Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) Adsorbents-Catalysts: Preparation and Characterization

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Al_2O_3-C_{act}-(CuO, Cr_2O_3 Co_3O_4) adsorbents-catalysts were prepared using Al_2O_3-C_{act} (alumina gel–activated carbon) adsorbent and different amount of CuO, Cr_2O_3 and Co_3O_4. The active components were incorporated into wet alumina gel–carbon mixture using different conditions (by sol-gel method and mixing a milled metal oxides). Equilibrium adsorptive capacity measurements of alcohol vapours were carried out in order to determine the influence of preparation conditions on the stability of prepared adsorbents–catalysts. Specific surface area of the prepared adsorbents-catalysts were measured by BET method. It was established that for adsorbent-catalyst produced by sol-gel method S_{BET} = 244.7 m^2/g. Surface area S_{BET} = 29.32 m^2/g was obtained for adsorbent-catalyst with metal oxides. On the basis of these results it was assumed that active carbon was lost in this adsorbent-catalyst during the preparation process. Sol-gel derived adsorbent–catalyst was tested for the oxidation of methanol vapours. Catalytic oxidation was carried out in fixed-bed reactor. Experimental data indicate that adsorptive capacity of the adsorbent–catalyst is (3.232 – 3.259) mg/m^3 CH_3OH at relative air humidity is 40 % – 50 %. During a fast heating of CH_3OH – saturated adsorbent-catalyst a part of adsorbate is converted to CO_2 and H_2O. Methanol conversion increases with increasing of adsorbent-catalyst heating rate.

Keywords: activated carbon, adsorbent-catalyst, metal oxides, oxidation, methanol.

1. INTRODUCTION

The spectrum of activated carbon applications for catalysis and adsorption is very wide. This is determined by carbon's ability to activate reactive substances. On the surface of carbon, radical centers ("trivalent carbon") are located, which catalyze various oxidation and reduction processes. Typical examples of carbon-catalyzed processes are chlorination (CO, SO_2, C_2H_2), dehydrochlorination ($C_2H_2Cl_4$), oxidation (H_2S, SO_2, NO), dehydration (C_2H_5OH, HCOOH), dissociation (H_2O_2) [1 – 10]. However, as mentioned before, the possibility of much greater use of activated carbon opens up when metals or various metal compounds are dispersed on the surface of carbon. In addition to the platinum-group metals, oxides of variable valence metals (Ni, Cu, Co, Mn, Cr) are the most active components of catalysts used for oxidation of organic compounds [11 – 20]. Interaction between oxygen molecules and oxide surface leads to formation of various oxygen radicals which react with organic molecules.

The usage of activated carbons as catalysts support is determined not only by the properties mentioned before but also by the high specific surface area and high adsorption capacity for adsorptive vapour, low selectivity and suitability for work in wet environments, relatively low cost, etc. However, in addition to those mentioned positive properties of activated carbon, they also have some limitations. In the presence of oxygen or other oxidizers their thermal resistance is reduced. Also, activated carbons are microporous what limits the transportation of adsorbates towards the active components.

Because of its abundance and low cost as well as excellent physical and chemical properties aluminum oxide is also very often used as a catalyst support [16, 21 – 25]. It is heat-resistant adsorbent with large transport pores. It is likely that alumina and activated carbon derivatives can be the basis for catalysts, where micro inserts of activated carbon perform the role of adsorbent and wide pore alumina part acts like a tray for catalysts active components. In order to produce heat resistant catalyst, we wanted to find the way to prevent a direct contact of activated carbons and alumina. Our previously produced alumina gel and activated carbons derivatives were more thermoresistant than pure activated carbons. In addition, 5 (weight) % additive of activated carbon highly increased the specific surface of alumina gel and slowed down the adsorption of water vapour on the surface of adsorbent [26]. Alumina and activated carbons derivatives can be used as adsorbents or as the base for catalyst. For the synthesis of adsorbents-catalysts as active components Cu, Cr and Co oxides were chosen: CuO as the most active oxide for VOC oxidation, Cr_2O_3 as additive which increases thermal resistance and activity of copper (mostly, if $CuCr_2O_4$ is formed during synthesis), Co_3O_4 as additive, which increases catalysts resistance to poisons.

