KAUNAS UNIVERSITY OF TECHNOLOGY

Kęstutis Čičinskas

"SANDWICH-TYPE" $Me_xO_y/\gamma Al_2O_3$ ADSORBENT-CATALYST IN ALCOHOL VAPOUR REMOVAL TECHNOLOGIES

Summary of the Doctoral Dissertation

Technological Science, Chemical Engineering (05T)

Kaunas, 2005

The research was carried out at Kaunas University of Technology Departament of Physical chemistry in the period of 2000–2004.

Scientific supervisor:

Assoc. Prof. Dr. Saulius KITRYS (Kaunas University of Technology, Technological Science, Chemical Engineering – 05T).

Council of Chemical Engineering sciences trend:

Prof. Dr. Habil. Alfredas Martynas SVIKLAS (Kaunas University of Technology, Technological Science, Chemical Engineering – 05T) – *chairman*;

Prof. Dr. Habil. Rimgaudas ABRAITIS (Institute of Architecture and Construction of Kaunas University of Technology, Technological Science, Chemical Engineering – 05T);

Assoc. Prof. Dr. Prutenis Petras JANULIS (Lithuanian University of Agriculture, Technological Science, Environmental Engineering and Land Management – 04T);

Prof. Dr. Algirdas ŠULČIUS (Kaunas University of Technology, Technological Science, Chemical Engineering – 05T);

Prof. Dr. Habil. Algirdas ŽEMAITAITIS (Kaunas University of Technology, Technological Science, Chemical Engineering – 05T).

Official opponents:

Prof. Dr. Habil. Aivaras KAREIVA (Vilniaus University, Physical Sciences, Chemistry – 03P);

Prof. Dr. Raimundas ŠIAUČIŪNAS (Kaunas University of Technology, Technological Science, Chemical Engineering – 05T).

The official defence of the disertation will be held at the open meeting of the Council of Chemical Engineering sciences trend at 11 a. m. on April 26, 2005 in the Dissertation Defence Hall at the Central Building of Kaunas University of Technology.

  Address: K. Donelaičio g. 73, LT – 44029, Kaunas, Lithuania
  Tel.: (370) 7 30 00 42, fax: (370) 7 32 41 44
  e-mail: mok.skyrius@ktu.lt

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

Kęstutis Čičinskas

SLUOKSNINIAI $Me_xO_y/\gamma Al_2O_3$ ADSORBENTAI-KATALIZATORIAI ALKOHOLIŲ GARŲ ŠALINIMO TECHNOLOGIJOSE

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Mokslinis vadovas:

Doc. dr. Saulius KITRYS (Kauno technologijos universitetas, technologijos mokslai, chemijos inžinerija – 05T).

Chemijos inžinerijos mokslo krypties taryba:

Prof. habil. dr. Alfredas Martynas SVIKLAS (Kauno technologijos universitetas, technologijos mokslai, chemijos inžinerija – 05T) – *pirmininkas*;

Prof. habil. dr. Rimgaudas ABRAITIS (Kauno technologijos universiteto Architektūros ir statybos institutas, technologijos mokslai, chemijos inžinerija – 05T);

Doc. dr. Prutenis Petras JANULIS (Lietuvos žemės ūkio universitetas, technologijos mokslai, aplinkos inžinerija ir kraštotvarka – 04T);

Prof. dr. Algirdas ŠULČIUS (Kauno technologijos universitetas, technologijos mokslai, chemijos inžinerija – 05T);

Prof. habil. dr. Algirdas ŽEMAITAITIS (Kauno technologijos universitetas, technologijos mokslai, chemijos inžinerija – 05T).

Oficialieji oponentai;

Prof. habil. dr. Aivaras KAREIVA (Vilniaus universitetas, fiziniai mokslai, chemija – 03P);

Prof. dr. Raimundas ŠIAUČIŪNAS (Kauno technologijos universitetas, technologijos mokslai, chemijos inžinerija – 05T).

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   Adresas: K. Donelaičio g. 73, LT – 44029, Kaunas, Lietuva
   Tel.: (370) 7 30 00 42, fax: (370) 7 32 41 44
   el. paštas; mok.skyrius@ktu.lt

Disertacijos santrauka išsiųsta 2005 m. kovo 25 d.

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INTRODUCTION

Relevance of the work. Adsorbent-catalysts are used in environmental technologies when concentration of pollutants in exhaust gases is low (tenths or hundredths of mg/m^3). In these cases traditional pollutant remove methods, such as combustion, direct catalysis, etc. are expensive and not efficient. The problem might be solved in unconventional way by using two treatment methods in one vessel: adsorption of pollutants at ambient temperature and catalytic oxidation of adsorbate by converting it into non-hazardous substances at higher temperatures. This approach is being used for controlling emissions of alcohols and volatile organic compounds (VOC). The use of adsorbent-catalysts allows the decrease in pollutant removal costs by 90%. Industrial catalysts from other processes, as well the mixtures of catalysts and adsorbents can be used in this technology. However, they must combine high surface area as characteristic for adsorbents and high mechanical and thermal stability, activity, long lifetime, resistance to poisoning as in catalysts. Thus toilered adsorbent-catalysts are more efficient.

The theory and technology of high temperature catalytic oxidation of organic compounds is well known. The most active catalysts are Pt family metals or transition metal oxides because of their ability to concentrate oxygen radicals on the surface. Oxygen radicals are responsible for VOC complete oxidation into carbon dioxide and water. However, the process rate and mechanism depend on temperature. When adsorbent-catalyst temperature is periodically changed, the rates of adsorption, desorption and catalytic oxidation, changes in amounts of VOC intermediate oxidation products become very important. They depend on nature of adsorbate and catalyst, its composition, specific surface characteristics and process conditions. The oxidation mechanism on adsorbent-catalyst for each adsorbate is individual. Systematic data on adsorption-catalytic oxidation of alcohols is lacking, therefore, further research on VOC removal is needed in order to create more efficient technology.

Aim of the work was to create the synthesis technology of "sandwich-type" $CuO/\gamma Al_2O_3$, $Co_3O_4/\gamma Al_2O_3$ and $MnO_2/\gamma Al_2O_3$ adsorbent-catalysts, determine their properties, and investigate their implementation in alcohols removal processes. In order to reach the aim of the work we had to complete these goals:

1. Experimentally determine the possibility to concentrate active components on surface of γAl_2O_3 granules;

2. To determine the composition of synthesized "sandwich-type" adsorbent-catalysts, the structure of active components, specific surface area and pore structure, thermostability;

3. To determine the adsorption capacity of adsorbent-catalyst for water and alcohol vapour;

4. To determine the initial temperature of alcohol complete oxidation and concentrations of reaction intermediates;

5. To determine activity of adsorbent-catalysts and optimal technological

parameters of their use in VOC removal processes;

6. To determine kinetic parameters and mechanism of processes;

7. To propose the recommendations for the use of adsorbent-catalysts in VOC removal technologies.

Scientific novelty and practical significance. A new way of manufacturing of "sandwich-type" CuO, Co_3O_4 and MnO_2 adsorbent-catalysts were investigated. γAl_2O_3 was used as catalyst support. Properties of the obtained products were investigated. Kinetic parameters and mechanism of methanol, propanol and butanol oxidation were experimentally determined in the range of $200–320^oC$. The connection between catalyst active component and oxidation intermediate products is presented. Technological parameters of adsorbent-catalyst use in alcohol removal processes were determined.

Approval and publication of research results. Results of the research are presented in 10 publications, one of them published in a journal "Chemical technology", one in „Journal of University of Chemical Technology and Metallurgy" (Bulgaria) and 3 reported in international conferences.

Structure and contents of the dissertation. Dissertation consists of introduction, literature survey, experimental part, results and discussion, conclusions, list of 198 references, list of 10 publications on dissertation topic and 4 appendixes. The main material is presented in 116 pages, including 19 tables and 75 figures.

Statements presented for defense:

1. Using inert gases and wet impregnation technology $CuO/\gamma Al_2O_3$, $Co_3O_4/\gamma Al_2O_3$ and $MnO_2/\gamma Al_2O_3$ adsorbent-catalysts with desired adjusted thickness of outside layer can be synthesized. Adsorbent-catalysts are mesoporous which have open 24–40 Å cylindrical-type pores.

2. Adsorbent-catalysts are hydrophilic. Under atmospheric relative humidity H_2O vapor condensation proceeds on surface influencing adsorption of alcohol vapor.

3. The most active "sandwich-type" adsorbent-catalyst in alcohol adsorption-oxidation processes is $CuO/\gamma Al_2O_3$ with 7.60–8.95 % CuO in outer layer of granules. Ratio of adsorbate desorption and oxidation rates depend on adsorbent-catalyst temperature. Oxidation reaction rate is prevailing, when temperature of reaction beginning is reached. Charge temperature depends on adsorbate amount on the surface of adsorbent-catalyst.

4. Parallel-consecutives mechanism is characteristic for catalytic oxidation of adsorbed alcohols. By increasing temperature of catalyst and decreasing molecular mass of adsorbate, the influence of side reactions decreases.

EXPERIMENTAL

"Sandwich-type" adsorbent-catalysts were prepared by impregnation of γAl_2O_3 using solutions of copper (II) acetate, cobalt (II) and manganese (II) nitrates. The impregnated samples were dried in air at 150 °C for 30 min and calcined in air at 350 °C for 150 min.

The activity of the adsorbent-catalysts and technological parameters of the process were determined using the experimental apparatus consisting of block of gas mixture preparation, reactor, temperature control and gas mixture analysis systems (Fig. 1). The quartz glass reactor was 35 mm in diameter and 110 mm in height (Fig. 2). The height of the adsorbent-catalyst bed in reactor was 60 mm.
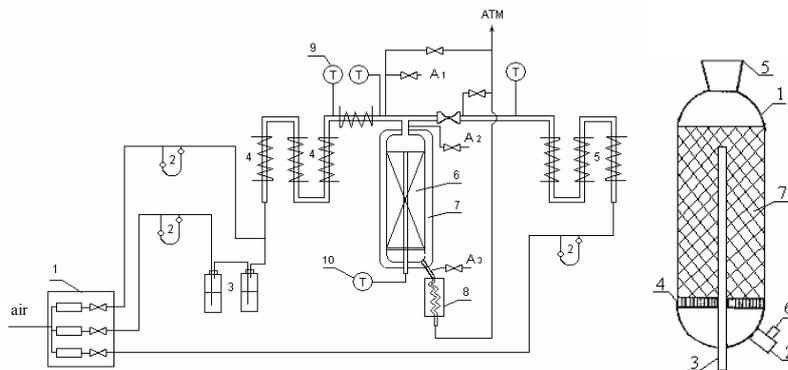
Fig. 1. Experimental aparatus scheme: 1– air pressure control device; 2 – flowmeter; 3 – scrubber; 4 – electric heater; 5 –air heater; 6 – catalytic reactor; 7 – insulation; 8 – cooler; 9– temperature control system; 10 – thermocouple; A_1, A_2 ir A_3 – sampling

Fig.2. Catalytic reactor: 1 – reactor frame; 2 – gas outlet; 3 – thermocouple; 4 – perforated partition wall; 5 – gas inlet; 6 – sampling; 7 – adsorbent-catalyst bed

Adsorbable (methanol, propanol and butanol) concentrations in preadsorptive gas were kept at 395.10–724.05 mg/m^3. Alcohol vapour adsorption performed at 25–30 °C and 5 l/min adsorption mixture flow (0.087 m/s linear flow rate). Adsorbate reactions were investigated using hot (190–320 °C) air flow. Adsorbate conversion was calculated according to the equation: $\alpha = \dfrac{\sum X_{ad} - \sum X_{des}}{\sum X_{ad}} \cdot 100$, where: $\sum X_{ad}$ is amount of adsorbate (mg/g); $\sum X_{des}$ is amount of desorbate (mg/g). Process apparent kinetic parameters were calculated by determining the adsorbate concentration change on the surface of catalyst as a function of reaction time. Pre-exponental and apparent activation energy was estimated via according to the logarithmic Arrhenius equation: $\ln k_T = \ln A - E_T/(RT)$, where: k_T is apparent reaction rate constant of adsorbate catalytic oxidation, A is pre-exponental factor, E_T is apparent activation energy.

