C atrankumas mažėja iki 27 %, metanolio konversijos laipsnis didėja iki 50 %.
3. Atrankaus metanolio oksidavimo iki formaldehido metu poreakcinėse dujose be formaldehido ir nesureagavusio metanolio nustatytos H_2 , CH_4 , CO , CO_2 , H_2O ir $HCOOH$ priemaišos. Greta metanolio oksidavimo reakcijų Cu/kvarcas katalizatoriaus paviršiuje vyksta ir žaliavų bei reakcijos produktų dehidrinimo ir terminio skilimo procesai. Šiuos eksperimentinius duomenis patvirtina apskaičiuotieji reakcijų termodinaminiai parametrai. Naudojant Cu/kvarcas katalizatorių 570–580 °C temperatūroje ir esant mažam 0,017 s dujų mišinio kontaktavimo su katalizatoriumi laikui susidaro paraformaldehido aerolis.
4. Cu/kvarcas katalizatorius, turintis 0,125 % vario, apie 250 kartų našesnis nei palyginimui panaudoti Cu–pėma–priedai katalizatoriai. Tyrimų sąlygomis jo savitasis našumas nustatytas 276,6 g/(min·m²).
5. Cu/kvarcas katalizatorių modifikuojant TiO_2 priedu (0,75 masės %) ir esant optimalioms technologinėms sąlygoms bendras metanolio sureagavimo laipsnis padidėjo nuo 32 % iki 54 %.
6. Naudojant 240–320 nm bangos ilgio UV spinduliuotę Cu/kvarcas ir Cu– TiO_2 /kvarcas katalizatorių paviršiuje greitėja metanolio ir reakcijos produktų dehidrinimo procesas didėjant H_2 koncentracijai poreakcinėse dujose.
7. Cu/kvarcas ir Cu– TiO_2 /kvarcas katalizatoriai yra mažiau atrankūs nei pramonėje naudojami gryno Ag ir Ag/nešiklis katalizatoriai. Tačiau juos galima taikyti kombinuotose metanolio perdirbimo technologinėse schemose, kuriose formaldehidai ir ypač paraformaldehidai yra šalutiniai produktai. Periodinės 400–500 t/metus formaldehido gamybos reaktoriuje Cu/kvarcas katalizatorius gali būti patalpintas 0,29–0,3 m skersmens ir 0,17–0,18 m storio sluoksniu.

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