2. EXPERIMENTAL

Preparation of adsorbent-catalyst. Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbents-catalysts were prepared as composites by adding various amounts of active components (Cu, Cr, Co gels (hydroxides) or oxides) into humid mixture of alumina gel and WS-42A type (Chemviron Carbon, Germany) activated carbon (5 % wt.) [26]. We tried to immobilize active components of adsorbent-catalyst by these methods:

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1) Adding Cu(II), Cr(IV) and Co(II/III) gel-type hydroxides into Al_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 °C and calcinated at 420 °C. The diameter of granules varied in the range of 1.5 mm – 2.0 mm, and the length from 5.0 mm 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 6.0 % (wt.) CuO, 2.0 % Cr_2O_3 and 2.0 % Co_3O_4 powder into Al_2O_3-C_{act} gel type composite. The obtained composites were further aged and thermally treated analogically to the 1st item.

Characterization of adsorbent-catalyst. The amounts of active components in the adsorbents-catalysts were estimated by atomic absorption spectrometry (AAS) using AASIN instrument (Carl 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}. 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. Experimental apparatus for research of equilibrium processes was used to measure the adsorption capacity [27]. Reactions on the surface of the adsorbent-catalyst was found to be theoretically possible for these reactions Gibbs energy change ($\Delta_r G_T^0$) 373 K – 1073 K temperature range [28].

Catalytic oxidation of methanol. Catalytic oxidation of methanol vapour was carried out in a fixed bed quartz reactor [27]. The initial concentration of alcohol vapour was analyzed using a gas chromatograph with a flame ionization detector (GC-FID Perkin Elmer Clarus 500). The exit gases from the reactor were analyzed using a gas chromatograph with a mass spectrometer system (GC-MS Perkin Elmer Clarus 500). CO and CO_2 quantities were tested online with a TESTO 445 gas meter.

3. RESULTS AND DISCUSSIONS

Properties of Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbents-catalysts. The results of X-ray diffraction (XRD) analysis showed that after thermal treatment both adsorbent-catalyst samples contained the oxides of active components (Fig. 1, (1) and (5) patterns.).

Peaks in X-ray diffractograms corresponded to characteristic peaks of CuO, Cr_2O_3 and Co_3O_4. Meanwhile, characteristic peaks of activated carbon (graphite) [11 – 13] can be obtained only in diffractogram of adsorbent-catalyst derived by mixing metal hydroxides (gels). The Al_2O_3-C_{act} (Figure 1, (3) pattern) has amorphous structure with crystalline particles [29 – 31]. The peaks are weakly expressed and characteristic to activated carbon, γAl_2O_3