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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.

The concentration of the methanol, propanol and butanol was determined by *Perkin Elmer Clarus 500* GC with a flame ionization detector using AT^{TM} WAX capillary column (30 m 0.32 mm i.d., 0.50 μm film thickness).

Characterization of adsorbent-catalysts

Differential thermal analysis (DTA) was carried out by computer control *DuPont 990* (USA) thermal analyzer. Parameters of DTA analysis: air atmosphere, max. temperature 800 ^{o}C, temperature increase 10 ^{o}C/min.

Metal loading in adsorbent-catalyst was determined by *Karl Zeiss Jena AAS1N* atomic absorption spectrometer (AAS).

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

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

CuO, Co$_3$O$_4$ and MnO$_2$ layer thickness in the granules of adsorbent-catalyst were determined by *МИН-8* optical polarization microscopy.

The XPS studies were performed by a *VG Escalab II* electron spectrometer using AlK$_\alpha$ 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.

IR spectroscopy was carried out with the help of *Perkin-Elmer FT – IR System Spectrum X* spectrometer. The tablets of specimen were prepared by using 1 mg of material and 200 mg of KBr.

The specific surface area of samples was measured by a BET surface area analyzer *Quantasorb* (Quantachrome, USA). The Quantasorb determines the surface area, total pore volume and pore size distribution of a sample 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 specific surface area was calculated by the BET equation using the data of the lower part of N$_2$ adsorption isotherm (0.05 < $p/p0$ < 0.35):

$$\frac{1}{X[(p/p_o)-1]} = \frac{C-1}{X_m C}\frac{p}{p_0} + \frac{1}{X_m \cdot C}$$ where: X is the mass of adsorbate, adsorbed on the

sample at relative pressure p/p_o, p the partial pressure of adsorbate, p_o the saturated vapour pressure of adsorbate, X_m the mass of adsorbate adsorbed at a coverage of one monolayer, C is a constant which is a function of the heat of the adsorbate condensation and heat of adsorption (C_{BET} is a constant).

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.

RESULTS AND DISCUSSION

Preparation of "sandwich-type" adsorbent-catalyst

"Sandwich-type" adsorbent-catalysts were prepared by wet impregnation of pure γAl_2O_3 pellets with aqueous solutions of active component salts. Before impregnation γAl_2O_3 cylindrical granules were regenerated at 300 °C for 2 hours in nitrogen atmosphere. Active component (metal oxide) content and layer thickness of the catalyst could by controlled by impregnation time (Fig. 3-5). The best results of CuO impregnation on the surface of γAl_2O_3 were obtained when Cu^{2+} ions concentration in aqueous solution was up to 54 g/l, the impregnation time being no longer then 90 min. At these conditions CuO layer thickness in adsorbent-catalyst is 0.25–0.35 mm, and CuO content in the outer layer of the granules is 7.60–8.95 wt%. A dark outer layer of CuO and white inner layer of γAl_2O_3 are observed in the crossection of granules. The best $Co_3O_4/\gamma Al_2O_3$ and $MnO_2/\gamma Al_2O_3$ adsorbent-catalysts were prepared using 30 g/l Co^{2+} or Mn^{2+} solutions, the impregnation time being no longer then 60 min.
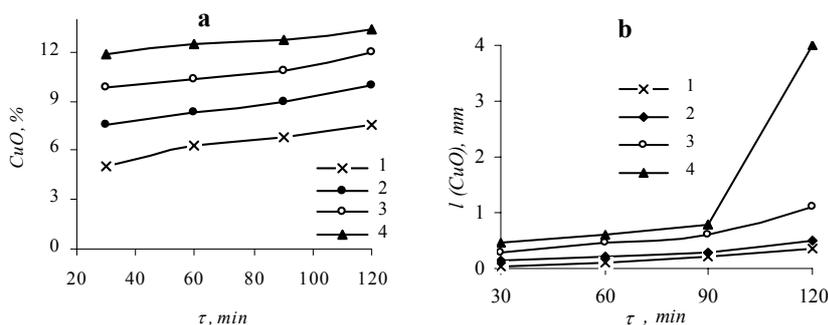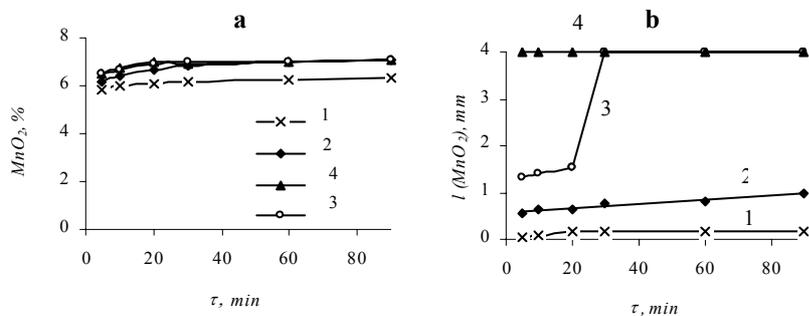

Fig 3. Dependence of CuO content (a) and layer thickness (b) in the granules of adsorbent-catalyst on the impregnation time at different Cu^{2+} concentrations in aqueous solutions (g/l): *1* – 30; *2* – 54; *3* – 90; *4* – 120
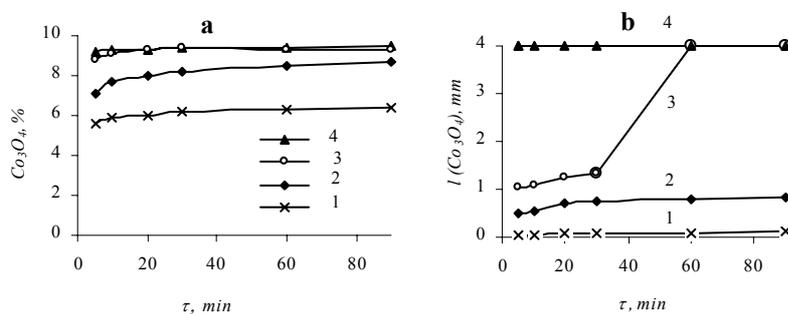
Fig 4. Dependence of Co_3O_4 content (a) and layer thickness (b) in the granules of adsorbent-catalyst on the impregnation time at different Co^{2+} concentrations in aqueous solutions (g/l): *1* – 10; *2* – 30; *3* – 50; *4* – 70

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Fig. 5. Dependence of MnO_2 content (a) and layer thickness (b) in the granules of adsorbent-catalyst on the impregnation time at different Mn^{2+} concentrations in aqueous solutions (g/l): *1* – 10; *2* – 30; *3* – 50; *4* – 70

Co_3O_4 and MnO_2 layer thickness varied in the range of 0.7–0.9 mm. The content of MnO_2 was 6.70–7.02 wt%, and that of Co_3O_4 – 8.01–8.54 wt%.

Properties of the "sandwich-type" adsorbent-catalyst

Active components of the adsorbent-catalysts are only metal oxides. Peaks of X-ray diffractograms corresponded to characteristic peaks of CuO, Co_3O_4 and MnO_2 (Fig. 6). Metal oxides were obtained by thermal treatment of metal salts at 350 ^{o}C. The conditions of thermal decomposition of metal salts have been investigated by a DTA.
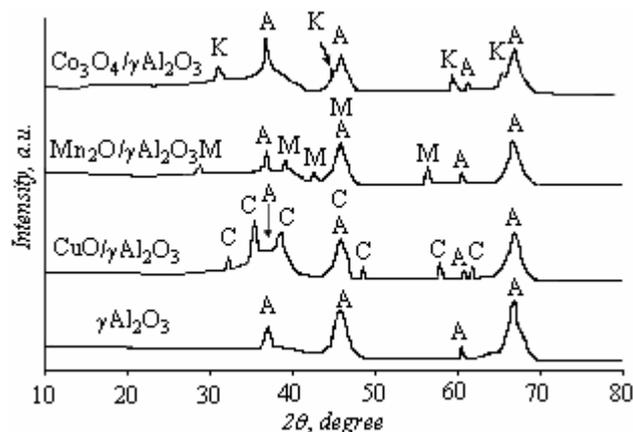
Fig. 6. X-ray diffraction patterns of adsorbent-catalysts. *Indexes:* A – γAl_2O_3; C – CuO; M – MnO_2; K – Co_3O_4

The results of XRD analysis were confirmed by the results of XPS and IR analysis of adsorbent-catalysts (Fig. 7, 8). Fig. 7a shows the XPS spectra for Cu 2p electrons of $CuO/\gamma Al_2O_3$ adsorbent-catalyst. The binding energy of the Cu $2p_{3/2}$ electrons is 933.9 eV, which is consistent with binding energies for Cu^{2+} in CuO. The main signals of the Co $2p_{3/2, 1/2}$ doublet (Fig. 7b) are separated by 15.7 eV in the case of $Co_3O_4/\gamma Al_2O_3$ (E_b = 780.2 and 795.3 eV). The presented binding

