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γAl_2O_3-C_{akt}-Me_xO_y ADSORBENTAI-KATALIZATORIAI: SINTEZĖ, SAVYBĖS IR PANAUDOJIMAS

Kaunas, 2005

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Gitana Dabrilaitė

γAl_2O_3-C_{act}-Me_xO_y ADSORBENTS-CATALYSTS: SYNTHESIS, PROPERTIES AND PRACTICAL APPLICATION

Summary of Doctoral Dissertation
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The research was carried out at Kaunas University of Technology Department of Physical chemistry in the period of 1999 – 2004.

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The official defence of the Dissertation will be held at the open meeting of the Council of Chemical Engineering sciences trend at 12 a.m. on March 31, 2005 in the Dissertation Defence Hall at the Central Building of Kaunas University of Technology (K. Donelaičio g. 73 – 403, Kaunas).

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The Dissertation is available at the library of Kaunas University of Technology (K. Donelaičio g. 20, Kaunas).

INTRODUCTION

Relevance of the work. The catalysts of transition metal oxides are widely used in environmental technologies for the removal of volatile organic compounds (VOC) from polluted exhaust gas. The theory of VOC catalytic oxidation into carbon dioxide and water vapour, technology peculiarities and activity of metal oxides are known. At high pollutant concentrations, the catalysts act effectively and economically if the temperature auto-thermally increases at least by 120 – 140 ºC during VOC mineralization. Otherwise, the flow of polluted gas has to be heated to the required temperature for catalysts (mostly 200 – 450 ºC). This can be applied to flows of pollutants where concentrations of VOC are low (hundreds of mg/Nm^3). Then a adsorptive-catalytic process should be more appropriate, which involves VOC adsorption at ambient temperatures and catalytic oxidation during thermal regeneration of adsorbent-catalysts. Currently theoretical and technological aspects of such processes are examined insufficiently. It is known that most perspective and effective are only tailored catalysts having a high specific surface area. As VOC oxidation reactions are exothermic, therefore, such adsorbent-catalysts have to be sufficiently thermo-stable.

Most catalysts used in various technologies are thermo-stable, but have small specific surface area (tens of m^2/g). The greatest adsorption capacity with respect to VOC is typical for activated carbon due to its especially high specific surface area (up to 3000 m^2/g). Since long time ago activated carbon has been used in chemical industry as hydrophobic adsorbents, acting in humid media. Carbon adsorbents in composition with gels or oxides of Ti, Al, Zr, Si are known, too. These composite adsorbents in comparison with activated carbon are more thermo-stable, and specific surface area can be regulated by changing the amount of activated carbon inserts and the conditions of synthesis.

Use of activated carbon or the above mentioned composite adsorbents in order to obtain catalysts was also examined. It is known that these materials were directly impregnated by active components of catalysts, such as Cr_2O_3, CuO, Co_3O_4, V_2O_5, MoO_3, WO_3 and others. However, due to direct contact of metal oxides and activated carbon in catalysts granules, they are not sufficiently thermo-stable. At 300–360 ºC activated carbon oxidizes, and specific surface area and activity of catalysts sharply decrease. Therefore, further investigations are needed in order to create more thermo-stable adsorbents-catalysts of high specific surface area, their production technology and define their use peculiarities in VOC removal processes.

Aim of the work was to create a production technology of thermo-stable adsorbents-catalysts using activated carbon and γAl_2O_3, CuO, Cr_2O_3, Co_3O_4, to determine their properties and use peculiarities in VOC removal technologies.

Activated carbon WS-42A (Chemviron Carbon) of high thermal stability was used in the experiments. CuO, Cr_2O_3 and Co_3O_4 were used as active components of the catalyst. In order to reach the aim of the work we had to complete these targets:

- to determine optimal mean of production and parameters of adsorbent-catalyst and its support;

- to determine specific surface area and pore structure;

- to determine adsorption capacity equilibrium and kinetic parameters for water, methanol, isobutanol and acetone vapours;

- to determine activity of adsorbent-catalyst and its use pecularities.

Scientific novelty and practical significance. Using sol-gel technology, the thermal resistance of the system activated carbon-Al_2O_3-Me_xO_y is increased by concentrating active components of catalysts in the shell of macroporous alumina. Relation between specific surface area and synthesis conditions, equilibrium and kinetic parameters of adsorption of alcohol, acetone, water vapour and catalytic activity in VOC removal technologies were determined.

Production technology of thermo-stable γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst with controlled pore structure was created and parameters of its use in VOC removal technologies were determined.

Approval and publication of research results. Results of the research are presented in 8 publications, 2 of them published in a journal "Chemical technology" and 1 reported in international conferences.

Structure and contents of the dissertation. Dissertation consists of introduction, literature survey, experimental part, results and discussion, parameters of technological use γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbents-catalysts, conclusions, list of 160 references, list of 8 publications on dissertation topic, notation and 2 appendixes. The main material is presented in 104 pages, including 26 tables and 58 figures.

Statements presented for defense:

1. Use of porous alumina gel in synthesis of catalyst do not decrease the specific surface area of activated carbon WS-42A micro-inserts and allows to avoid direct contact of activated carbon with active catalyst components (CuO, Cr_2O_3 and Co_3O_4). Metal oxide gels added into adsorbent are concentrated in macroporous Al_2O_3. Catalytic reactions of desorbate mineralization into carbon dioxide occur in this part of catalyst at high temperatures.

2. γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst containing 5 wt. % of activated carbon is thermo-stable up to 450 ºC.

3. Adsorption capacity of adsorbent-catalyst charge with respect to VOC at small concentrations (Henry region) is proportional to the amount of active carbon insert in the catalyst. Macroporous γAl_2O_3 covers the carbon in the catalyst, and serves for the transfer of reagents.

4. Both catalyst support γAl_2O_3-C_{act} and catalyst containing CuO, Cr_2O_3 and Co_3O_4 are hydrophobic. Volatile organic compounds will be adsorbed firstly in the humid gas.

5. γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst is characterized by sufficient activity and is suitable for adsorptive-catalytic removal of alcohols from exhaust gas. Catalyst support (γAl_2O_3-C_{act}) can be used as adsorbent in humid gas flows.

EXPERIMENTAL

Chemical materials used in the work were chemically or analytically pure reagents.

γAl_2O_3 was prepared at room temperature and atmospheric pressure according to the following procedure. 1 M NaOH was poured into 1 M $Al_2(SO_4)_3$ solution under vigorous stirring. The obtained precipitates were filtered, washed by distilled water until negative reaction with respect to SO_4^{2-} ion (using $BaCl_2$ solution), aged for various time, dried at 120 ^{o}C for 4 h, heated at 420 ^{o}C for 4 h, granulated and sifted through the sieve of 3 – 5 mm. The same procedure was applied for the synthesis of γAl_2O_3 - C_{act} composites. Activated carbon granules (up to 50 μm in diameter) were mixed into 1 M $Al_2(SO_4)_3$ solution before the precipitation of gel. γAl_2O_3-C_{act}-CuO, γAl_2O_3-C_{act}-(CuO, Cr_2O_3), γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) composites were prepared by adding various amounts of active components (crushed up to 50 μm) into humid mixture of alumina gel and activated carbon. The prepared composites were aged for 12 days, granulated by pressing them through sprinneret, dried at 120 ^{o}C for 4 h and heated at 420 ^{o}C for 4 h. Diameter of granules was 1 – 1,5 mm. Cu, Cr and Co gels were prepared similarly to Al_2O_3. 1 M solutions of Cu, Cr and Co nitrates were used for synthesis. γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) (synthesized from gels) was prepared by mechanically mixing composite of humid alumina gel-carbon and Cu, Cr and Co gels. The obtained mixtures were aged for 12 days, granulated by pressing them through sprinneret, dried at 120 ^{o}C for 4 h and heated at 420 ^{o}C for 4 h. Diameter of granules was 1 – 1.5 mm.

Experimental apparatus of research of equilibrium processes was used to measure the adsorption capacity, and consisted of block of gas mixture preparation, flow rate regulation and measurement systems, and thermostated adsorption cell with the balances. Investigations of adsorptive-catalytic oxidation were performed

using the experimental apparatus made from quartz glass, consisting of block of gas mixture preparation, reactor, temperature control and gas mixture analysis systems.

Methanol concentration was measured by Perkin Elmer Clarus 500 gas chromatograph equipped with flame ionization detector or photocolorimetrically (selective methanol oxidation by potassium permanganate into formaldehyde). Formaldehyde concentration in the gas mixture was estimated photocolorimetrically at λ = 584 nm using photoelectric colorimeter FEK-56M. Method is based on formaldehyde reaction with chromotropic acid in strongly acid medium.