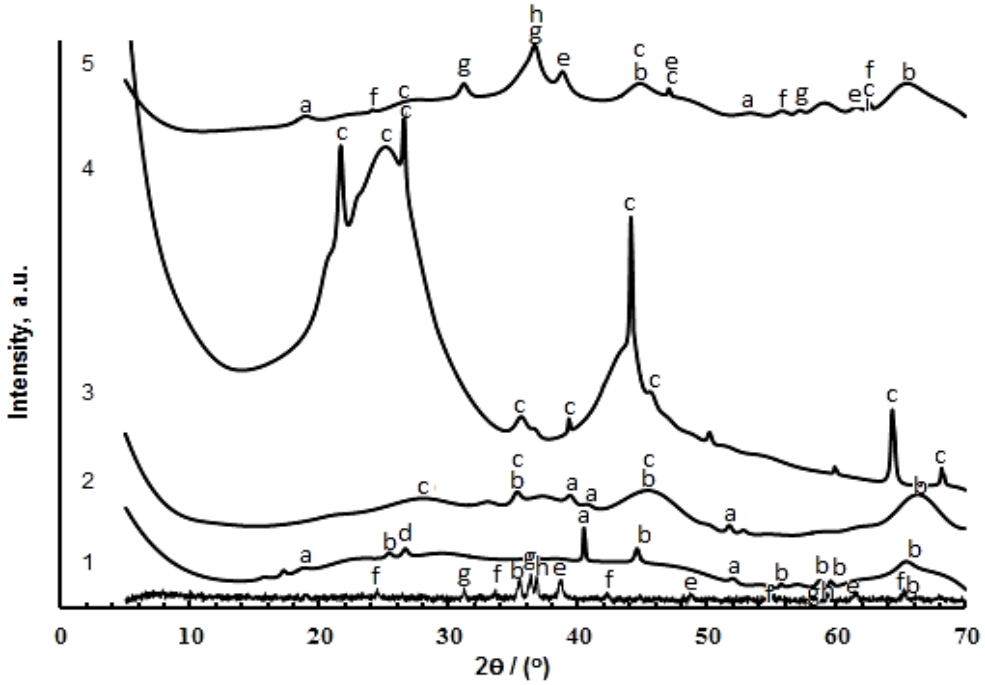

Fig. 1. XRD patterns of: 1 – Al_2O_3-C_{act}-(CuO,Cr_2O_3,Co_3O_4) derived from oxides; 2 – alumina gel, 3 – Al_2O_3-C_{act}, 4 – activated carbon; 5 – Al_2O_3-C_{act}-(CuO,Cr_2O_3,Co_3O_4) derived from gels. Indexes: a – AlO(OH), b – γ Al_2O_3, c – carbon, d – Al_2SO_4, e – CuO, f – Cr_2O_3, g – Co_3O_4, h – $CuCr_2O_4$, i – CuCoO

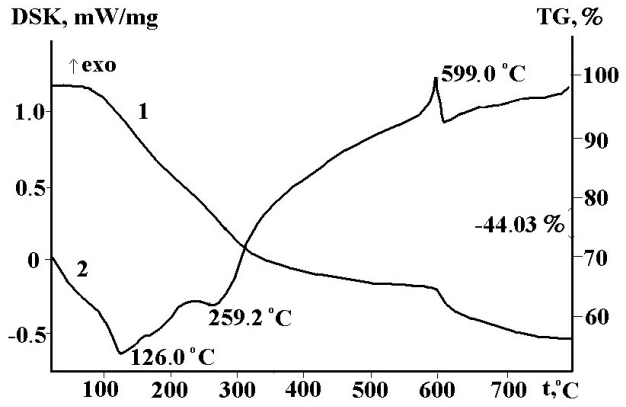

Fig. 2. Curves of thermal analysis of humid Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst produced using the gels of metal hydroxides:
1 – Thermogravimetry (TG);
2 – Differential Scanning Calorimetry (DSC)

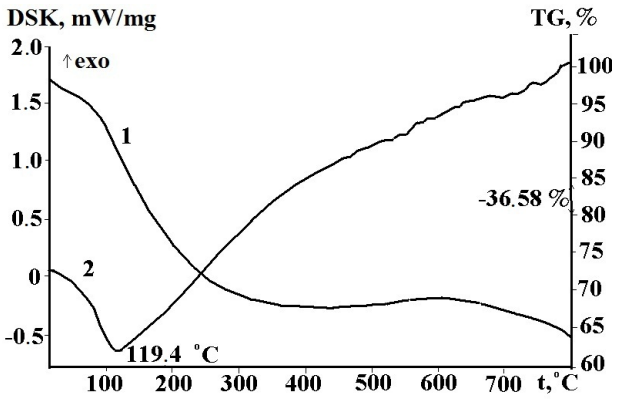

Fig. 3. Curves of thermal analysis of humid Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst produced using the powders of metal oxides:
1 – Thermogravimetry (TG);
2 – Differential Scanning Calorimetry (DSC)

and boehmite (AlO(OH)).