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energies can be attributed to the Co_3O_4. The peaks of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ (see Fig. 7c) are located at 642.4 and 654.1 eV respectively. Thus, the spin–orbit splitting of Mn 2p is 11.7 eV, which is very similar to that of MnO_2.
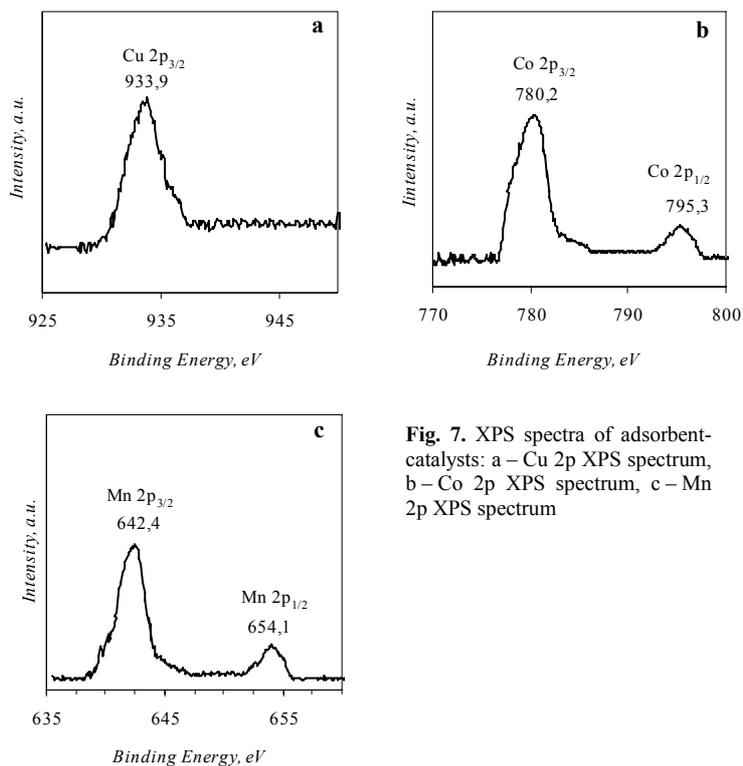

Fig. 7. XPS spectra of adsorbent-catalysts: a – Cu 2p XPS spectrum, b – Co 2p XPS spectrum, c – Mn 2p XPS spectrum

In all IR spectrograms (Fig. 8) γAl_2O_3 show a broad band ranging from 900 to 550 cm^{-1} and weak bands at 1180 and 1275 cm^{-1}. A broad band ranging from 650 to 400 cm^{-1} (with maximum at ~ 500cm^{-1}) and absorption bands at 375 cm^{-1} are assigned to the CuO. Co_3O_4 samples show two bands located at 664 and 565 cm^{-1}. IR spectra of MnO_2 show a broad band ranging from 700 to 500 cm^{-1} and bands at 420 and 350 cm^{-1}. The infrared spectra of the all studied samples show a broad band with a maximum centered about 3430 cm^{-1} together with a band at 1630 cm^{-1} which correspond to adsorbed molecular water.

Results of specific surface area (S_{BET}) measurements are presented in Table 1. C_{BET} constant values for outer and inner layer of adsorbent-catalysts are calculated to be $C_{BET(outer)}$=133.4–150.2 and $C_{BET(inner)}$=103.0–144.1. It is known that the most accurate results of S_{BET} measurements are obtained when C_{BET} is 50–250. BET equation gives a linear plot when $1/X[(p_o/p − 1]$ is plotted versus p/p_o, coefficient of determination $R^2 > 0.98$. It was established that there is no significant difference between specific surface areas of outer and inner layers of adsorbent-
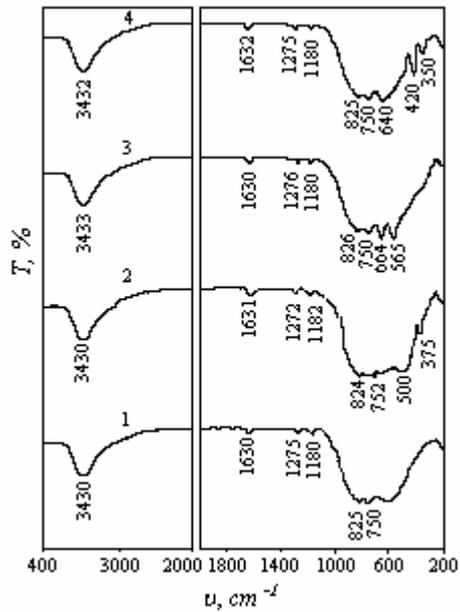
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Fig. 8. FT-IR spectra of the adsorbent-catalysts: 1 – γAl_2O_3, 2 – $CuO/\gamma Al_2O_3$, 3 – $Co_3O_4/\gamma Al_2O_3$, 4 – $MnO_2/\gamma Al_2O_3$

catalyst granules: $S_{BET(outer)} = 133.40–150.29$ m^2/g, $S_{BET(inner)} = 148.66–171.03$ m^2/g.

Research results show that a phenomenon of hysteresis is observed for adsorbent-catalyst (Fig. 9): isotherms of adsorption and desorption do not coincide at relative pressures $p/p_o > 0.4$. Cylindrical pores of 24–40 Å radii prevail in $CuO/\gamma Al_2O_3$ adsorbent-catalyst (Fig. 10). They are determined by a surface structure of γAl_2O_3.

Additional of CuO active component reduced the total volume of pores from $\Sigma V_{p(inner)} = 0.329$ cm^3/g in inner layer to $\Sigma V_{p(outer)} = 0.225$ cm^3/g in outer layer of "sandwich-type" adsorbent-catalyst granules.

Table 1. BET equation parameters

| Part of adsorbent-catalyst granule	Parameters of BET equation		Mass of adsorbate monolayer X_m, g	Specific surface area S_{BET}, m^2/g	Constant $C_{BET} = \dfrac{1}{I \cdot X_m}$	Correlation coef. R^2
	Slope, $S=tg\alpha$	Intercept, I				
$CuO/\gamma Al_2O_3$ outer	2259.0	15.13	0.00044	150.29	150.2	0.999
$CuO/\gamma Al_2O_3$ inner	1963.4	13.72	0.00051	171.03	144.1	0.998
$Co_3O_4/\gamma Al_2O_3$ outer	1560.2	11.71	0.00064	149.61	133.4	0.990
$Co_3O_4/\gamma Al_2O_3$ inner	3092.7	23.26	0.00032	155.28	134.0	0.999
$MnO_2/\gamma Al_2O_3$ outer	1847.0	13.51	0.00054	133.40	137.1	0.999
$MnO_2/\gamma Al_2O_3$ inner	2838.6	27.73	0.00035	148.66	103.0	0.997
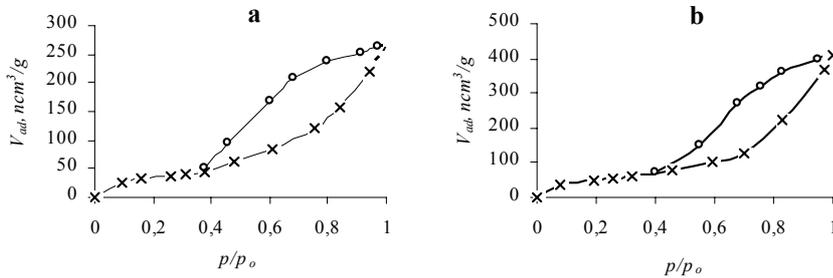
Fig. 9. The isotherm of N$_2$ adsorption-desorption by CuO/γ-Al$_2O_3$ outer (a) and inner (b) layers at 77 K
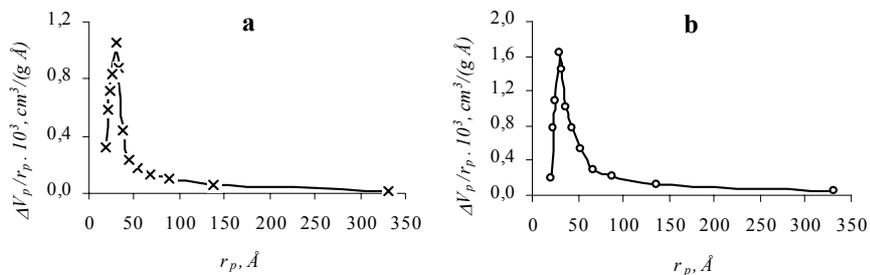
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Fig 10. Differential volume pore size distribution of CuO/γ-Al$_2$O$_3$ outer (a) and inner (b) layers

"Sandwich-type" adsorbent-catalyst in methanol, propanol and butanol oxidation reactions

Temperature and intermediates of oxidation reaction. Temperature of oxidation initiation of methanol, propanol and butanol vapour was determined of feeding the reactor with a mixture of alcohol vapour and humid air (φ = 30–50 %) at a constant rate. In order to compare the activity of CuO/γAl$_2$O$_3$, Co$_3$O$_4$/γAl$_2$O$_3$ and MnO$_2$/γAl$_2$O$_3$ catalysts, were carried out additional experiments with industrial Pt catalyst (amount of Pt 0.35 wt%, ceramic support, granules of 2.5–3.0 mm in diameter and 10 mm in long) (Fig. 11).
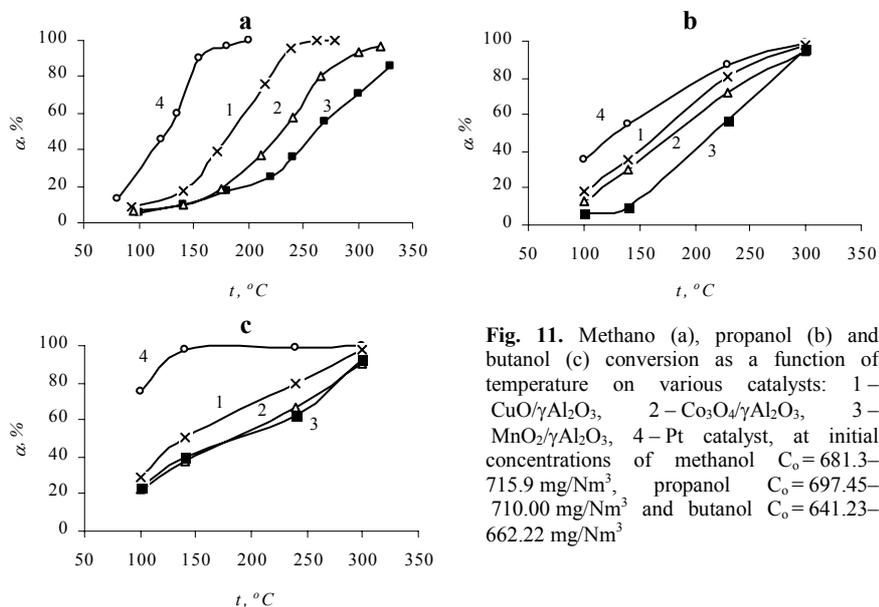

Fig. 11. Methano (a), propanol (b) and butanol (c) conversion as a function of temperature on various catalysts: 1 – CuO/γAl$_2$O$_3$, 2 – Co$_3$O$_4$/γAl$_2$O$_3$, 3 – MnO$_2$/γAl$_2$O$_3$, 4 – Pt catalyst, at initial concentrations of methanol C$_o$ = 681.3–715.9 mg/Nm^3, propanol C$_o$ = 697.45–710.00 mg/Nm^3 and butanol C$_o$ = 641.23–662.22 mg/Nm^3