Amounts of active components in the adsorbents-catalysts were estimated by atomic absorption spectrometry (AAS) using AASIN instrument (Karl Zeiss Jena, Germany). Mineral composition of the prepared adsorbent-catalysts was examined by X-ray diffraction (XRD) analysis using DRON-6 (Bourevestnik, Russia) diffractometer with Ni-filtered CuK_{α} radiation. Images of the surface and chemical composition of adsorbent-catalysts were obtained by Oxford ISIS Leo 440i scanning electron microscope (SEM).

Differential scanning calorimetry-thermogravimetry (DSC-TG) was used to analyze the thermal effects occurring in a sample during heat treatment. DSC-TG analysis was performed with a NETZSCH (Germany) calorimeter under air atmosphere with a rate of heating 10 °C min^{-1}. Differential thermal analysis (DTA) was performed by DuPont 990 analyser (USA) under air atmosphere up to 800 ºC with a rate of heating 10 °C min^{-1}.

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, Dalla Valle scheme using entire N_2 desorption isotherm at 77 K.

RESULTS AND DISCUSSION

1. Synthesis and properties of adsorbents-catalysts

Synthesis of γAl$_2$O$_3$. During the synthesis of alumina gel from solution of 1 M aluminum salt and caustic soda, the highest specific surface area is obtained when solution pH $\sim$ 10. We determined experimentally the dependence of the alumina gel amount on solution pH. The largest amount of precipitates is obtained at pH $\sim$ 5 – 6, and the biggest diameter of pores is observed when pH $\sim$ 8. The biggest amount

of gel was obtained when solution pH $\sim 5 - 6$. Only very small amount of precipitate was obtained at pH ~ 10.

During the aging process of alumina gel, the specific surface area is decreasing. During aging the stronger carcass is being formed, and this is very important in production of adsorbents and catalysts. By heating the samples of not aged alumina gel, the powdery Al_2O_3 were obtained. Aging of the alumina gel for up to 24 days showed that if the period of aging is extended, the stronger Al_2O_3 is obtained. Samples aged for 24 days formed a firm monolith. Efforts to age the precipitated alumina gel in the mother solution did not turn to be successful. Even in the presence of the biggest amount of precipitate (pH $\sim 5 - 6$) only the traces of precipitate of alumina gel remained in the solution after a period of a day.

Results of X-ray diffraction analysis showed that peaks typical for low-temperature γAl_2O_3 and bohmite dominate in the produced adsorbent. Thermal analysis of aged humid adsorbent showed that the largest endothermic effect in DSC curve is observed at the increase of the temperature from room temperature up to 200 ^{o}C. In this temperature range the water is removed. Further heating of sample resulted in smaller changes of TG and DSC curves. Up to 400 ^{o}C the weight of sample still decreases, but over 400 ^{o}C remains constant. DSC curve slowly increases at the interval of temperatures of $200 - 600$ ^{o}C. It can be attributed to the formation of Al_2O_3 gel structure and appearance of low-temperature γAl_2O_3.

Synthesis of γAl_2O_3-C_{act} composites. For the production of γAl_2O_3-C_{act} adsorbents we used the sol-gel method by adding the activated carbon to the produced Al_2O_3 gel. In our research we used WS-42A (Chemviron Carbon, Germany) activated carbon of high thermal stability, widely used in the industry. This carbon is designed for cleaning the gas from organic compounds and may be regenerated thermally. We added various amounts of activated carbon (granulated up to 50 μm) into 1 M $Al_2(SO_4)_3$ solution and added 1 M NaOH by portions. The obtained gel was mixed with a stirrer ($140 - 160$ rpm) for 1 min. Later the obtained composites were filtered. The gel was washed by distilled water in order to remove residual SO_4^{2-} ions and aged for 12 days. Further the gels were granulated by extrusion, dried at 120 ^{o}C for 4 h and heated at 420 ^{o}C for 4 h. The obtained γAl_2O_3-C_{act} adsorbents granules were $1.5 - 2.0$ mm in diameter and $5.0 - 6.0$ mm in length. The experimental results showed that alumina gel absorbs in the solution less than 8.5 % (wt.) of activated carbon at the above indicated conditions. Upon addition of larger amounts of activated carbon to the solution, free carbon remains in the solution and gels are contaminated.

The measurements of specific surface area (S_{BET}) of the obtained adsorbents were performed and the dependence of S_{BET} on the synthesis conditions was determined (Table 1). It was established that $S_{BET} \sim 940$ m^2/g for activated carbon. S_{BET} of produced alumina gel varies between 7.9 and 30.7 m^2/g, depending on the aging duration and heating temperature. This indicates that the produced alumina gels could be attributed to the macroporous gels. When the amount of added carbon is increased to 1.7 – 5 % (wt.), the surface of adsorbents increases. The highest value we were able to reach was $S_{BET} = 280.4$ m^2/g. The best γAl_2O_3-C_{act} composite were obtained by using ~ 5 % (wt.) of activated carbon, keeping solution pH ~ 8 and time of contact until filtration ~ 1 min.

Differential thermal analysis showed that composites of alumina gel-activated carbons are thermally stable up to 450 ºC. The oxidation of pure activated carbon starts at 400 ºC.

Table 1. Synthesis conditions of adsorbent specimens and their specific surfaces areas

Composition of adsorbents	Duration of aging, days	Heating temperature, ºC	Specific surface area (S_{BET}) of adsorbents, m^2/g
activated carbons	-	-	~ 940
alumina gel	24	150	7,9
alumina gel	24	230	9,7
alumina gel	12	420	30,7
alumina gel + 1,7 % activated carbons	24	150	92,7
alumina gel + 3,3 % activated carbons	24	150	147,3
alumina gel + 5 % activated carbons	24	150	228,8
alumina gel + 5 % activated carbons	12	420	280,4
alumina gel + 5 % activated carbons	24	420	149,4

Synthesis of γAl_2O_3-C_{act}-Me_xO_y adsorbent-catalyst. We tried to immobilize active components of catalyst by these means:

1) Adding Cu(II), Cr(IV) and Co(II/III) gel-type hydroxides into γAl_2O_3-C_{act} gel. Separately produced gels were mixed. After aging it was possible to granulate the composite having 85 – 90 % Al_2O_3-C_{act} and 10 – 15 % of metal hydroxides. An increase in the amount of hydroxides caused the granules to become powdery after heating. The obtained gels were aged for 12 days, granulated in an extrusive way, dried at 120 ºC and heated at 420 ºC. The diameter of granules varied in the range of 1.5 – 2.0 mm, and the length from 5.0 to 6.0 mm. The best sample had 6.8 % (wt.) CuO, 3.1 % Cr_2O_3 and 2.0 % Co_3O_4.

2) Adsorbents-catalysts were also produced by adding the 50 μm fraction of CuO, Cr_2O_3 and Co_3O_4 powder and their various mixtures into γAl_2O_3-C_{act} gel type composite. The obtained composites were further aged and thermally treated analogically to the 1st item.

The results of the research showed that after thermal treatment all catalyst samples contained the oxides of active components. Peaks in X-ray diffractograms corresponded to characteristic peaks of CuO, Cr_2O_3 and Co_3O_4.

Thermal analysis of humid samples showed that catalysts loose their humidity at $\sim$ 120 ^{o}C (Figure 1). The endothermic effect at 250 – 260 ^{o}C is being observed for catalyst, which is produced by using hydroxides and it is attributed to thermal dissociation of metals hydroxides. The exothermic effect above 580 ^{o}C showed the destruction of catalyst structure. The endothermic effect due to evaporation of humidity was found at $\sim$ 120 ^{o}C for catalysts produced by adding the powder of metal oxides (Figure 2). TG curve falls consecutively, and that of DSC rises if temperature is increased. This lets to maintain that metal oxides can be slowly reduced by activated carbon.
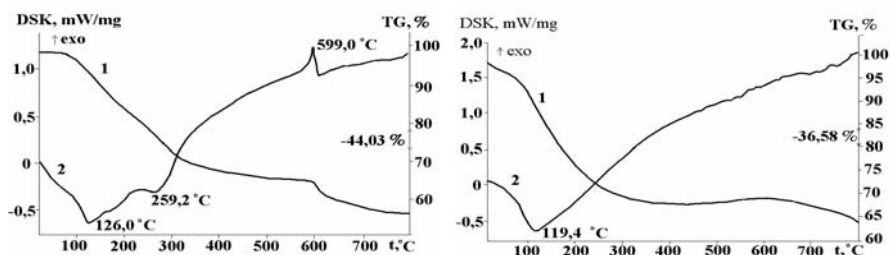
Figure 1. Curves of thermal analysis of humid γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst produced using the gels of metal hidroxides: *1* – Thermogravimetry (TG); *2* – Differential Scanning Calorimetry (DSC)

Figure 2. Curves of thermal analysis of humid γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst produced using the powders of metal oxides: *1* – Thermogravimetry (TG); *2* – Differential Scanning Calorimetry (DSC)

In order to confirm this assumption, we performed preliminary tests for all obtained adsorbent-catalysts according to their equilibrium adsorption capacity. The results of these measurements show that adsorption capacity is proportional to the added amount of activated carbon only for catalyst which is produced by adding gel type metals hydroxides. If metal oxides are added in the form of powders, the adsorption capacity of thermally treated charge of adsorbent-catalyst is significantly smaller and is close to that of macroporous γAl_2O_3. This shows that using powdery oxides, due to their direct contact with activated carbon, the latter is oxidized

during thermal treatment of humid catalysts. In this case one obtain Al_2O_3-metal oxide catalysts having small specific surface area. These assumptions were confirmed by BET measurements for catalyst having CuO, Cr_2O_3 and Co_3O_4 powder. The S_{BET} value we found was 29.32 m^2/g, which is close to that for macroporous γAl_2O_3 ($S_{BET} = 30.7$ m^2/g).