Thermal analysis of humid samples showed that catalysts lose water at ~ 120 °C (Fig. 2). The endothermic effect at 250 °C – 260 °C is attributed to thermal dissociation of metal hydroxides [32]. The exothermic effect above 580 °C showed the destruction of catalyst structure. The endothermic effect due to evaporation of water was found at ~120 °C for catalysts produced by adding the powder of metal oxides (Fig. 3). TG curve falls consecutively, and that of DSC rises if temperature is increased. This lets to assume that metal oxides can be slowly reduced by activated carbon.

In order to confirm this assumption, we performed preliminary tests for both obtained adsorbent-catalysts according to their equilibrium adsorption capacity (Table1). The results of these measurements show that adsorption capacities increase only for adsorbent-catalyst which is produced by adding gel type metals hydroxides. If metal oxides are added in the form of powder, the adsorption capacity of thermally treated adsorbent-catalyst is significantly lower.

This shows that during thermal treatment of humid catalysts, when using powdery oxides, activated carbon becomes oxidized (due to their direct contact). In this case one obtains Al_2O_3-C_{act}-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 powders. The calculated S_{BET} value was 29.32 m^2/g, which is close to that for macroporous Al_2O_3 (S_{BET} = 30.7 m^2/g) [33]. Adsorbent-catalyst prepared from gels S_{BET} = 244.7 m^2/g is nearly equal to Al_2O_3-C_{act} by specific surface area (S_{BET} = 280.43 m^2/g).

The experimental results were validated by findings of thermodynamic calculations (Table 2). By comparing the standard Gibbs potentials ($\Delta_r G_T^0$) it can be noticed that all reactions, except (3), can be proceeded at low temperatures, and carbon inserts remain intact at high temperatures only if no contact with metal oxides is present.

Table 1. Adsorption equilibrium capacity for methanol and isobutanol vapors at 25 °C and (748 – 756) mm Hg

Composites	The amount of adsorbed methanol $\sum X^p_{met}$, mg/g	The amount of adsorbed isobutanol $\sum X^p_{but}$, mg/g
Al_2O_3-C_{akt}	61.4	34.3
Al_2O_3-C_{akt}-(CuO, Cr_2O_3, Co_3O_4) prepared from gels	111.1	59.5
Al_2O_3-C_{akt}-(CuO, Cr_2O_3, Co_3O_4) prepared from oxides	8.6	5.2

Table 2. Standard Gibbs potentials of reactions

Reactions		ΔG_T^0, kJ/mol at various temperatures t, °C						
		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
$C + ½\ O_2 \rightarrow CO$	(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