It was observed that CuO/γAl$_2$O$_3$ is highly active catalyst for the oxidation of all alcohols. Oxidation of CH$_3$OH starts at t$_{st}$=130 ^{o}C, and that of C$_3$H$_7$OH and

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C$_4$H$_9$OH at t$_{st}$ ≈ 100–110 ^{o}C. Industrial Pt catalyst exhibited slightly higher catalytic performance for these reactions. Using "sandwich-type" Co$_3$O$_4$/γAl$_2$O$_3$ and MnO$_2$/γAl$_2$O$_3$ adsorbent-catalysts oxidation reactions of alcohols start at higher temperatures (150–200 ^{o}C). The concentration of intermediates in reaction products depends on oxidation temperature, type of used catalyst and alcohol. The lowest amount of intermediates was formed on the surface of CuO/γAl$_2$O$_3$ adsorbent-catalyst. At 300 ^{o}C methanol was completely oxidized to CO$_2$ and H$_2$O. Meanwhile oxidation degree α of propanol reaches 97.9 %, and that of butanol is 99,7 %. A more through study of the reaction products revealed that propanal, propane, butanal and butane were formed as intermediates. Co$_3$O$_4$/γAl$_2$O$_3$ and MnO$_2$/γAl$_2$O$_3$ catalysts formed more intermediates in the reaction products (formaldehyde, propylether, butylether and tetrahydrofuran are also present). Over these catalysts oxidation degree α of alcohols was less then 93–95 % at 300 ^{o}C.

Adsorption capacity of water, methanol, propanol and butanol vapour

Water vapour adsorption. Water vapour adsorption isotherms are characteristic to hydrophilic adsorbents (Fig. 12).The shape of isotherms indicates a weak bond between adsorbent and adsorbate. In this case water vapour condensation in pores of adsorbent is possible at ambient air humidity. Thermodynamic possibility of water vapour condensation in adsorbent-catalyst pores was calculated according to Kelvin equation. At ambient humidity above 47 % the prevailing pores (24–40 Å) will be filled by water due to its capillary condensation (Fig. 13).
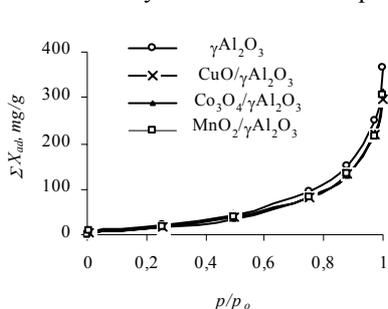

Fig. 12. Water vapour adsorption isotherms on prepared adsorbent-catalysts and pure γAl$_2$O$_3$ at 20 ^{o}C
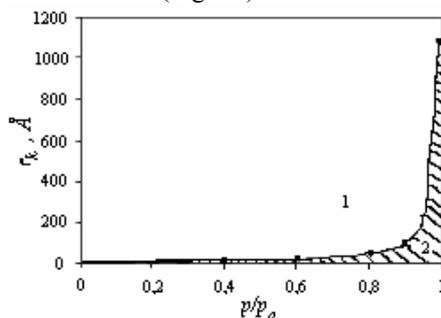
Fig. 13. r$_k$ dependence of open pores of adsorbent-catalyst on water vapour quantity in the preadsorptive gas (1 – region of open pores; 2 – region of water vapour condensation in the pores)

Such water vapour adsorption will influence the VOC adsorption from humid gas mixtures. In this case, the adsorption of VOC vapour can be accompanied by the VOC absorption in condensed water. Consequently, the time of adsorbent equilibrium adsorption should increase, and desorption of organic compounds should decrease.

Adsorption of methanol, propanol and butanol vapour. Adsorption measurements were carried out on CuO/γAl$_2$O$_3$ adsorbent-catalyst, γAl$_2$O$_3$ and Pt catalyst

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(Fig. 14-16). The concentration of alcohols in the preadsorptive air – vapour mixture was varied in the range of 395–627 mg/Nm^3. Equilibrium adsorption experiments were performed only for methanol. It was found that adsorption capacities of γAl_2O_3, $CuO/\gamma Al_2O_3$ and Pt catalyst are 3.491–3.518, 3.407–3.429 and 3.410 mg/g respectively.

CuO/γAl_2O_3 adsorbs 29.352 mg/g of propanol vapour. Equilibrium adsorption was not reached during 700 min. (Fig. 15). In the industrial processes, the adsorption is usually carried out for 5–6 hours. Under the same conditions, γAl_2O_3 adsorbs 22.344 mg/g, Pt catalyst adsorbs 22,205 mg/g of propanol vapour.

Butanol vapour adsorption is similar to that of propanol. At 611.30–628.34 mg/Nm^3 butanol concentration in preadsorptive air – vapour mixture (42–56 % relative air humidity) CuO/γAl_2O_3 adsorbent-catalyst adsorbs 24.456 mg/g of butanol vapour. Adsorption capacities of γAl_2O_3 and Pt catalyst are 26.632 and 27.317 mg/g respectively (Fig. 16).
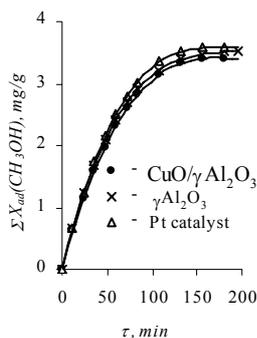

Fig. 14. Integral adsorption of methanol vapour (C_o= 395.10 – 415.20 mg/Nm^3) as a function of time for: 1 – CuO/γAl_2O_3, 2 – γAl_2O_3, 3 – Pt catalyst
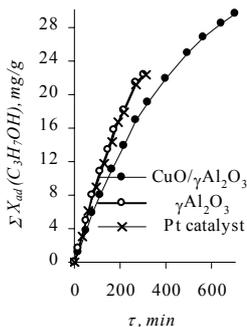
Fig. 15. Integral adsorption of propanol vapour as a function of time for: 1 – CuO/γAl_2O_3 (C_o = 558.32 mg/Nm^3), 2 – γAl_2O_3 (C_o = 724.05 mg/Nm^3), 3 – Pt catalyst (C_o = 625.00 mg/Nm^3)
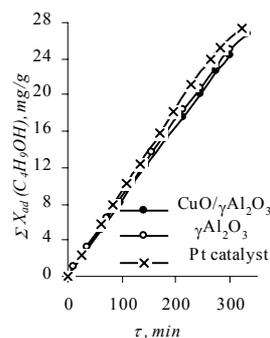
Fig. 16. Integral adsorption of butanol vapour as a function of time for: 1 – CuO/γAl_2O_3 (C_o = 627.41 mg/Nm^3), 2 – γAl_2O_3 (C_o = 611.30 mg/Nm^3), 3 – Pt catalyst (C_o = 628.34 mg/Nm^3)

Technological and kinetic parameters of adsorbate complete oxidation

In adsorption-catalytic oxidation technology the regeneration of adsorbent-catalyst bed (containing VOC adsorbate) is performed in such way that adsorbate would be converted into CO_2 and H_2O vapour. Adsorbate oxidation reaction with air oxygen proceeds at elevated temperatures, thus thermal charge regeneration is the only acceptable method. Thermal regeneration can be performed by several methods: 1) heating of VOC saturated catalyst, 2) feeding a hot air to the adsorbent-catalyst bed. It is known that during the heating of catalyst without air flow, the destruction of adsorbate into carbon can occur. This process decreases the specific surface area of catalyst bed. Beside, the structure of catalyst can be destroyed. Such processes can be avoided by feeding a hot air to the reactor, and, thus, keeping the concentration of oxygen in excess. Depending on technological conditions, the reactions of adsorbate on the surface of catalyst bed can be

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accompanied by adsorbate desorption. Technological process depends on the properties of adsorbate and catalyst.

Adsorbed methanol reactions on the surface of adsorbent-catalyst

The active $CuO/\gamma Al_2O_3$ adsorbent-catalyst adsorbs 3.410–3.429 mg/g of methanol and 25–40 mg/g of water vapour at 20–25 ^{o}C. Feeding hot air to the reactor, adsorbate oxidation degree α (into CO_2 and H_2O vapour) depends on time at which reaction initiation temperature (t_{st}) is reached. Methanol oxidation degree α=90–95 % can be reached if adsorbent-catalyst would be heated at 67–70 ^{o}C/(cm·min) rate (Fig. 17). γAl_2O_3 support does not oxidize methanol up to 320 ^{o}C.
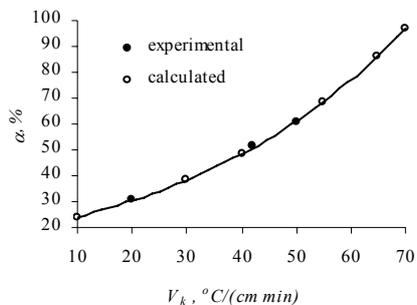
Fig. 17. Dependence of methanol oxidation degree α on heating rate V_k of adsorbent-catalyst bed

On the bases of the obtained data (Fig. 18), kinetic parameters of adsorbate complete oxidation were calculated according to the following equation: $\ln W = \ln k_T + n \cdot \ln (X_o - X_\tau)$, where $W = dX/d\tau$ is adsorbate oxidation rate, k_T is apparent reaction rate constant, n is apparent order of reaction, X_o is initial amount of adsorbate, X_τ is amount of desorbate at reaction time τ.
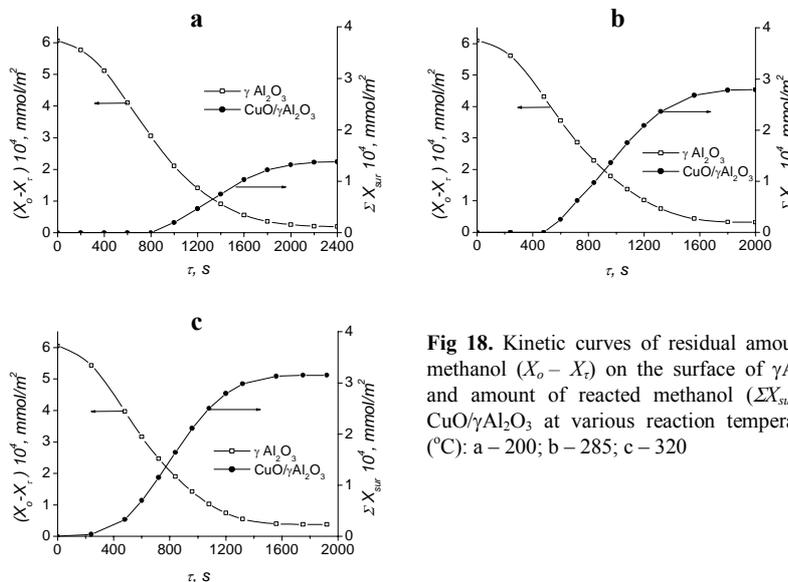
Fig 18. Kinetic curves of residual amount of methanol $(X_o - X_\tau)$ on the surface of γAl_2O_3, and amount of reacted methanol (ΣX_{sur}) on $CuO/\gamma Al_2O_3$ at various reaction temperatures (^{o}C): a – 200; b – 285; c – 320