The experimental results were validated by findings of thermodynamic calculations (Table 2). By comparing the standard Gibbs potentials it can be noticed that all reactions, except (3), can proceed at low temperatures, and carbon inserts can remain at high temperatures only if no contact with metal oxides is present.

Table 2. Standard Gibbs potentials of reactions

Reactions		ΔG_T^0, kJ/mol, at various temperatures, ^0C						
		100	200	300	400	500	600	800
$C + O_2 \rightarrow CO_2$	(1)	-398,2	-396,5	-395,7	-395,4	-395,2	-395,1	-394,7
$C + \frac{1}{2} O_2 \rightarrow CO$	(2)	-153,3	-156,4	-163,5	-171,3	-179,4	-187,5	-204,1
$C + H_2O \rightarrow H_2 + CO$	(3)	73,5	64,5	52,1	39,0	25,5	11,9	-18,5
$C + CuO \rightarrow Cu + CO$	(4)	-29,8	-41,2	-55,0	-67,1	-80,0	-92,3	-117,2
$C + 2CuO \rightarrow Cu_2O + 2CO$	(5)	-243,2	-271,8	-299,6	-327,9	-355,8	-384,0	-436,9

On the basis of these results for further investigations we used only catalyst having CuO, Cr_2O_3 and Co_3O_4 and which was produced from hydroxides of these metals. Such adsorbent-catalyst is characterized by sufficient thermal stability and had high specific surface area which is influenced by activated carbon additive. These properties are determined by the fact, that adding gel type metal hydroxides into γAl_2O_3-C_{act} gel type composite using our synthesis method, metal oxides are localized in the porous alumina gel and do not make a direct contact with activated carbon.

Specific surfaces areas and pore structure of γAl_2O_3-C_{act} and γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O composites. For the detailed examination of specific surface we have chosen the best γAl_2O_3-C_{act} composite having ~ 5 % of activated carbon and the best γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst produced by using the gels of metal hydroxides. For comparison we measured specific surface area and pore characteristics of alumina gel prepared in identical conditions.

Calculations of specific surface area (S_{BET}) were performed by using primary part of N_2 adsorption-desorption hysteresis when $p/p_o < 0.30$ (Figure 5). Clear arch is seen in isotherms of hysteresis (point A), which shows that N_2 monomolecular layer has formed. By plotting $1/X(p/p_0)-1$ as a function of p/p_o, linear BET plots are obtained (Figures 3 and 4), and their R^2 fluctuates in the range of $0,9990 – 0,9993$.

These results show that S_{BET} = 280.43 m^2/g for γAl$_2$O$_3$-C$_{act}$ adsorbent, and S_{BET} = 244.7 m^2/g for catalyst. C_{BET} constant value for catalyst is calculated to be 168.7 and that for γAl$_2$O$_3$-C$_{act}$ is 337.83. C_{BET} numeral value allows to evaluate validity of BET measurements. It is known that the most accurate results of S_{BET} are obtained when C_{BET} is 50 – 250. In our case, the calculated high values of C_{BET} were conditioned by additive of microporous activated carbon.
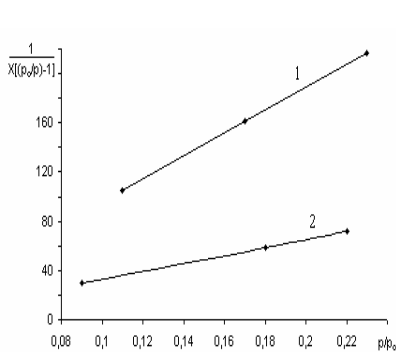
Figure 3. N$_2$ adsorption isotherm at 77 K in BET plot: *1* – γAl$_2$O$_3$; *2* – γAl$_2$O$_3$-C$_{act}$ having 5 % (wt.) of activated carbon (X – weight of adsorbate, g)
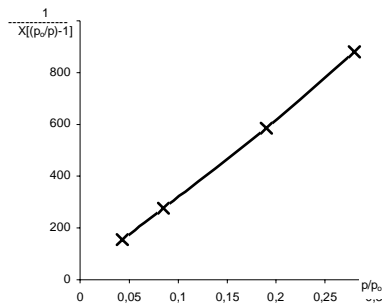
Figure 4. N$_2$ adsorption isotherm of γAl$_2$O$_3$-C$_{act}$-(CuO, Cr$_2$O$_3$, Co$_3$O$_4$) adsorbent-catalyst at 77 K in BET plot

It is possible to forecast the pore form of adsorbents according to de Boer classification of hysteresis isotherms (Figure 5). Collateral depth-type forms are typical to the produced γAl$_2$O$_3$. The phenomenon of hysteresis ends in the range of low relative pressures p/p$_o$ = 0.24, isotherm is narrow, isotherm sharply rises as p/p$_o$ approaches to 1. The form of dominant pores is changed by 5 % additive of activated carbon: typical spherical forms appear alongside the collateral depths. Hysteresis isotherm of this absorbent becomes larger at relative pressures p/p$_o$ = 0.5 – 0.8 and the phenomenon of hysteresis ends when p/p$_o$ = 0.37. Spherical forms of pores prevail in the catalyst: when p/p$_o$ = 0.6 – 0.95 the broad part of hysteresis isotherm can be seen, and when p/p$_o$ decreases up to 0.4, the phenomenon of hysteresis finishes. This approximate evaluation of the form of pores is supported by the comparison of S_{BET} results with the total specific surface ΣA, calculated according to scheme of C. Orr, J. M. Dalla Valle. It has been determined that S_{BET} = 30.67 m^2/g and ΣA = 73.5 m^2/g for produced γAl$_2$O$_3$. For γAl$_2$O$_3$-C$_{act}$ adsorbent S_{BET} = 280.43 m^2/g, and ΣA = 239.1 m^2/g. In the case of γAl$_2$O$_3$-C$_{act}$-(CuO, Cr$_2$O$_3$, Co$_3$O$_4$) catalyst S_{BET} = 244.7 m^2/g, and ΣA = 502.98 m^2/g.

The results show that we have evaluated the form of pores of γAl$_2$O$_3$-C$_{act}$

adsorbent rather accurately, while the polydispersal structure is typical for γAl_2O_3 and catalyst regarding the form of pores when the collateral depths are supplemented by the capillaries of bigger radius.

These assumptions are confirmed by the calculations of integral and differential distribution of pores according to their diameters (Table 3). The pores of $16 - 20$ Å radius prevail in $\gamma Al_2O_3-C_{act}$ adsorbent, and there are not much of pores of other radii. The pores of $10 - 15$ Å and $25 - 45$ Å radii prevails in γAl_2O_3, and pores of $18 - 20$ Å and $24 - 27$ Å radius prevails in catalyst.
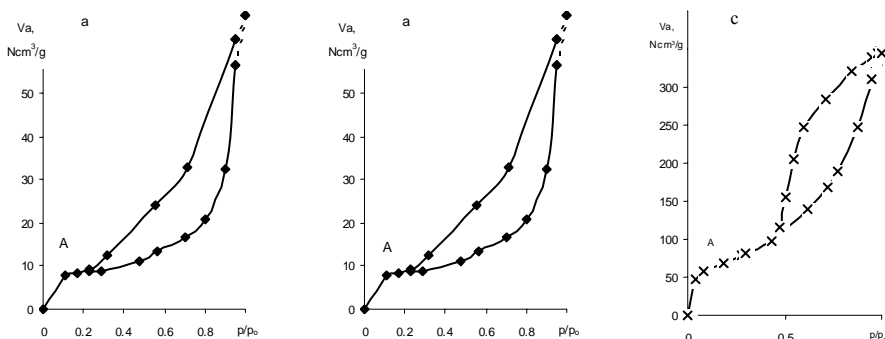
Figure 5. N_2 Adsorption-desorption isotherms at 77 K: $a - \gamma Al_2O_3$; $b - \gamma Al_2O_3-C_{act}$, having 5 % (wt.) of activated carbon, c $- \gamma Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4)$ adsorbent-catalyst