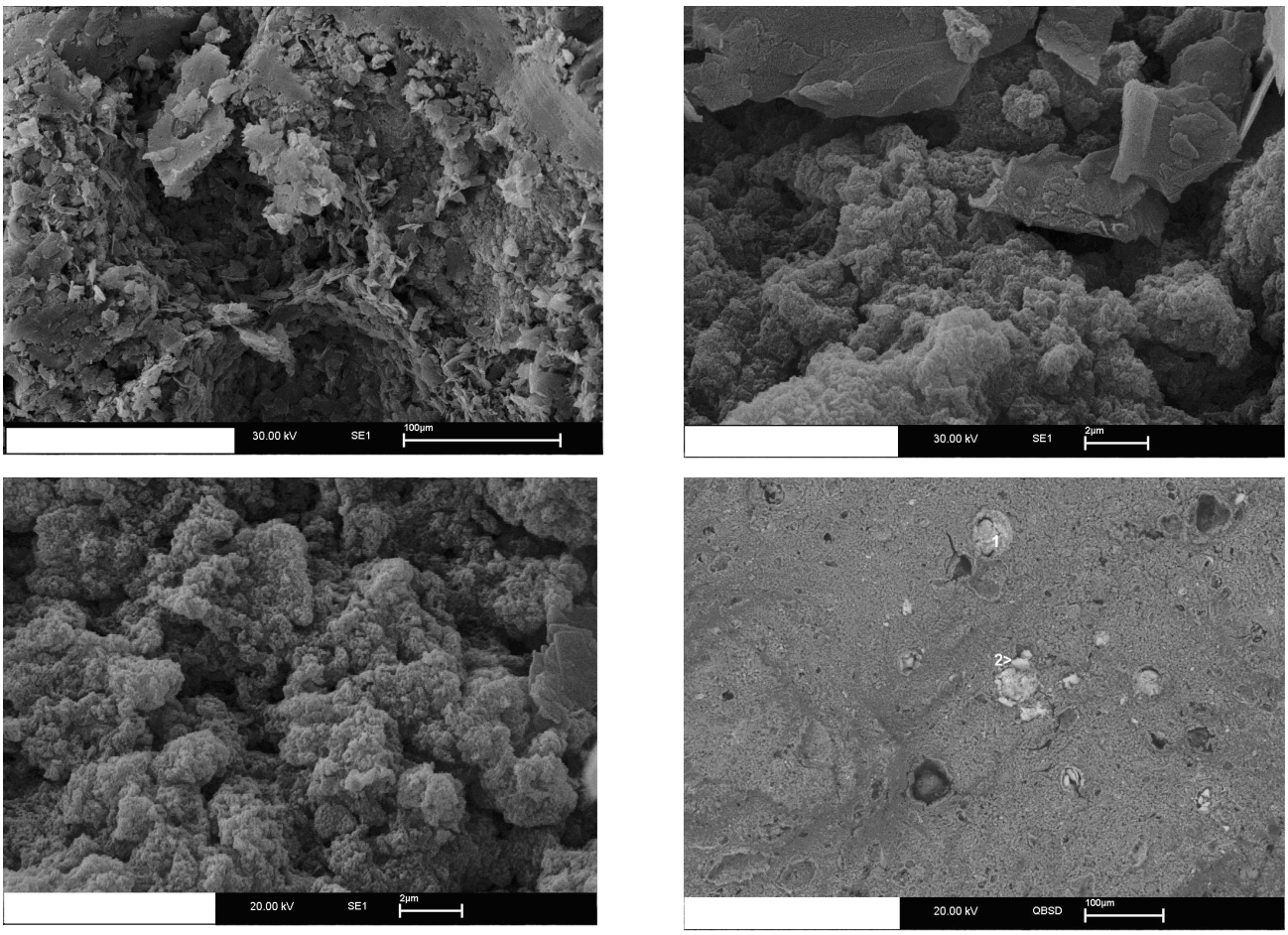

Fig. 4. SEM images of Al_2O_3-C_{akt}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst prepared by using gel-type hydroxides at different scales

On the basis of these results, for further investigations adsorbent-catalyst prepared by using gel-type hydroxides was used. Such adsorbent-catalyst is characterized by sufficient thermal stability and had a high specific surface area, which is influenced by activated carbon additive. These properties are determined by the fact, that using our synthesis method when adding gel type metal hydroxides into Al_2O_3-C_{act} gel type composite, metal oxides are localized in the porous alumina gel and do not make a direct contact with activated carbon (Fig. 4).

Specific surface area and pore structure. Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst was chosen for the detailed examination of specific surface.

Calculations of specific surface area (S_{BET}) were performed by using primary part of N_2 adsorption-desorption hysteresis when $p/p_0 < 0.30$ (Fig. 5) [34].

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_0, linear BET plots are obtained (Fig. 6), and their reliability coefficient R^2 is 0.9993.