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Under our experimental conditions, order of reaction with respect to oxygen should be closed to zero, as the concentration of oxygen exceeded many times the concentration of adsorbate. It was established that the reaction rate as a function of $(X_o - X_\tau)$ in logarithmic plot gives a straight line (Fig. 19). The slope and intercept of these plots determine the values of n_T and $\ln k_T$, respectively. The values of reaction order and rate constant are given in table 2. The plot of $\ln k_T$ versus $1/T$ gives a straight line (Fig. 20). The intercept of this plot as $\ln A$, and the slope $tg\alpha = \dfrac{E_T}{R}$. Apparent activation energy (E_T) and pre-exponential factor (A) of the Arrhenius equation $k = A \cdot e^{-\frac{E_T}{RT}}$ were calculated 81.42 kJ/mol and 958.53, respectively.
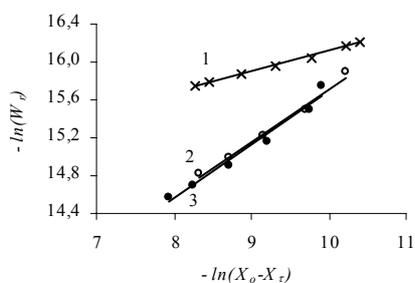
Fig. 19. Reaction rate of methanol oxidation as a function of $(X_o - X_\tau)$ in logarithmic plot at various reaction temperatures (^oC): 1 – 200; 2 – 285; 3 – 320
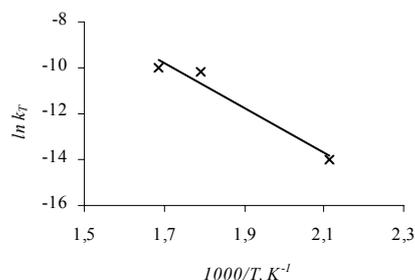
Fig. 20. Dependence of apparent reaction constant of methanol oxidation on the reaction temperature in Arrhenius plot

Table 2. The apparent kinetic parameters of methanol oxidation

t, ^oC	200	285	320
$k_T \cdot 10^5$, 1/(m^2·s)	0.09	3.70	4.49
n_T	0.22	0.55	0.57

The obtained data let us to conclude, that at temperature above t_{st} methanol oxidation can be related to kinetic controlled reactions. This process can by controlled by varying the reaction temperature. Using GC/MS system no formation of methanol oxidation intermediates (CO, formaldehyde and formic acid) in the temperature range from 200 to 320 ^oC was detected.

Adsorbed propanol reactions on the surface of adsorbent-catalyst

It was observed that the temperature of CuO/γAl$_2$O$_3$ catalyst autothermally increase during the oxidation of propanol. Increment of temperature depends on the propanol amount on the surface of adsorbent-catalyst (Fig. 21). The intermediates of propanol oxidation estimated using GC/MS analysis system (Fig. 22).
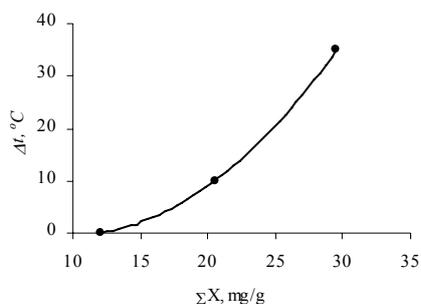
Fig. 21. Increment of temperature as a function of adsorbed propanol amount ($\sum X$) at 240–245 ºC reaction temperature
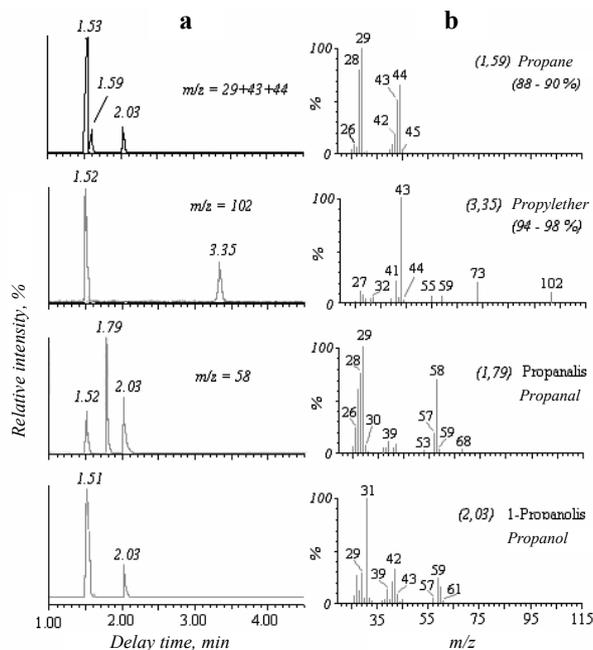

Fig. 22. Characteristic chromatograms (a) and mass spectrums (b) of product gas mixtures during propanol oxidation over CuO/γAl$_2$O$_3$

The concentrations of propanol oxidation intermediates (propanal, propane and propylether) depend on reaction temperature (Fig. 23). Increasing the initial amount of adsorbed propanol, the amount of intermediates increase. Propanol oxidation degree α = 70.4 % at 290 ºC and at heating rate V_k = 35.8 °C/(cm·min) of charge upper layer. Increasing V_k values up to 62–67 °C/(cm·min), the α will reach 92–96 %. The apparent kinetic parameters of propanol oxidation were calculated similarly as in the case of methanol oxidation (Fig. 24, 25, table 3)
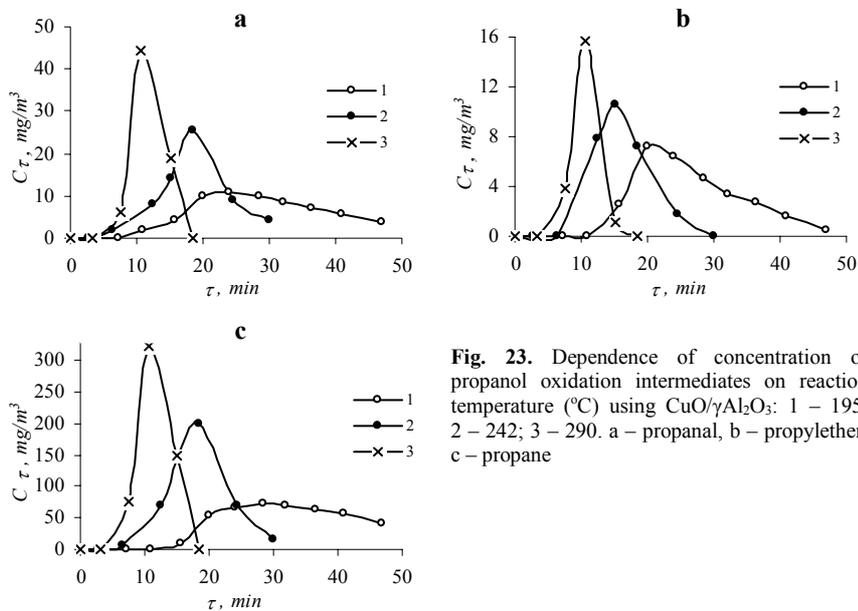
18

Fig. 23. Dependence of concentration of propanol oxidation intermediates on reaction temperature ($^{\circ}$C) using CuO/γAl$_2$O$_3$: 1 – 195; 2 – 242; 3 – 290. a – propanal, b – propylether, c – propane
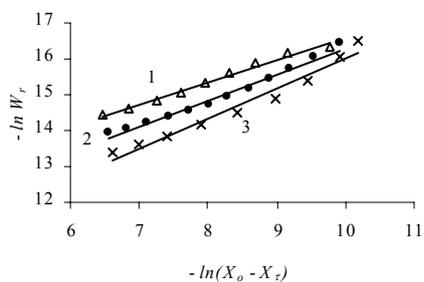

Fig. 24. Reaction rate of propanol oxidation as a function of $(X_o - X_\tau)$ in logarithmic plot at various reaction temperatures ($^{\circ}$C): 1 – 195; 2 – 242; 3 – 290
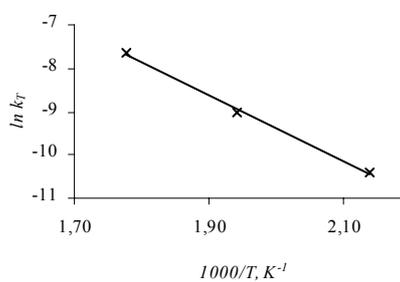

Fig. 25. Dependence of apparent reaction constant of propanol oxidation on the reaction temperature in Arrhenius plot

Table 3. The apparent kinetic parameters of propanol oxidation

t, $^{\circ}$C	$k_T \cdot 10^5$, 1/(m$^2 \cdot$s)	n_T	$- \ln k_T$	$1/T \cdot 10^3$, K^{-1}	$\ln A$	A	tgα=E/R	E_T, kJ/mol	Correlation coef. R^2
195	3.05	0.62	10.398	2.14					
242	12.19	0.73	9.012	1.94	5.7832	324.80	7586.6	63.07	0.998
290	47.25	0.84	7.657	1.78					

Adsorbed butanol reactions on the surface of adsorbent-catalyst

During oxidation of adsorbed butanol we also observed an autothermal increment of catalyst temperature with respect to the amount of adsorbate. This effect starts at 250 $^{\circ}$C and is accompanied with sharp decrease in butanol concentration in product gas stream. Butanal, butylether, butane and tetrahydrofuran (THF) were detected as butanol oxidation intermediates (Fig. 27, 28). At 57–64 °C/(cm·min) heating rate of adsorbent-catalyst bed the butanol oxidation degree will reach 90–95 %.