Table 3. Parameters of specific surface of adsorbents and catalyst

Adsorbent or catalyst	Mean radius of pores $\bar{r}_p$, Å	Total volume of pores ΣV_p, cm^3/g	Total surface area calculated according to hysteresis isotherm ΣA, m^2/g
γAl_2O_3	32.13	0.118	73.5
$\gamma Al_2O_3-C_{act}$	20.02	0.332	239.1
$\gamma Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4)$	25.96	0.652	502.98

2. Adsorption capacity of $\gamma Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4)$ adsorbent-catalyst

Adsorption capacity for water vapours. Adsorption capacity for water vapour is determined by properties of catalyst support ($\gamma Al_2O_3-C_{act}$ composite). Therefore, we performed analyses of water vapour adsorption by this composite and its constituents (hydrophilic γAl_2O_3 and hydrophobic activated carbon WS-42A). The maximum adsorption capacity of water vapour was measured using $13.52 - 16.63$ mg/Ndm^3 concentration of water vapour in the preadsorptive mixture of air and water vapour. At these conditions water vapour was in equilibrium with

the liquid water at 15 – 18 °C (relative air humidity φ ~ 100 %, relative pressures p/p_o ~ 1, adsorption pressure is close to atmospheric). Equilibrium adsorption capacity for water vapour of alumina gel and γAl_2O_3-C_{act} adsorbents are close to each other and vary between 7.82 to 8.03 mmol/g. An equilibrium adsorption capacity of water vapour for activated carbon $\sum X^p_{H_2O}$ = 22,92 mmol/g and is due to higher specific surface of carbon. Adsorption is slow, its equilibrium can be reached only within 24 – 72 hours. As relative air humidity decreases up to 66 – 70 %, equilibrium is reached within 48 h for all adsorbents. Quantity of equilibrium adsorbed water $\sum X^p_{H_2O}$ is similar for all adsorbents and varies from 2.48 to 5.9 mmol/g. If adsorption temperature increases up to 30 °C, water vapour is adsorbed only by γAl_2O_3 and γAl_2O_3-C_{act} (Figure 6). The found equilibrium adsorption capacity for alumina gel was 1.98 mmol/g, and for γAl_2O_3-C_{act} 0.86 mmol/g. Equilibrium was reached also very slowly, within 150 – 300 min. Pure activated carbon do not adsorb the water vapour. γAl_2O_3-C_{act} does not adsorb water vapour over 40 °C, too. Only hydrophilic γAl_2O_3 absorbed it. Equilibrium water vapour adsorption capacity for alumina gel $\sum X^p_{H_2O}$ = 0.19 mmol/g, equilibrium was reached within 120 min. Alumina gel do not adsorb the water vapour over 50 °C, too.
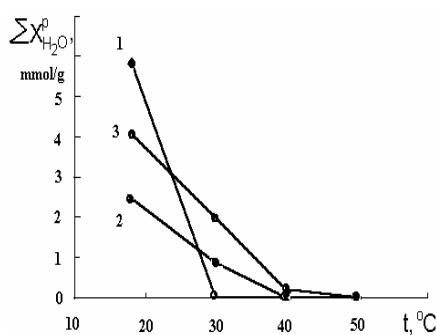

Figure 6. Equilibrium quantity of adsorbed water at various temperatures and relative air humidity φ = 66 – 70 % for adsorbents:

1 – activated carbon; 2 – γAl_2O_3-C_{act}; 3 – γAl_2O_3.

After estimation of specific surfaces area of catalyst support γAl_2O_3-C_{act} and its constituents (Table 4) we can see, that our produced catalyst is hydrophobic with respect to water vapour adsorption capacity.

This feature is determined by the presence of carbon of high surface area in the catalyst. Meanwhile, the influence of hydrophilic macroporous γAl_2O_3 can be recognized as insignificant. Furthermore, water is adsorbed very slowly: during the first adsorption hour 0.5 – 0.6 mmol/g water vapour is absorbed on γAl_2O_3-C_{act} composite in the range of medium relative humidity. Above 40 °C water is not adsorbed at all. These experimental results are also supported by water vapour adsorption isotherms obtained over H_2SO_4 – H_2O solutions at the stationary conditions with constant partial pressure of water vapour (Figure 7).

γAl_2O_3-C_{act} water vapour isotherms are ascribed to be of the 3rd type isotherms, and WS-42A carbons are ascribed to the 5th type isotherms. A rise towards the axis of relative pressures is typical for them, which indicates a weak bond between adsorbent and adsorbate. Isotherms of this type are omitted in the calculations due to great inaccuracy.

Table 4. Dependence of quantity of equilibrium adsorbed water on specific surface area of adsorbents

Adsorbent	Specific surface area S, m^2/g	Ratio $\Sigma X^p_{H_2O}$ / S, $mmol/m^2$	Equilibrium adsorption capacity $\Sigma X^p_{H_2O}$, mmol/g
$\varphi = 66 - 70\%$, $t = 18\,^oC$			
WS-42A activated carbon	~940	0.006	5.91
γAl_2O_3	30.7	0.133	4.09
γAl_2O_3-C_{act}	280.4	0.009	2.48
$\varphi = 100\%$, $t = 15 - 18\,^oC$			
WS-42A activated carbon	~940	0.024	22.92
γAl_2O_3	30.7	0.303	7.82
γAl_2O_3-C_{act}	280.4	0.032	8.03
$\varphi = 64 - 72\%$, $t_s = 30\,^oC$			
WS-42A activated carbon	~940	0	0
γAl_2O_3	30.7	0.077	1.98
γAl_2O_3-C_{act}	280.4	0.003	0.86

In this case water vapour condensation in meso and micro pores is possible after reaching the equilibrium conditions. The possibility of water vapour condensation in adsorbents pores (Figure 8) is calculated according to Kelvin equation.
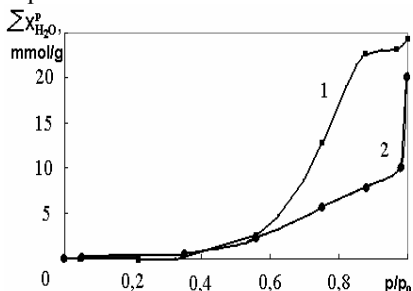

Figure 7. Water vapour adsorption isotherm at 20 ^oC: 1 – WS-42A activated carbon;
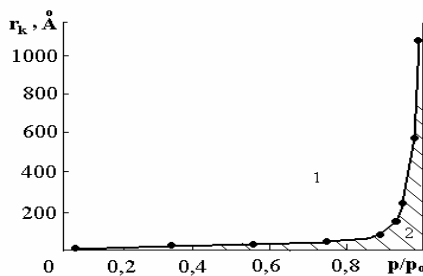
2 – γAl_2O_3-C_{act} adsorbent

Figure 8. r_k dependence of open pores of adsorbents on water vapour quantity in the preadsorptive gas (1 – region of open pores; 2 – region of water vapour condensation in the pores)

We determined that 18 – 20 Å radius pores prevail in the obtained adsorbent-catalyst and its support. Then the prevailing pores would be filled by water at the equilibrium conditions and relative humidity over 40 %. This assumption is approximate, as the examined catalyst is hydrophobic and the equilibrium is reached very slowly.

Adsorption capacity for alcohol vapours. For experimental runs we used methanol and isobutanol vapour mixtures with air. Maximum adsorption capacity of adsorbents for methanol vapour was measured using a high 251 – 1460 g/Nm^3 methanol concentration of preadsorptive air-vapour mixture for activated carbon, $\gamma Al_2O_3-C_{act}$ and $\gamma Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4)$. Methanol vapour were in equilibrium with the liquid methanol at 25, 35, 45, 55 and 65 ^oC (partial pressure $p/p_o \sim 1$, adsorption pressure is close to atmospheric). The findings indicate (Table 5) that the greatest adsorption capacity for methanol vapour is proportional to specific surface area. Adsorption of methanol, contrariwise to water vapour, is very rapid, and adsorption equilibrium is reached within 2 – 40 minutes. Comparing these findings with the previous ones we can maintain, that water vapour do not compete with methanol in the inner surface of adsorbent charge and do not determine the parameters of methanol adsorption.