As noticed, specific surface area for adsorbent-catalyst is $S_{BET} = 244.7$ m^2/g (for Al_2O_3 $S_{BET} = 30.7$ m^2/g, for Al_2O_3-C_{act} $S_{BET} = 280.4$ m^2/g [33]). C_{BET} constant value is calculated to be 168.7 and that allows to evaluate validity of BET measurements (Table 3). 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.

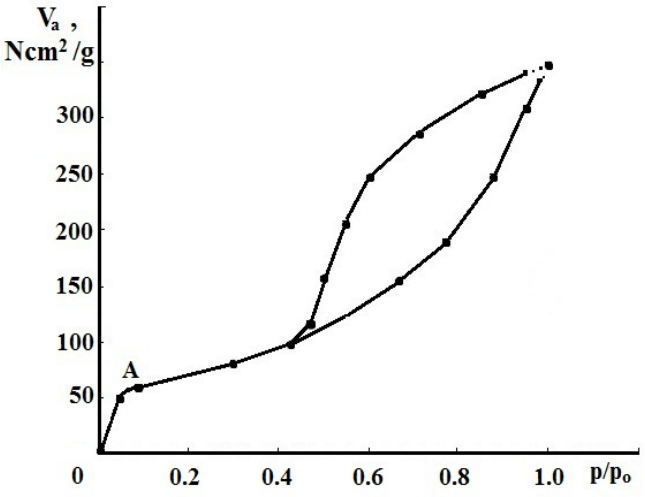

Fig. 5. N_2 adsorption-desorption isotherms at 77 K for adsorbent-catalyst

Table 3. Calculated parameters of specific surface area (S_{BET})

BET equation constants		Capacity of monolayer $X_m = \frac{1}{S+I}$, g	Specific surface area S_{BET}, m^2/g	Constant $C_{BET} = \frac{1}{I \cdot X_m}$
Slope, $tg\alpha = S$	Intercept, I			
3053.3	17.97	0.00033	244.7	168.7