The following apparent kinetic parameters of adsorbate oxidation were estimated: reaction order n_T ranges from 0.58 to 0.86, activation energy $E_T = 54.89$ kJ/mol, pre-exponental $A = 64.06$ (Fig. 29, 30, table 4).Such parameters can be related to kinetics controlled reactions.
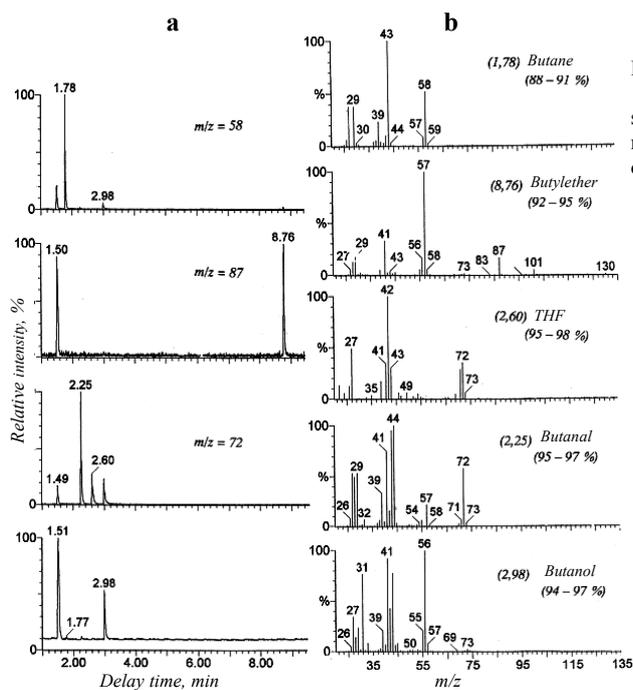

Fig. 27. Characteristic chromatograms (a) and mass spectrums (b) of product gas mixtures during butanol oxidation over CuO/γAl$_2$O$_3$

On the bases of the obtained kinetic and technological data it can be concluded, that CuO/γAl$_2$O$_3$ adsorbent-catalyst is effective for complete oxidation of adsorbate into CO$_2$ and H$_2$O vapour at 260–320 $^{\circ}$C. Charges with adsorbed alcohols should be quickly heated (60–70 $^{\circ}$C/(cm·min)) in order to achieve initial temperature of alcohol complete oxidation. At these conditions oxidation degree $\alpha > 90$ %. On the contrary, the adsorbate desorption process is dominating at lower temperature and catalyst heating rate.
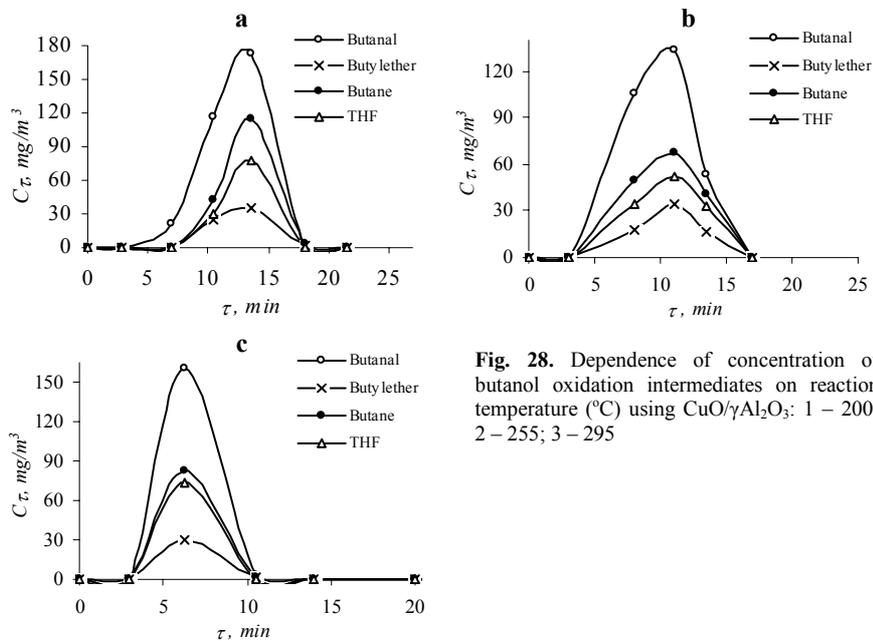
a

b

c

Fig. 28. Dependence of concentration of butanol oxidation intermediates on reaction temperature (°C) using CuO/γAl$_2$O$_3$: 1 – 200; 2 – 255; 3 – 295
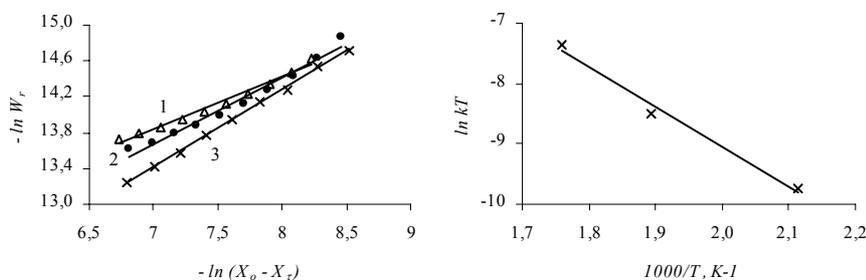
Fig. 29. Reaction rate of butanol oxidation as a function of $(X_o - X_\tau)$ in logarithmic plot at various reaction temperatures (°C): 1 – 200; 2 – 255; 3 – 295

Fig. 23. Dependence of apparent reaction constant of butanol oxidation on the reaction temperature in Arrhenius plot

Table 4. The apparent kinetic parameters of butanol oxidation

t, °C	$k_T \cdot 10^5$, 1/(m^2·s)	n_T	- lnk_T	$1/T \cdot 10^3$, K^{-1}	lnA	A	tgα=E/R	E$_T$, kJ/mol	Correlation coef. R^2
200	5.87	0.58	9.7431	2.11					
255	20.55	0.74	8.4899	1.89	4.1598	64.06	6602.1	54.89	0.988
295	62.81	0.86	7.3728	1.76					

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Apparent reaction rate constant, activation energy and pre-exponental of alcohol oxidation are characteristics for kinetics controlled reactions. In this case, the reaction rate increases with temperature. Activation energies (E_{Tdes}) of physical desorption of methanol, propanol and butanol are 12.24, 11.25 and 10.63 kJ/mol, respectively. The values of pre-exponental factor vary from 0.001 to 0.019. The rate of this process slightly increases with temperature. By increasing molecular mass of adsorbate, its initial temperature of oxidation decreases. In this case, the amount of intermediates increases. The γAl_2O_3 support of adsorbent-catalyst is active in propanol and butanol oxidation.

The order of reaction with respect to oxygen should be closed to zero, due to its excess, and that with respect to adsorbate n_T is closed to one.

**Peculiarities of the process mechanism**

The experimental results show that investigated process is dual in respect of temperature:

1. Physical adsorption of alcohols is prevailing at ambient temperature and it is described by well-known Langmuir mechanism:

$$\left| R\text{–}OH \right|_{gas} \rightleftarrows \left| R\text{–}OH \right|_{ads.} - \Delta H_{ads.}$$

At equilibrium conditions adsorption heat is closed to apparent activation energy of adsorption. This heat is approximately equal to desorption activation energy E_{Tdes} during adsorbate desorption. For the investigated adsorbates E_{Tdes} ranged from 10.63 to 12.24 kJ/mol. These values prove the physical nature of adsorption. By increasing the temperature and decreasing the concentration of adsorbable in the gases, adsorbates will necessary desorbs. Such character of adsorption determines dual mechanism of adsorbate removal.

2. At elevated temperatures process proceeds according to the scheme:
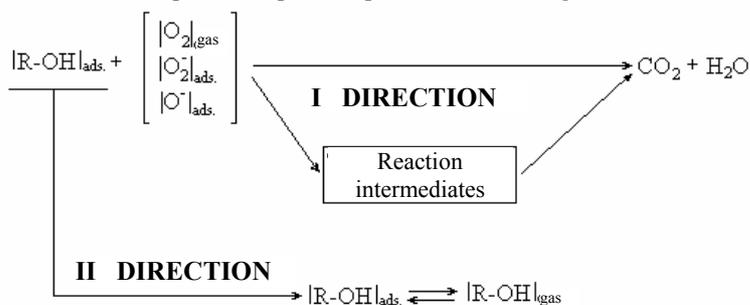
The scheme consists of two main directions. First direction determines the existence of oxidation intermediates in reaction products. Otherwise, second direction determines the presence of non-reacted alcohol in reaction products, due to its physical desorption. This direction decreases the efficiency of alcohol removal. It was determined, that second direction is dominant when temperature is lower than temperature of adsorbate oxidation initiation (t_{st}). t_{st} is a different for each adsorbate and adsorbent-catalyst. For highly active $CuO/\gamma Al_2O_3$ adsorbent-catalyst, oxidation of methanol, propanol and butanol starts at 130, 110 and 100 ^{o}C

respectively. Depending on temperature and oxidation conditions, contribution of second direction ranged from 19.0 to 69.6 %. The elimination of second direction was failed as it is impossible to heat instantly the surface of adsorbent-catalyst to $t > t_{st}$. In order to achieve this temperature we spent 3–4 minutes, while some part of desorbate did not react to CO_2 and H_2O.

First direction is desirable and dominant. The main amount of adsorbate is completely oxidized to CO_2 and H_2O vapour during these reactions. It was observed the increment of temperature on the adsorbent-catalyst bed is accompanied with sharp decrease of non-reacted adsorbate. The presence of reaction intermediates together with final oxidation products (CO_2 and H_2O) was detected. The concentration of intermediates depends on the final reaction temperature (t_r). When $t_r > t_{st}$ and difference t_r - t_{st} is low, aldehydes are dominant intermediate species. By increasing the difference t_r - t_{st} , the amounts of side products decrease. Such character of reactions is known: the existence of oxidation intermediates is explained by the formation of various oxygen radicals on the surface of catalyst. Both oxygen ion-radicals (O_2^- and O^-) and molecular oxygen (O_2) participate in these reactions. Langmuir-Hinshelwood and Eley-Rideal mechanism are used to describe the above mentioned reactions.