Table 5. Dependency of adsorption capacity for methanol on temperature (C_o- concentration of methanol over the solution)

Adsorbent	ΣX^p_{met}, mg/g				
	t=25 ^oC $C_o = 250$ g/Nm^3	t=35 ^oC $C_o = 290$ g/Nm^3	t = 45 ^oC $C_o = 630$ g/Nm^3	t = 55 ^oC $C_o= 970$ g/Nm^3	t = 65 ^oC $C_o = 1460$ g/Nm^3
WS-42A activated carbons	300.48	296.19	285.40	271.43	283.81
$\gamma Al_2O_3-C_{act}$	61.40	51.51	48.49	34.79	78.08
$\gamma Al_2O_3-C_{act}$ -(CuO, Cr$_2$O$_3$, Co$_3$O$_4$)	111.14	75.23	60.53	54.53	56.17

As the temperature increases the quantity of adsorbed methanol vapour decreases almost in a linear dependence. Only after reaching the region of overheated vapour (65 ^oC temperature) the quantity of adsorbed methanol increases. In the range of small concentrations of methanol vapour (0.2 up to 10 g/Nm^3 at 25 ^oC) WS-42A pure carbon adsorption capacity increases from 1.44 to 78 mg/g. $\gamma Al_2O_3-C_{act}$ adsorption capacity for methanol increases in the range of 0.14 – 5.22 mg/g at the same conditions. Adsorption capacity of $\gamma Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4)$ catalyst increases in the range of 0.08 – 7.20 mg/g. At 55 ^oC all adsorbents adsorb very small (several mg/g) quantities of methanol vapour (Figure 9).

Maximum adsorption capacity for isobutanol vapour was measured in preadsorptive air-vapour mixtures having 45 – 519 g/Nm^3 of isobutanol at various temperatures. Isobutanol vapour were in equilibrium with the liquid isobutanol at 25, 35, 45, 55 and 65 ^{o}C (partial pressure $p/p_o \sim 1$, adsorption pressure is close to atmospheric). Results indicate (Table 6), that equilibrium adsorption capacity of adsorbents (the same as in the case of adsorption of methanol), are the greatest for activated carbon WS-42A, and the least for $\gamma Al_2O_3-C_{act}$ and depend on the specific surface area. Adsorption equilibrium is reached also rather rapidly.
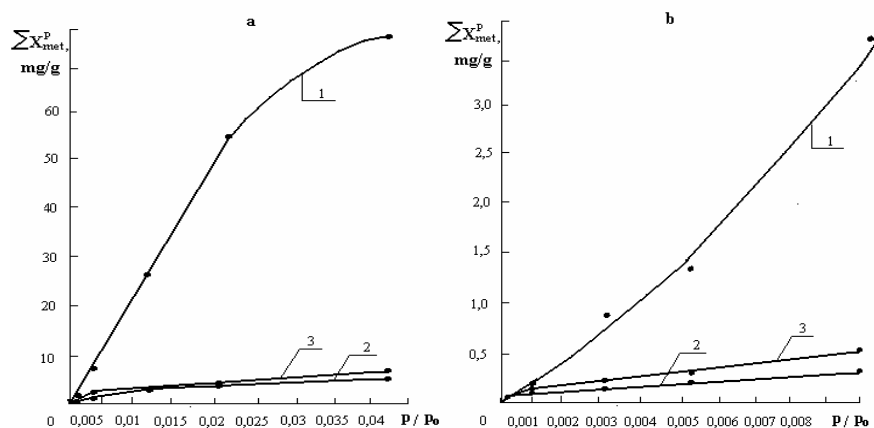

Figure 9. Isotherms of methanol vapour adsorption in the range of low concentrations: **1** – WS-42A activated carbon, **2** – $\gamma Al_2O_3-C_{act}$, **3** – adsorbent-catalyst $\gamma Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4)$; **a** – t = 25 ^{o}C, **b** – t = 55 ^{o}C

If adsorption temperature increases, adsorption equilibrium is reached faster. Equilibrium of adsorbent-catalyst is reached within 20 min under our experimental conditions. As the temperature increases, the quantity of adsorbed isobutanol decreases in a linear dependence.

In the range of low concentrations (Henry adsorption region, from 0.2 up to 10 g/Nm^3 at 25 ^{o}C) activated carbon adsorption capacity increases from 0.1 to 53 mg/g. $\gamma Al_2O_3-C_{act}$ adsorption capacity for isobutanol increases from 0.07 to 36.0 mg/g in the same conditions. $\gamma Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4)$ charge adsorption capacity increases from 0.04 to 7.20 mg/g. At 55 ^{o}C activated carbon WS-42A adsorb 0.08 – 40 mg/g of isobutanol vapour. $\gamma Al_2O_3-C_{act}$ adsorbs 0.06 – 7.90 mg/g, and $\gamma Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4)$ adsorbs 0.01 – 3.20 mg/g (Figure 10) of isobutanol vapour.

Table 6. Dependency of adsorption capacity for isobutanol on temperature (C_o- concentration of isobutanol over the solution)

Adsorbent	ΣX^P_{but} mg/g				
	t = 25 ºC C_o = 45 g/Nm^3	t = 35 ºC C_o = 89 g/Nm^3	t = 45 ºC C_o = 172 g/Nm^3	t = 55 ºC C_o = 297 g/Nm^3	t = 65 ºC C_o = 519 g/Nm^3
WS-42A activated carbon	287.85	269.7	259.38	253.30	232.3
γAl_2O_3-C_{act}	34.31	30.49	28.76	26.24	25.04
γAl_2O_3-C_{act} -(CuO, Cr$_2$O$_3$,Co$_3$O$_4$)	59.49	40.62	31.04	26.08	23.88

As compared with the findings on adsorption of methanol vapour, the known correlation for the produced adsorbent-catalyst samples can be observed: as adsorbable molecular mass increases, the equilibrium adsorption capacity increases. Also the less volatile isobutanol is adsorbed at higher temperatures, when the adsorption of water and methanol vapour does not occur.
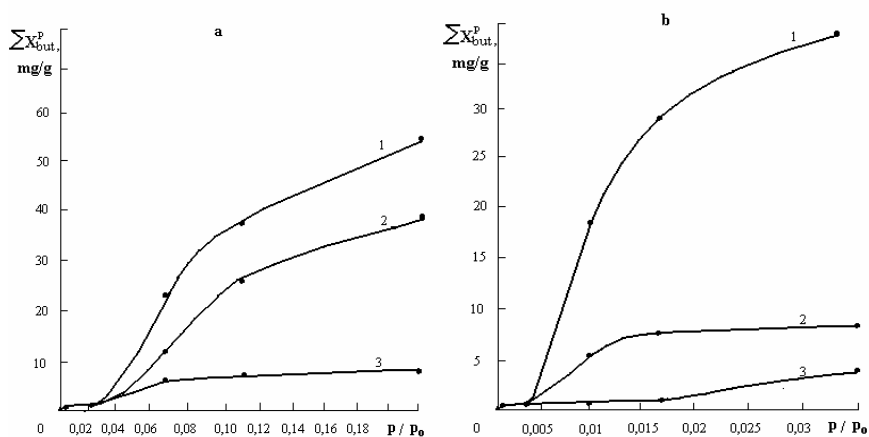

Figure 10. Isotherms of isobutanol vapour adsorption in the range of low concentrations:
1 – WS-42A activated carbon, 2 – γAl_2O_3-C_{act}, 3 – γAl_2O_3-C_{act} -(CuO, Cr$_2$O$_3$, Co$_3$O$_4$);
a – t = 25 ºC, **b** – t = 55 ºC

Adsorption capacity for acetone vapours. Activated carbons (as WS-42A in our case) are widely used for the removal of acetone and cyclic hydrocarbons from flue gas. Thermal stability and combustibility of adsorbents limit their use in adsorption technology. It is common not to overpass the temperature of 200 ºC in order to avoid accidents during regeneration. Our prepared catalyst and especially its support (γAl_2O_3-C_{act}) are thermally more stable than activated carbon. Therefore, in our opinion, it is important to measure their adsorption capacity for acetone vapour.

The maximum adsorption capacity of adsorbents was measured using acetone vapour concentration of 758 g/Nm^3 in the preadsorptive air-vapour mixture. Acetone vapours were in equilibrium with the liquid acetone at 22 ^oC (partial pressure $p/p_o \sim 1$, adsorption pressure is close to atmospheric). Kinetic plots of adsorption are presented in the Figure 11. Adsorption equilibrium settles within 30 minutes. When acetone concentration in preadsorptive vapour-air mixture was $6.00 - 35.13$ g/Nm^3, equilibrium adsorption capacity of WS-42A activated carbon and γAl_2O_3 - C_{act} (adsorption at $36 - 37$ ^oC) is less than maximum and varies in the range of $99.2 - 177$ mg/g for activated carbon and $3.8 - 13.5$ mg/g for γAl_2O_3-C_{act}. Adsorption equilibrium for activated carbon is reached within 20 minutes, and for γAl_2O_3-C_{act} within 30 minutes.
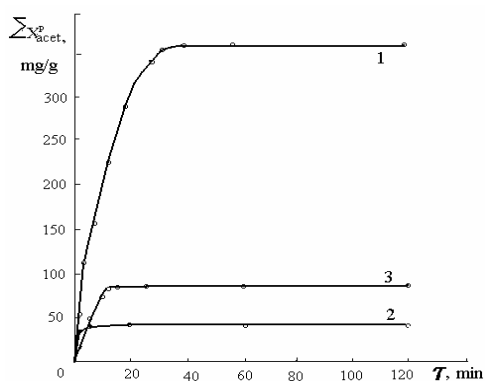
Picture 11. Acetone equilibrium adsorption capacity $\sum X^p_{acet}$ as a function of time at $\varphi = 36 - 48$ % for adsorbents:
1 – WS-42A Activated Carbon,
2 – γAl_2O_3-C_{act},
3 – γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4)

The obtained results indicate that Al_2O_3-C_{act} charge suits for acetone vapour adsorption technology, too. Less specific surface area determines the less adsorption capacity compared to activated carbon WS-42A. However, greater thermal stability, and at the same time the faster regeneration can compensate this shortage at higher than 200 ºC temperature.