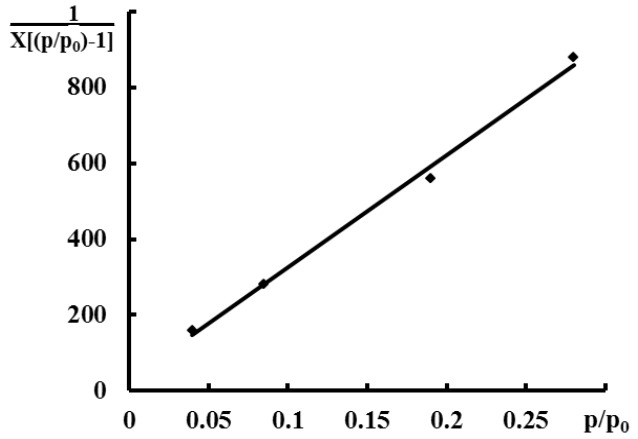

Fig. 6. N_2 adsorption isotherm at 77 K in BET plot

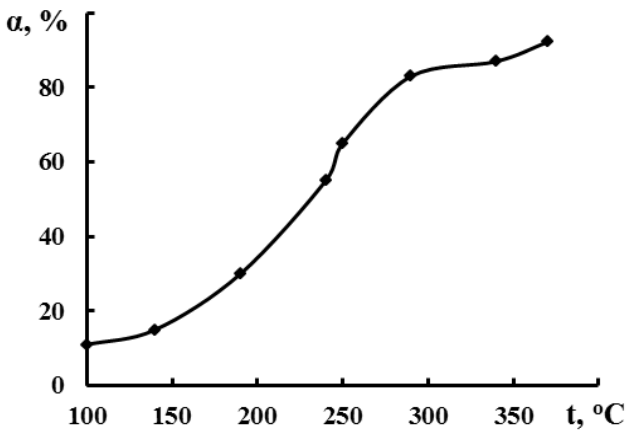

Fig. 7. Dependence of methanol oxidation degree on temperature

It is possible to forecast the pore form of adsorbents according to de Boer classification [35] of hysteresis isotherms (Fig. 5). Spherical forms of pores prevail in the catalyst: when $p/p_0 = 0.6 - 0.95$ the broad part of hysteresis isotherm can be seen, and when p/p_0 decreases down to 0.4, the phenomenon of hysteresis ends. 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 [36]. It has been determined that $S_{BET} = 244.7$ m^2/g, and $\Sigma A = 502.98$ m^2/g. The results show that regarding the form of pores the polydispersial structure is typical for catalyst when the slit-like pores 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. The pores of 1.8 nm – 2.0 nm and 2.4 nm – 2.7 nm radius prevails catalyst, mean radius of pores $\bar{r}_p = 2.6$ nm (for Al_2O_3 $\bar{r}_p = 3.2$ nm, for Al_2O_3-C_{act} $\bar{r}_p = 2.0$ nm), total volume of pores $\Sigma V_p = 0.652$ cm^3/g (for Al_2O_3 $\Sigma V_p = 0.118$ cm^3/g, for Al_2O_3-C_{act} $\Sigma V_p = 0.332$ cm^3/g).

Activity of Al_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 °C) temperatures, which are tested towards cyclic hydrocarbon (mostly benzene) oxidation.

We tested Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) catalyst activity in methanol vapour oxidation using two technologies:

1) at constant temperature of catalyst bed;

2) in the cyclic adsorptive-catalytic process.

We maintained the methanol concentration at inlet gas to be 800 mg/Nm^3. Inlet mixture humidity was equal to relative air humidity and varied in the range of 40 % – 50 % (8 – 12 g/Nm^3). As inlet mixture CH_3OH is constantly supplied, methanol vapour reaction with air oxygen starts when average temperature in adsorbent-catalyst load reaches 100 °C. As temperature rises, methanol oxidation degree increases up to 92.2 % at 370 °C (Fig. 7).

When temperature of flow of methanol vapour – humid air mixture reaches 150 °C – 300 °C, methanol is oxidized not only to CO_2 and H_2O, but also into intermediate oxidation product formaldehyde (Fig. 8).

The largest quantity of formaldehyde (~100 mg/Nm^3) is formed when average temperature of adsorbent-catalyst bed is 235 °C. As temperature increases above 235 °C, formaldehyde concentration decreases. At 350 °C formaldehyde is not found. This indicates that the process proceeds according to the well known parallel-consecutive mechanism of oxidation [37].

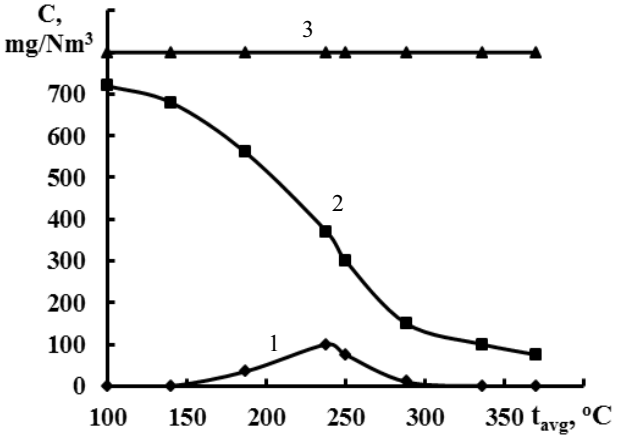

Fig. 8. Dependence of methanol and formaldehyde concentrations in exit gases at an average temperature of adsorbent-catalyst bed (linear flow rate is 0.088 m/s): 1 – CH_2O; 2 – CH_3OH, 3 – CH_3OH concentration in inlet gas

The activity of Al_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 bed was saturated with methanol vapour at 25 °C – 30 °C. Dynamic adsorption capacity of adsorbent-catalysts ΣX_{CH3OH} was found to be (3.232 – 3.259) mg/cm^3.