For the active $CuO/\gamma Al_2O_3$ adsorbent-catalyst were detected:

- the oxidation of adsorbed methanol occurs directly to the CO_2 and H_2O vapour, without forming any intermediates at 320 ^{o}C;
- the oxidation of adsorbed propanol and butanol occurs by a parallel-consecutive mechanism. Scheme of propanol oxidation at 290 ^{o}C:
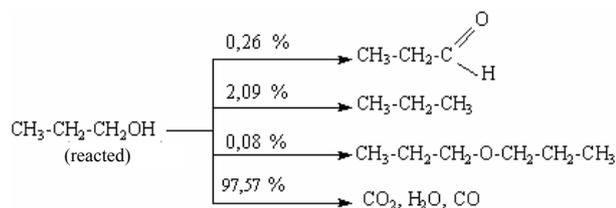
Scheme of butanol oxidation at 295 ^{o}C:

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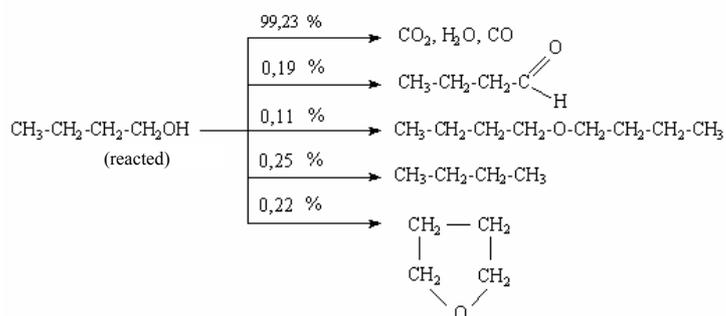
Reactions of adsorbate catalytic oxidation are not hindered by the adsorbed water vapour. It was established that the adsorbed water vapour condenses in adsorbent-catalyst pores, and have a positive influence. It is known that pyrolysis of organic adsorbates by forming elemental carbon can occur at elevated temperatures. The possibility of pyrolysis increases with increasing the molecular mass of adsorbed compound. In our case, the pyrolysis of reaction intermediates is highly probable. Formed carbon can block pores of adsorbent-catalyst and decrease the adsorption capacity. In our investigation activity and adsorption capacity of adsorbent-catalyst remained constant during experimental runs. We expect that adsorbed water vapour stimulate well-known carbon gasification reaction:

$$C + H_2O_{(g)} \rightleftharpoons CO + H_2 \xrightarrow{\text{ambient } O_2} CO_2 + H_2O$$
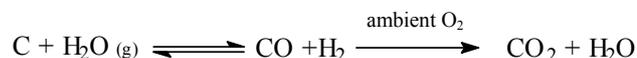
The formation of alkanes (propane and butane) during the adsorbate oxidation was determined too. In the catalytic oxidation of organic compounds these substances are formed due to thermal decomposition or hydrogenation reactions. In the present work these compounds were determined at 220–250 °C. Their formation proves the possibility of adsorbate pyrolysis.

Peculiarities and technological recommendations of CuO/γAl₂O₃ adsorbent-catalyst use

The maximum operation temperature and thermal stability

In order to achieve alcohol oxidation degree α = 90–95 %, the temperature of 300 – 320 °C is sufficient, the heating rate being 65–70 °C/(cm·min). Increasing temperature and heating rate, the oxidation degree of adsorbates approaches to 100 %. Phase transformations in γAl_2O_3 support can starts at temperatures above 500 °C. This process diminishes the specific surface area of Al_2O_3. $CuO/\gamma Al_2O_3$ adsorbent-catalyst is not recommended to use at temperatures above 500 °C. This limiting temperature can be suddenly achieved during oxidation process, especially, in the propanol and butanol. The increment of temperature depends on the amount of the adsorbate on the surface of catalyst (Fig. 21, 26). Temperature increment is also determined by heat of adsorbate complete oxidation, reaction rate, heat of water vapour desorptio and evaporation in catalyst pores, mass and heat transfer parameters. The heats of complete oxidation at 300 °C are calculated according to the laws of Hess and Kirchoff: for methanol $\Delta_r H_T^o$ = - 678.6 kJ/mol (- 21.21 J/mg), for propanol $\Delta_r H_T^o$ = - 1790.7 kJ/mol (- 29.85 J/mg) and for butanol $\Delta_r H_T^o$ = - 2509.4 kJ/mol (- 33.91 J/mg). On the bases of obtained kinetic results the reaction rate at 190–320 °C can be calculated according to the following equations:

- methanol oxidation

$$W_r = k_T \cdot (X_o - X_\tau)^{n_T} = A \cdot e^{-E_T/R \cdot T} \cdot (X_o - X_\tau)^{n_T} = 958.53 \cdot e^{-81420/8,314 \cdot T} (X_o - X_\tau)^{n_T} =$$
$$= 958.53 \cdot e^{-\frac{9793,12}{T}} \cdot (X_o - X_\tau)^{n_T}$$

where: T is temperature of catalyst, K;

n_T is apparent order of reaction (Fig. 31).

- propanol oxidation

$$W_r = 324.80 \cdot e^{-\frac{7586,00}{T}} \cdot (X_o - X_\tau)^{n_T}$$

- butanol oxidation

$$W_r = 64.06 \cdot e^{-\frac{6602,10}{T}} \cdot (X_o - X_\tau)^{n_T}$$
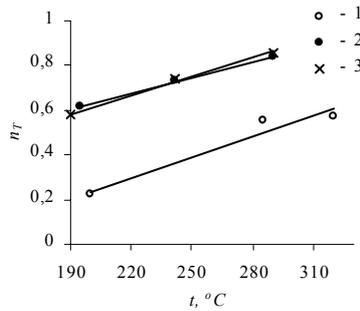

Fig. 31. The apparent reaction order as a function of catalyst temperimenture for: 1 – methanol, 2 – propanol, 3 – butanol

The increment of temperature does not allow reaching equilibrium adsorption for alcohols on the surface of adsorbent-catalyst. The following values of adsorption capacity ΣX are recommended for various alcohol vapour:

- methanol   close equilibrium
- propanol   < 30 mg/g
- butanol   < 20 mg/g

Below these values, catalyst temperature increment $\Delta t < 120\ ^o\text{C}$ and the catalyst temperature in the oxidation process will not exceed $450\ ^o\text{C}$.

Exploitation time and activity variations

The best $CuO/\gamma Al_2O_3$ samples were maintained for six month in the experimental apparatus for cyclic dual function runs (adsorption – catalytic oxidation). Charge adsorption capacity (ΣX) and catalytic activity practically have remained constants during the exploitation time (Fig. 32, 33).

Catalyst activity and exploitation temperatures of $CuO/\gamma Al_2O_3$ and industrial Pt catalysts are similar. The use of $CuO/\gamma Al_2O_3$ is advantageous because of the lower amount of reaction intermediates as compared to Pt catalyst.
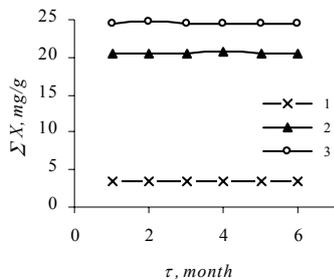
Fig. 32. CuO/γAl$_2$O$_3$ adsorption capacity (ΣX) as a function of time for: 1 – methanol (C$_o$ = 395.1–415.2 mg/Nm^3); 2 – propanol (C$_o$ = 555.00–562.12 mg/Nm^3, τ$_{ad}$ = 6 h); 3 – butanol (C$_o$ = 611.17–628.34 mg/Nm^3, τ$_{ad}$ = 6 h)

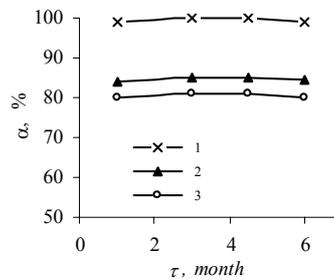**Fig. 33.** Alcohols oxidation degree (α) at 240 – 250 ºC as a function of CuO/γAl$_2$O$_3$ exploitation: 1 – methanol (C$_o$ = 395.1–415.2 mg/Nm^3); 2 – propanol (C$_o$ = 555.00–562.12 mg/Nm^3); 3 – butanol (C$_o$ = 611.17–628.34 mg/Nm^3)

Recommended characteristics of reactor

Experimentally obtained data allow to recommend "sandwich-type" CuO/γAl$_2$O$_3$ adsorbent-catalyst for the use in VOC removal technology. For this purpose, the most suitable is "tablet-like" adsorber-reactor containing second supplementary protective catalyst bed (Fig. 34).

Polluted gas stream is passing through a radial adsorbent-catalyst bed (2). At this moment the valve (6) is opened, and the valve (7) is closed. The end of adsorption is determined by automatic analyzer according to the maximum allowable concentration of pollutant. Afterwards, the valve (6) is closed, heater (9) is turned on and the regeneration gas is feeding to the reactor. Oxidation reactions of adsorbate start in catalyst bed (2). In order to destroy the non-reacted adsorbate, the gas stream is passing through a reactor (3) and is released by the outlet (8). The supplementary reactor can contain the same adsorbent-catalyst or other known VOC oxidation catalyst.

Reactor measurement depend on polluted gas flow rate, amount of pollutant, type of catalyst, etc. "Sandwich-type" CuO/γAl$_2$O$_3$ adsorbent-catalyst is particularly suitable for butanol oxidation. Taking
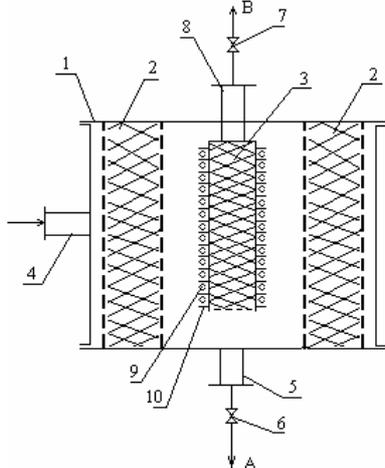

Fig. 34. Scheme of adsorber-reactor: 1 – frame, 2 –adsorbent-catalyst bed, 3 –supplementary catalytic bed, 4 – polluted and regeneration gas inlet, 5 – post-adsorptive gas outlet, 6, 7 – valves, 8 – regeneration gas outlet, 9 – heater, 10 – heat exchanger

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into account the obtained experimental data, the adsorption capacity of butanol vapour should be less than 20 mg/g (2 kg/100 kg). At the same time, about 4–5 kg/100 kg of water vapour will be adsorbed. Butanol is adsorbed at constant 0.4 kg/(100 kg·h) rate and limiting values of adsorption capacity reached in 4.5–5 hour. Similar loading will be obtained by feeding 4000 m^3/h of air pollutant at 100 mg/m^3 concentration of butanol.

Assuming 0.2 m/s optimal linear velocity per 4000 m^3/h gas flow, the bed of adsorbent-catalyst would be of 1.5 m in inside diameter, 0.7 m in outside diameter and 1.2 m in height. The bed thickness is about 0.4 m. The supplementary reactor contains 0.1 m^3 of the same catalyst (1.2 m in height and 0.32 m in diameter), if the flow rate of regeneration gas varies from 200 to 1000 m^3/h. The regeneration at 300–350 $^{\circ}$C will last ≤ 30 min, the ratio τ_{ads}/τ_{reg} being 9÷10. It means that technological scheme can be composed at least of two adsorber-reactors.

CONCLUSIONS

1. "Sandwich-type" adsorbent-catalysts were synthesized by wet impregnation of γAl_2O_3 granules (4 mm in diameter) with aqueous solutions of active component salts under N_2 atmosphere, dried and thermally treated at 150–350 $^{\circ}$C. The active components (CuO, Co_3O_4 or MnO_2) were concentrated in 0.3–0.7 mm outer layer of γAl_2O_3 granules.