3. Activity of γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst

It is customary to test an activity of VOC oxidation catalysts in CO or alcohol oxidation reactions. Exception is made by catalysts acting at high (> 550 ºC) temperatures, which are tested towards cyclic hydrocarbon (mostly benzene) oxidation.

We tested γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) catalyst activity in methanol vapour oxidation using two technologies:

1) At stationary temperature of catalyst charge;
2) In the cyclic adsorptive-catalytic process.

We maintained the methanol concentration in preadsorptive gas to be 800 mg/Nm^3. Pre-reactionary mixture humidity equaled to relative air humidity and varied in the range of 40 – 50 % (8 – 12 g/Nm^3). Methanol vapour reaction with air oxygen starts, as pre-reactionary mixture CH_3OH is constantly supplied and when average temperature of adsorbent-catalyst layer is 100 ^{o}C. As temperature rises, methanol oxidation degree increases and it reaches to 92,2 % at 370 ^{o}C (Figure 12).

As temperature of flow of methanol vapour – humid air is 150 – 300 ^{o}C, methanol is oxydated not only into CO_2 and H_2O vapour, but also into intermediate
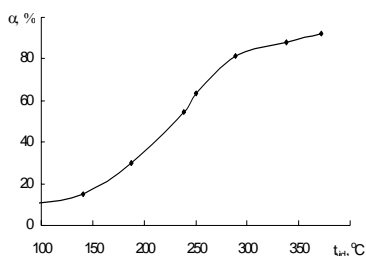

Figure 12. Dependence of methanol oxidation degree on temperature

oxidation product (formaldehyde). The largest quantity of formaldehyde (~100 mg/Nm^3) is formed as average temperature of adsorbent - catalyst layer is 235 ^{o}C.

As temperature increases above 235 ^{o}C, formaldehyde concentration decreases. At 350 ^{o}C formaldehyde is not found. This indicates that the process proceeds according to the well known parallel-consecutive mechanism of oxidation.

The activity of γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst was also investigated in the cyclic adsorptive-catalytic oxidation process of methanol vapour. Firstly, adsorbent-catalyst charge was saturated with methanol vapour at 25 – 30 ^{o}C. The found dynamic adsorption capacity of adsorbent-catalysts ΣX_{CH3OH} was 3.232 – 3.259 mg/cm^3. If the charge of adsorbent-catalyst saturated with methanol vapour is quickly heated by a flow of hot air (320 – 525 ^{o}C) methanol conversion into CO_2 and H_2O vapour occurs (Table 7). The findings indicate, that if the linear flow rate of hot air is 0.088 m/s and if heating rate of charge upper layer is 50 ^{o}C/(cm·min), then methanol vapour response degree is $\alpha = 47.4$ %. Formaldehyde is formed (0.055 mg/cm^3) only regenerating the charge with air flow of 320 ^{o}C and slowly heating the catalyst. Under our experimental conditions we did not find formaldehyde upon fast heating.

Table 7. Dependence of adsorptive-catalytic oxidation degree on the rate of temperature rise

Adsorption time, min	Initial concentration of methanol vapour mg/Nm^3	Adsorbed CH_3OH quantity ΣX_{ads}, mg/cm^3	Heating rate w_k of charge upper layer, ^0C/(cm·min)	Regeneration time, min	Regenerated CH_3OH quantity ΣX_{reg}, mg/cm^3	CH_3OH oxidation degree α, %
90	851.67	3.247	17.3	42	2.827	12.9
90	842.0	3.232	32.3	38	2.591	19.8
90	856.15	3.259	50.0	32	1.713	47.4

The quantities of methanol reacted to CO_2 and H_2O vapour or desorbed depend on heating rate of catalyst charge in post-reactive gas (Figure 13). As the heating rate of catalyst charge increases, the fraction of reacted CH_3OH increases, too.
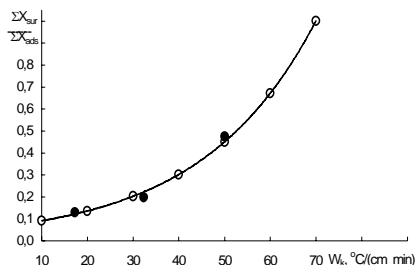

Figure 13. Dependence of reaction degree on heating rate of adsorbent-catalyst charge (• – experimental, ◦ – calculated)

The obtained results can be described by the following equation:

$$\frac{\sum X_{sur}}{\sum X_{ads}} = 0{,}0609\, e^{0{,}04 w_k},$$ which with 2 % error allows to choose w_k values in order to

reach methanol oxidation degree from 92 to 95 %. It was calculated from equation that such values of reaction degree would be reached if adsorbent-catalyst would be heated at 67 – 70 ^{o}C/(cm min) rate.

PARAMETERS OF TECHNOLOGICAL USE OF γAl$_2$O$_3$-C$_{act}$-(CuO, Cr$_2$O$_3$, Co$_3$O$_4$) ADSORBENTS-CATALYSTS

Thermostability and temperature of maximum use of adsorbent-catalyst. The results of performed analysis indicate that the stability of the produced catalyst structure at high temperatures is determined by these factors:

— Thermostability of catalyst support γAl$_2$O$_3$-C$_{aCt}$;
— Elimination of direct contact of reductant (activated carbon) and oxidizer (oxides of metals, especially, the most active CuO).

The latter factor was eliminated by choosing the optimum mean of adsorbent-catalyst synthesis.

The thermal stability of the support is determined by properties of its constituents. It is known that during thermal treatment of adsorbents the structural changes occur, as alumina gel $(Al(OH)_3)$ at 150 $^{\circ}$C becomes AlO(OH), and at 300 – 450 $^{\circ}$C it slowly transforms to Al_2O_3. Analysis of thermal stability (Figure 14) show that fast structural changes of aged adsorbents occur up to 200 $^{\circ}$C. Losses of weight at 100 – 250 $^{\circ}$C are attributed to the water desorption and to the above mentioned phase changes. As temperature increases in the range of 350 – 600 $^{\circ}$C a slow formation of γAl_2O_3 starts. Heating temperature higher than 450 $^{\circ}$C in the air atmosphere is acceptable only for alumina gel. Activated carbon used for synthesis is thermally stable up to 400 $^{\circ}$C, and at higher temperatures they oxidize. Weight of produced pure alumina gel samples decreases until temperature reaches 550 $^{\circ}$C, and further does not change. γAl_2O_3-C_{act} adsorbent is stable up to 450 $^{\circ}$C.
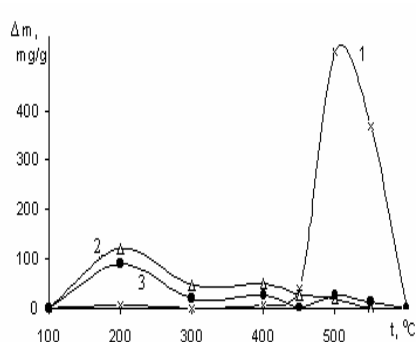

Figure 14. Dependence of differential weight changes on temperature of humid adsorbents in air: *1* – activated carbon (dry); *2* – alumina gel; *3* – alumina gel having 5 % of activated carbon
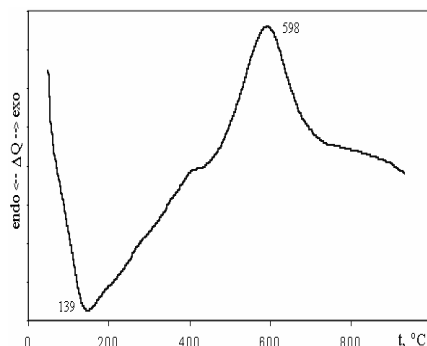
Figure 15. Differential thermal analysis (DTA) pattern of γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst

The results of differential thermal analysis also validate the findings (Figure 15). The best samples of catalyst can operate at temperatures up to 450 $^{\circ}$C. It has been determined that catalyst looses carbon effectively above 500 $^{\circ}$C. Then its specific surface area sharply decreases from 244.7 m^2/g to 16.45 m^2/g.