When the load of adsorbent-catalyst, saturated with methanol vapour, is quickly heated by a flow of hot air (320 °C – 525 °C), methanol conversion into CO_2 and H_2O occurs (Table 4). This indicates that if the linear flow rate of hot air is 0.088 m/s and if the heating rate of beds upper layer is 50 °C /(cm·min), methanol vapour oxidation degree is $\alpha = 47.4$ %. Formaldehyde is formed (0.055 mg/cm^3) only when regenerating the bed with air flow of 320 °C and slowly heating the catalyst. Under our experimental conditions we did not find formaldehyde upon fast heating.

Table 4. Dependence of adsorptive-catalytic oxidation degree on the rate of temperature rise

Adsorption time, min	Initial concentration of methanol vapour, mg/Nm^3	Amount of adsorbed CH_3OH ΣX_{ads}, mg/cm^3	Heating rate w_k of upper layer of catalyst bed °C/(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	842.00	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 converted to CO_2 and H_2O vapour or desorbed depend on heating rate of catalyst bed in post-reactive gas (Fig. 9). As the heating rate of catalyst load increases, the fraction of reacted CH_3OH increases too.

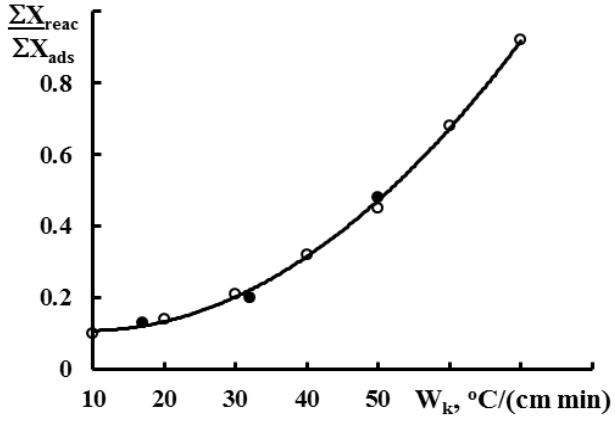

Fig. 9. Dependence of conversion degree and heating rate of adsorbent-catalyst bed (• – experimental, ◦ – calculated)

The obtained results can be described by the equation: $\frac{\sum X_{reac}}{\sum X_{ads}} = 0.0609 \cdot e^{0,04 W_k}$, $(\sum X_{reac} = \sum X_{ads} - \sum X_{reg})$, which with 2 % of error allows choosing w_k values in order to reach methanol oxidation degree from 92 % to 95 %. It was calculated from equation that such values of oxidation degree would be reached if adsorbent-catalyst would be heated at 67 – 70 °C/(cm min) rate.

The maximum working temperature of adsorbent-catalyst is about 500 °C. Reaching this temperature catalyst loses carbon inserts: specific surface area S_{BET} decreases from 244.7 m^2/g to 16.45 m^2/g.

4. CONCLUSIONS

Thermostable up to about 500 °C Al_2O_3-C_{act}-(CuO, Cr_2O_3, Co_3O_4) adsorbents-catalysts were obtained using sol-gel technology. At higher temperatures activated carbon is lost. The best samples have 5 % of activated carbon, 6.8 % CuO, 3.1 % Cr_2O_3 and 2.0 % Co_3O_4.

The specific surface area of Al_2O_3-C_{akt}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst depends on the amount of WS-42A activated carbon. It was found that S_{BET} = 244.7 m^2/g. The system is mesoporous, as 1.8 nm – 2.0 nm and 2.4 nm – 2.7 nm radius pores prevail and their total volume is ΣV_p = 0.652 cm^3/g.

Oxidation degree of methanol depends on heating rate of Al_2O_3-C_{akt}-(CuO, Cr_2O_3, Co_3O_4) adsorbent-catalyst bed. At 400 °C – 420 °C when heating rate w_k = (67 – 70) °C/(cm min), the methanol oxidation degree reaches 92 % – 95 %.

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