2. Adsorbent-catalysts are mesoporous. The outer layer of $CuO/\gamma Al_2O_3$ adsorbent-catalyst contains 7.60–8.95 wt.% of CuO, and its specific surface area $S_{BET} = 150.29$ m^2/g. Similarly, $Co_3O_4/\gamma Al_2O_3$ adsorbent-catalyst contains 8.01–8.54 wt.% of Co_3O_4 and $S_{BET} = 149.51$ m^2/g. MnO_2 content in $MnO_2/\gamma Al_2O_3$ adsorbent-catalyst is 6.70–7.02 wt.% and $S_{BET} = 133.40$ m^2/g. The pores of 24–40 Å radii are dominant. During catalyst synthesis, the specific surface area of outer granule layer decreased by 4–12 % as compared to γAl_2O_3 support.

3. Adsorbent-catalysts are hydrophilic. Their adsorption capacity for water vapour depends on the relative humidity φ of gas mixture. 35–45 mg/g of water is adsorbed at $\varphi = 40$–50 %. When $\varphi > 47$ %, a capillary condensation of water vapour starts in dominant catalyst pores.

4. Alcohol oxidation over $CuO/\gamma Al_2O_3$ starts at 100–130 $^{\circ}$C. $Co_3O_4/\gamma Al_2O_3$ and $MnO_2/\gamma Al_2O_3$ are less active: alcohol vapour is oxidized only above 140– 80 $^{\circ}$C and more reaction intermediates are formed on the surface of these charges.

5. Adsorption capacity of adsorbent-catalyst depends on the adsorbable concentration in gas mixture. 3.407–3.429 mg/g of methanol, 12.153–29.552 mg/g of propanol and 8.545–24.456 mg/g of butanol vapour were adsorbed at 20–25 $^{\circ}$C and at low concentrations (395–627 mg/Nm^3) of alcohol vapour in humid preadsorptive gas.

6. Adsorbate oxidation degree α depends on amount of adsorbate and heating rate V_k of adsorbent-catalyst charge. Using $CuO/\gamma Al_2O_3$, oxidation degree $\alpha = 90$–95 %, if $V_k = 60$ $^{\circ}$C/(cm·min). Catalyst charge temperature autothermally increases during propanol and butanol oxidation.

7. Apparent reaction order of adsorbate oxidation varies from 0.22 to 0.86. Apparent activation energies E_T of methanol, propanol and butanol oxidation were calculated to be 81.42, 63.07, 54.89 kJ/mol, respectively, and they are characteristic for kinetics control reactions. Activation energies of alcohol physical desorption varied from 10.63 to 12.24 kJ/mol. Depending on amount of adsorbate in catalyst charge the parallel-consecutive reactions are dominant during adsorbate oxidation at 200–320 ^{o}C. As the catalyst temperature is increased, the amount of reaction intermediates is decreased.

8. $CuO/\gamma Al_2O_3$ adsorbent-catalyst is recommended for the use in radial adsorber-reactor. The catalyst is thermostable up to 500 ^{o}C.

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CURRICULUM VITAE

Born	in 1976 03 10 in Biržai;
In 1994	graduation from Kėdainiai M. Daukša secondary school;
1994–1998	bachelor's degree studies at Kaunas University of Technology, Faculty of Chemical Technology; Bachelor of Science in Chemical Engineering;
1998–2000	master's degree studies at Kaunas University of Technology, Faculty of Chemical Technology; Master of Science in Chemical Engineering;
2000–2004	doctoral degree studies at Kaunas University of Technology, Faculty of Chemical Technology;
Scientific publications:	10, on the subject of dissertation;
For contacts:	e-mail: kestutis.cicinskas@ktu.lt

SLUOKSNINIAI Me$_x$O$_y$/γAl$_2$O$_3$ ADSORBENTAI-KATALIZATORIAI ALKOHOLIŲ GARŲ ŠALINIMO TECHNOLOGIJOSE

Reziumė

Alkoholių ir kitų lakių organinių junginių (LOJ) šalinimui iš dujinių atliekų adsorbentai-katalizatoriai naudojami kuomet teršalų koncentracijos dujinėse išlakose yra mažos (dešimtys ar šimtai mg/m^3). Tuomet tradiciniai nukenksminimo metodai tokie kaip sudeginimas, tiesioginė katalizė ir kt. yra brangūs arba nepakankamai efektyvūs. Šią problemą tikslinga spręsti netradiciniu būdu – viename aparate apjungiant du prioritetinius nekoncentruotų išlakų valymo metodus: aplinkos temperatūroje – teršalų adsorbciją specialių įkrovų paviršiuje, aukštesnėje temperatūroje – adsorbtyvo katalizinį oksidavimą į nekenksmingas medžiagas. Adsorbentuose-katalizatoriuose turi derėti adsorbentams būdingas didelis savitasis paviršius ir katalizatoriams reikalingi mechaninis ir terminis patvarumas, aktyvumas, ilgas tarnavimo laikas, atsparumas kataliziniams nuodams ir pan.

Kiekvienam adsorbatui adsorbcinio-katalizinio oksidavimo mechanizmas yra individualus. Periodiškai kintant adsorbento-katalizatoriaus temperatūrai adsorbcijos, desorbcijos, reakcijų greičių, priemaišų kiekių pokyčiai tampa ypač svarbūs. Jie priklauso nuo adsorbato ir katalizatoriaus prigimties, sudėties, savitojo paviršiaus parametrų ir technologinių sąlygų. Pastaruoju metu sistemingų alkoholių adsorbcinio-katalizinio oksidavimo duomenų trūksta, todėl yra aktualūs tyrimai kuriant geriausias LOJ šalinimo adsorbentais-katalizatoriais technologijas.

Darbo tikslas buvo sukurti sluoksninių CuO, Co$_3$O$_4$ ir MnO$_2$ adsorbentų-katalizatorių sintezės technologiją, nustatyti jų savybes ir panaudojimą alkoholių garų šalinimo technologijose. Pagal eksperimentinius rezultatus buvo apskaičiuoti alkoholių (metanolio, propanolio ir butanolio) mikropriemaišų ore adsorbcinio-katalizinio oksidavimo kinetiniai parametrai 200–320 ^{o}C temperatūroje, bei eksperimentiškai nustatytas šio proceso mechanizmas. Pateikti katalizatorių aktyviųjų komponentų ir tarpinių oksidavimo junginių sąryšio rezultatai. Nustatyti įkrovų panaudojimo LOJ šalinimui technologiniai parametrai. Pateiktos rekomendacijos naudojant sukurtus adsorbentus-katalizatorius LOJ šalinimo technologijose

Remiantis tyrimų duomenimis padarytos šios išvados:

1. Sluoksniniai adsorbentai-katalizatoriai buvo susintetinti impregnuojant azoto aplinkoje 4 mm skersmens nešiklio γAl$_2$O$_3$ granules vandeniniuose metalų druskų tirpaluose ir jas džiovinant bei kaitinant 150–350 ^{o}C temperatūroje. Aktyvieji komponentai (CuO, Co$_3$O$_4$ arba MnO$_2$) buvo koncentruojami išoriniame granulės paviršiuje 0,3–0,7 mm storio sluoksniu.

2. Adsorbentai-katalizatoriai yra mezoporiai. CuO/γAl$_2$O$_3$ adsorbento-katalizatoriaus išoriniame granulės sluoksnyje yra 7,60–8,95 % CuO, o savitojo paviršiaus plotas S$_{BET}$ = 150,29 m^2/g. Analogiškai Co$_3$O$_4$/γAl$_2$O$_3$ adsorbente-katalizatoriuje yra 8,01–8,54 % Co$_3$O$_4$ ir S$_{BET}$ = 149,51 m^2/g. MnO$_2$/γAl$_2$O$_3$

adsorbente-katalizatoriuje yra 6,70–7,02 % MnO_2 ir $S_{BET} = 133,40$ m^2/g. Vyrauja 24–40 Å spindulio poros. Sintezės metu granulės išorinis sluoksnis praranda 4–12 % savitojo paviršiaus ploto lyginant su nešikliu γAl_2O_3.

3. Adsorbentai-katalizatoriai yra hidrofiliniai. Adsorbentų-katalizatorių geba adsorbuoti vandens garus priklauso nuo dujinės terpės santykinio drėgnio φ. Esant $\varphi = 40$–50 % adsorbentai-katalizatoriai adsorbuoja 35– 5 mg/g H_2O garų. Didėjant φ virš 47 % vyraujančiose katalizatoriaus porose prasideda H_2O garų kapiliarinė kondensacija.

4. $CuO/\gamma Al_2O_3$ įkrova pradeda oksiduoti alkoholių garus pasiekus 100–130 ^{o}C. $Co_3O_4/\gamma Al_2O_3$ ir $MnO_2/\gamma Al_2O_3$ yra mažiau aktyvūs: alkoholių garai oksiduojami tik viršijus 140– 80 ^{o}C. Be to pastarųjų įkrovų paviršiuje susidaro daugiau alkoholių oksidavimo tarpinių junginių.

5. Adsorbentų-katalizatorių prisotinimo adsorbatų garais laipsnis priklauso nuo pastarųjų koncentracijos dujinėje terpėje. Esant mažoms 395–627 mg/Nm^3 alkoholių garų koncentracijoms drėgnose priešadsorbcinėse dujose ir esant 20 – 25 ^{o}C temperatūrai buvo adsorbuota 3,407–3,429 mg/g metanolio, 12,153–29,552 mg/g propanolio ir 8,545–24,456 mg/g butanolio garų.

6. Adsorbatų visiško oksidavimo laipsnis α priklauso nuo įkrovos prisotinimo adsorbatu laipsnio ir jos kaitinimo greičio (V_k). Esant $V_k = 60$ ^{o}C/(cm·min) visiško oksidavimo laipsnis α $CuO/\gamma Al_2O_3$ įkrovoje sieks 90–95 %. Oksiduojant propanolį ir butanolį įkrovos temperatūra autotermiškai didėja.

7. Adsorbatų oksidavimo reakcijos tariamasis laipsniai yra nuo 0,22 iki 0,86. Tariamosios oksidavimo reakcijų aktyvacijos energijos E_T būdingos kinetinei sričiai ir apskaičiuotos metanoliui $E_T = 81,42$ kJ/mol, propanoliui $E_T = 63,07$ kJ/mol ir butanoliui $E_T = 54,89$ kJ/mol. Adsorbatų fizikinės desorbcijos $E_{T(des)}$ yra 10,63–12,24 kJ/mol. Adsorbatų oksidavimo metu 200–320 ^{o}C temperatūroje, priklausomai nuo įkrovos prisotinimo laipsnio, vyrauja lygiagrečiai-nuoseklios oksidavimo reakcijos. Didėjant katalizatoriaus temperatūrai tarpinių oksidavimo junginių koncentracijos mažėja.

8. $CuO/\gamma Al_2O_3$ adsorbentą-katalizatorių rekomenduojama naudoti radialiniuose adsorberiuose – reaktoriuose. Katalizatorius gali stabiliai veikti temperatūroje iki 500 ^{o}C.