Use of adsorption analysis results for technological calculations. The results of adsorption analysis permit to maintain that adsorbent-catalyst can be used most effectively when the concentrations of organic admixture are very small This is so called Henry region, when the inner surface of charges is filled at constant rate. This corresponds to relative pressure $p/p_o < 0.1$.

Adsorbable isotherms are presented in the Figure 16. Henry region can be with sufficient accuracy described by linear equation

$$\Sigma X_{ad} = b\left(\frac{p}{p_0}\right),$$

where: b – adsorption coefficient; $b = \dfrac{k_{ad}}{k_{des}}$, where: k_{ad} – adsorption rate constant, k_{des} – desorption rate constant. Mathematical equations are generally deduced from Langmuir isotherm equation: $\Theta = \dfrac{X}{X_{max}} = \dfrac{bp}{1+bp}$ or $\dfrac{X}{X_{max}} = \dfrac{b(p/p_0)}{1+b(p/p_0)}$. It is possible to eliminate the denominator if $p/p_0 < 0.1$ and equation becomes similar to our used one.
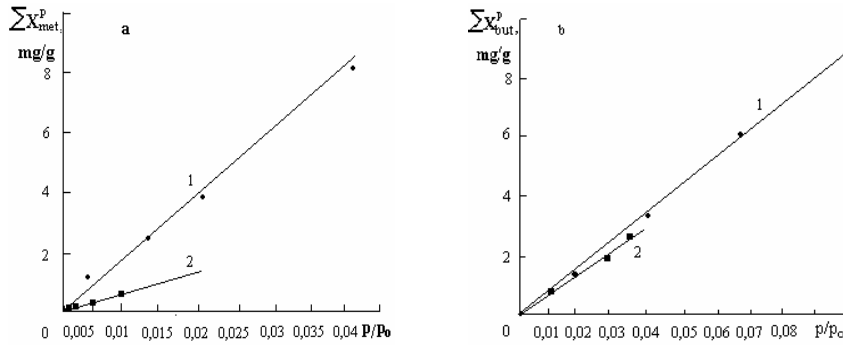

Figure 16. Adsorption isotherms of adsorbent-catalyst when adsorbable is: a) methanol; b) isobutanol (1 – t = 25 ºC; 2 – t = 55 ºC)

Adsorption coefficient b at various temperatures is calculated according to the equation $b = b_0 e^{-\Delta H_{ads}/RT}$, which is a line in semilogarithmic plot (Figure 17). Pre-exponential logarithm $\ln b_0$ is equal to the length of intercepted section in y axis, and adsorption heat ΔH_{ads} is calculated as $tg\alpha = -\Delta H_{ads}/R$ (table 8)

Table 8. Adsorption heats for various adsorbates

Adsorbate	Adsorption temperature T, K	1/T	b	lnb	Pre-exponent b_0	ΔH_{ads}, kJ/mol	R^2
Methanol	298	0.0033	200	5.3	0.00022	34.03	0.999
	328	0.0030	57	4.0			
Isobutanol	298	0.0033	100	4.6	2.03399	9.46	0.999
	328	0.0030	70	4.2			

The obtained results prove physical nature of adsorption and are used for the calculation of parameters of adsorbent-catalysts equilibrium at 25 – 55 °C and $p/p_0 = 0,1$. An equation for methanol vapour adsorption can be expressed in this

form: $\Sigma X_{max} = b_0 e^{-\Delta H_{ads}/RT\cdot 10^{-3}}(p/p_0) = 0,00022 \cdot e^{34,03/RT\cdot 10^{-3}}(p/p_0)$, where R is universal gas constant, J/molK; T is temperature, K; p/p_0 partial pressure. Similar equation for isobutanol vapour is: $\Sigma X_{max} = b_0 e^{-\Delta H_{ads}/RT\cdot 10^{-3}}(p/p_0) = 2,03399 \cdot e^{9,46/RT\cdot 10^{-3}}(p/p_0)$.
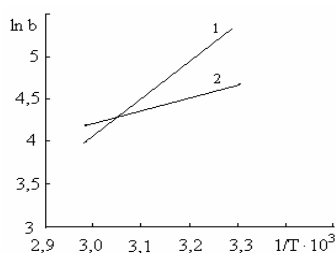

Figure 17. Adsorption coefficient b for adsorbates in semilogarithmic plot: 1 – for methanol, 2 – for isobutanol

Recommended technological scheme and characteristics of reactor. Taking into account the obtained results, a cylinder form radial adsorbers-reactors are the most suitable for the use (Figure 18). Reactors of this construction are known and used in thermo-catalytic processes of VOC removal at 360 – 450 ºC. Reactors are isolated and equipped with heaters or gas burners for the catalyst charge regeneration. Instantaneous load of adsorbent-catalyst would be of 1.11 m³/s according to gas flow and 1.11 g/s according to pollutant if assuming that the flow rate is 4000 m³/h and concentration of organic pollutants is 1000 mg/Nm³ as it is often met in industry. At 25 ºC γAl_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst would adsorb from 2.0 to 8.07 mg/g of methanol vapour depending on the linear rate of contaminants flow. Furthermore, in this Henry adsorption region ($p/p_0 < 0.004$), the charge would be saturated at constant rate (495 kg (~ 1.24 m³) every hour).

Generally adsorbers are used when linear rate is v = 0.2 m/s. Assuming that the flow rate of cleaning gas is 1.11 m³/s, an area of contact is $F_k = \dfrac{w}{v} \cong 5,6$ m².

This corresponds to radial layer of adsorbent catalyst in height $H_{sl} = 1.5$ m, inner and outer diameters being 1.2 and 2.4 m, respectively. The geometrical volume of layer cavity would be 5.1 m³. It would be possible to place about 2.5 – 2.6 m³ of adsorbent-catalyst in the geometrical volume, taking filling coefficient k = 0.5, and arranging in layer radial thickness of 0.6 m. Such layer would operate about 1.5 – 2 h at 20 – 25 ºC, if the concentration of organic pollutants is 800 – 1000 mg/Nm³.

According to results of performed analysis, adsorbent-catalyst saturated with adsorbable vapour has to be regenerated within ~ 30 min and as total oxidation reactions of adsorbate occur. Regeneration gas has to be provided for this

purpose at 0.65 – 0.8 m/s linear rate (0.28 m^3/s flow rate) and heated up to 350 – 400 °C. It is common that treated gas waste or ambient air is used as regeneration gas.
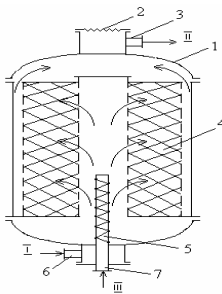

Figure 18. Scheme of radial adsorbent-reactor:
1 – frame with heat isolation, 2 – explosive membrane,
3 – cleaned gas flow, 4 – adsorbent-catalyst layer,
5 – heater, 6 – polluted gas flow, 7 – regeneration gas flow.

Gas can be heated by electric heaters, burners or in thermal tube. 140 kJ/s of heat should be used in order to heat the regeneration gas from the ambient up to 400 °C.

This quantity of heat corresponds to the heat, which is obtained during combustion of 4 l/s (14.4 m^3/h) of natural gas (when Q_d = 35.7 MJ/m^3). Considering the periodic regeneration of charge such quantity needed for heating can be qualified as small. Ratio τ_{ads}/τ_{reg} = 4. As it > 1, VOC removal is done by adsorbents – catalysts in several adsorbers-reactors connected in parallel (not less then two), when one of them adsorb pollutants periodically, and the second is regenerated when full oxidation reactions of adsorbates occur (Figure 19)
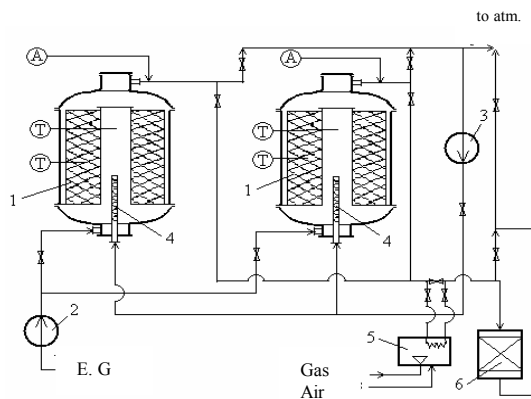

Figure 19. Recommended technological scheme of VOC removal 1- radial adsorber- reactor,
2, 3 – ventilators of polluted and regeneration gas,
4 – heaters of regeneration gas,
5 – additional thermal tube,
6 – additional catalyst

Cycle of adsorption is completed according to signal of analyzers A (having reached maximum allowable concentration value). Then adsorber-reactor is disconnected by automatic valves and its control system from the flow of polluted gas, regeneration gas is supplied and the heaters are switched on. Additional equipment is used in many schemes: thermal tube (5) and reactor of additional catalyst (6) are needed for protection during technological troubles.

About $0.1 - 0.2$ m^3 of our used adsorbent-catalyst or one of previously analyzed CuO catalyst can be placed in apparatus (6). Using apparatus (6) it is heated up to ~ 250 ºC before apparatuses (1). The results of carried out analyses of methanol oxidation allow to maintain that high $85 - 90$ % degree of adsorbate mineralization into carbon dioxide and water vapour can be reached in apparatuses (1). Oxidation degree will approach towards 100 % if jointly using apparatus (6) in the process.

Support (γAl_2O_3-C_{act}) of adsorbent-catalyst γAl_2O_3-C_{act}-(CuO, Cr$_2$O$_3$, Co$_3$O$_4$) can be used as more thermostable adsorbent replacing the activated carbon. Ordinary adsorption technology and radial adsorbers are used in this case.

CONCLUSIONS

1.   Thermostable γAl_2O_3-C_{act}-(CuO, Cr$_2$O$_3$, Co$_3$O$_4$) adsorbents-catalysts were obtained using sol-gel technology. Optimal parameters of their production are as follows: solution pH ~ 8, contact time of gels 1 min, aging duration 12 days, heating
temperature 420 °C. The best samples have 5 % of activated carbon, 6.8 % CuO, 3.1 % Cr$_2$O$_3$ and 2.0 % Co$_3$O$_4$.

2.   Adsorbent-catalyst can be used at temperatures up to 450 °C. At higher temperatures activated carbon is lost.

3.   The specific surface area of γAl_2O_3-C_{akt}-(CuO, Cr$_2$O$_3$, Co$_3$O$_4$) adsorbent-catalyst is determined by the amount of WS-42A activated carbon. It was found that $S_{BET} = 244.7$ m^2/g. The system is mesoporous, as $18 - 20$ Å and $24 - 27$ Å radius pores prevail and their total volume is $\Sigma V_p = 0.652$ cm^3/g.

4.   Adsorbent-catalyst and its support γAl_2O_3-C_{akt} are hydrophobic. Water vapour is adsorbed very slowly, and equilibrium adsorption capacity is reached after 72 h.

5.   Adsorption capacity of adsorbents-catalysts for methanol, isobutanol and acetone vapour is characteristic for the physical adsorption. At relative pressure $p/p_o \leq 0.1$ and $25 - 65$ °C, the adsorption heats for methanol and isobutanol vapour are 34.03 and 9.46 kJ/mol, respectively.

6.   Oxidation degree of adsorbate depends on heating rate of γAl_2O_3-C_{akt}-(CuO, Cr$_2$O$_3$, Co$_3$O$_4$) adsorbent-catalyst charge. At $400 - 420$ °C when heating rate $w_k = 67 - 70$ ^{0}C/(cm min), the methanol oxidation degree α reaches $92 - 95$ %.

7.   Radial adsorber-reactor is suggested for VOC removal. At 4000 m^3/h flow of polluted gas with methanol vapour, it uses $2.5 - 2.6$ m^3 of adsorbent-catalyst.

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γAl_2O_3-C_{akt}-Me_xO_y ADSORBENTAI-KATALIZATORIAI: SINTEZĖ, SAVYBĖS IR PANAUDOJIMAS

Reziumė

Pereinamųjų metalų oksidų katalizatoriai gamtosaugos technologijose plačiai naudojami lakių organinių junginių (LOJ) šalinimui iš užterštų išmetamų dujų. Žinomi bandymai naudoti aktyvintas anglis ar jų kompozicijas su Al, Ti, Si ir kt. oksidais katalizatorių gamybai. Šios medžiagos tiesiogiai impregnuotos katalizatorių aktyviaisiais komponentais – Cr_2O_3, CuO, Co_3O_4, V_2O_5, MoO_3, WO_3 ir kt. Tačiau dėl metalų oksidų ir aktyvintų anglių tiesioginio kontakto katalizatorių granulėse jie yra nepakankamai termiškai atsparūs: esant 300 – 360 ^oC aktyvintos anglys oksiduojasi, katalizatorių savitasis paviršiaus plotas ir aktyvumas staiga sumažėja. Todėl yra aktualūs tolesni tyrimai, siekiant sukurti patvaresnių didelio savitojo paviršiaus LOJ šalinimo adsorbentų-katalizatorių gamybos technologiją ir ištirti panaudojimo ypatumus.

Šio darbo tikslas buvo sukurti termiškai atsparių adsorbentų-katalizatorių, naudojant aktyvintas anglis ir γAl_2O_3, CuO, Cr_2O_3, Co_3O_4 oksidus, gamybos technologiją, nustatyti jų savybes ir panaudojimo ypatumus.

Tyrimams pasirinkome didelio terminio atsparumo aktyvintas anglis WS-42A (Chemviron Carbon). Katalizatoriaus aktyviaisiais komponentais naudojome žinomus CuO, Cr_2O_3, Co_3O_4 oksidus. Zolių-gelių technologijos būdu padidintas sistemos aktyvintos anglys-Al_2O_3-Me_xO_y terminis atsparumas koncentruojant katalizatoriaus aktyviuosius komponentus stambiaporio aliuminio oksido apvalkale. Nustatyta savitojo paviršiaus ir sintezės sąlygų sąryšis, alkoholių, acetono ir vandens garų adsorbcijos pusiausvirieji ir kinetiniai parametrai, katalizinis aktyvumas LOJ šalinimo technologijose. Sukurta termoatsparaus ir valdomos porėtos struktūros adsorbento - katalizatoriaus γAl_2O_3-C_{akt}-(CuO, Cr_2O_3, Co_3O_4) gamybos technologija ir nustatyti jo panaudojimo LOJ šalinimo technologijose parametrai.

Remiantis tyrimų duomenimis padarytos šios išvados:

1. Termoatsparūs iki 450 ˚C γAl_2O_3-C_{akt}-(CuO, Cr_2O_3, Co_3O_4) adsorbentai-katalizatoriai buvo gauti naudojant zolių-gelių technologiją. Optimalūs gamybos parametrai yra: terpės pH ~ 8, žaliavų reakcijos trukmė 1 min., sendinimo trukmė 12 parų ir iškaitinimo temperatūra 420 ˚C. Geriausiuose bandiniuose yra 5 % C_{akt}, 6,8 % CuO, 3,1 % Cr_2O_3, 2,0 % Co_3O_4.

2. Adsorbentas-katalizatorius gali būti naudojamas iki 450 ˚C temperatūros. Esant didesnei temperatūrai prarandamos aktyvintos anglys.

3. Adsorbento-katalizatoriaus γAl_2O_3-C_{akt}-(CuO, Cr_2O_3, Co_3O_4) savitojo paviršiaus plotą lemia WS-42A aktyvintų anglių kiekis. S_{BET} rastas 244,7 m^2/g. Sistema mezoporė, vyraujant 18 – 20 Å ir 24 – 27 Å spindulio poroms ir esant jų suminiam tūriui $\Sigma V_p = 0,652$ cm^3/g.

4. Adsorbentas-katalizatorius ir jo pagrindas γAl_2O_3-C_{akt} yra hidrofobiniai. Vandens garai adsorbuojami labai lėtai, pusiausviroji adsorbcijos geba pasiekiama po 72 h.

5. Adsorbentų-katalizatorių geba adsorbuoti metanolio, izobutanolio ir acetono garus būdinga fizikinei adsorbcijai. Esant santykiniam slėgiui $p/p_o \leq 0,1$ ir 25 – 65 ˚C temperatūrai metanolio garų adsorbcijos šiluma $\Delta H_{ads} = 34,03$ kJ/mol, izobutanolio garų $\Delta H_{ads} = 9,46$ kJ/mol.

6. Adsorbento-katalizatoriaus γAl_2O_3-C_{akt}-(CuO, Cr_2O_3, Co_3O_4) aktyvumas metanolio garų adsorbcinio-katalizinio oksidavimo procese priklauso nuo įkrovos kaitinimo greičio w_k. Pasiekus 400 – 420 ˚C temperatūrą ir esant $w_k = 67 – 70$ ˚C/(cm min) metanolio oksidavimo laipsnis α bus 92 – 95 %.

7. Lakių organinių junginių šalinimui pasiūlytas radialinis adsorberis-reaktorius. Esant 4000 m^3/h užterštų metanolio garais dujų srautui pakanka 2,5 – 2,6 m^3 adsorbento-katalizatoriaus.

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