

Deactivation of Cu - Cr/ γ -alumina Catalysts for Combustion of Exhaust Gases

Krasimir Ivanov, Dimitar Dimitrov, Boyan Boyanov

Abstract—The paper relates to a catalyst, comprising copper-chromium spinel, coated on carrier γ -Al₂O₃. The effect of preparation conditions on the active component composition and activity behavior of the catalysts is discussed. It was found that the activity of carbon monoxide, DME, formaldehyde and methanol oxidation reaches a maximum at an active component content of 20 – 30 wt. %. Temperature calcination at 500°C seems to be optimal for the γ -alumina supported CuO-Cr₂O₃ catalysts for CO, DME, formaldehyde and methanol oxidation. A three months industrial experiment was carried out to elucidate the changes in the catalyst composition during industrial exploitation of the catalyst and the main reasons for catalyst deactivation.

It was concluded that the CuO-Cr₂O₃/ γ -alumina supported catalysts have enhanced activity toward CO, DME, formaldehyde and methanol oxidation and that these catalysts are suitable for industrial application. The main reason for catalyst deactivation seems to be the deposition of iron and molybdenum, coming from the main reactor, on the active component surface.

Keywords—catalyst deactivation, CuO-Cr₂O₃ catalysts, deep oxidation.

I. INTRODUCTION

THE modern catalysts, used for removing harmful components from exhaust gases are: (i) catalysts with complex composition, coated on different carriers, which often comprise of one to several layers active metal-metal oxide phases. Most frequently the active metals have been Pt, Rh, Pd, as well as Au during the last years, and the active oxides are 3d-transition metals such as Cu, Cr, Ni, Mn, Co, etc.; (ii) mixed oxide catalysts, comprising one or more metal oxides, more often CuO, Cu-Co, Cu-Mn and Cu-Cr [1, 2]. Due to the cost and limited availability of noble metals, considerable attention has been paid to transition metals and their oxides. One of the most effective catalyst systems for CO oxidation is based on a combination of copper and chromium oxides [3, 4]. In spite of the many scientific and patent publications the characteristics of CO and hydrocarbon oxidation on Cu-Cr oxide catalyst with spinel structures are not well understood and there is no clear definition of the role of each metal [5]. According to Laine and co-workers [6] the electron transfer between copper and chromium leads to the inhibition of the reduction of the Cu-Cr catalysts and thus copper is the main active species for CO oxidation. Monnier

et al. suggested that Cu⁺ is the active site responsible for CO chemisorptions over this catalyst [7]. More often the catalysts activity is associated with formation of different Cu-Cr species such as CuCr₂O₄ and Cu₂Cr₂O₄ [8], and the role of chromium is attributed to a limitation of the extent of copper reduction.

Many works have been devoted to the study of hydrocarbon oxidation because of its large industrial application and problems with exhaust emissions. It is known that copper and mixed copper-chromium oxides are effective catalysts for propane, n-butane and methane oxidation [9, 10]. No data are known about deep oxidation of CO, dimethyl ether (DME) and methanol mixture on this type of catalysts. As it is known [11, 12] the catalytic oxidation of methanol on oxide catalysts is accompanied by toxic products formation, mainly CO and dimethyl ether. The high concentration of these compounds in the outlet gases requires the using of an additional reactor for their complete oxidation. Usually these reactors are adiabatic and the oxidation takes place on oxide catalysts, which are most often supported upon different supports [13, 14].

Our previous work [15] indicates that supported Cu-Cr oxide catalysts are effective for deep oxidation of methanol, CO and DME. Evaluation of the possibility for removing harmful components from methanol oxidation exhaust gases needs a more complex investigation. This work aims to elucidate the changes in the catalyst composition during industrial exploitation of the catalyst, and the main reasons for catalyst deactivation.

II. EXPERIMENTAL

1. Catalyst preparation and characterization

Commercial γ -Al₂O₃ F-2000 with particle size of 4.8 mm and total pore volume of 0,5 cm³/g was used as a carrier. The catalysts were prepared by co-impregnation method [4, 5]. Appropriate amounts of copper nitrate and CrO₃ were dissolved in de-ionized water and γ -Al₂O₃ was added, so that the volume ratio solution/carrier was 2:1. The mixture was kept at 20 °C during 12 h and then filtered; the residue was dried for 12 h in air, and after that for 2 h at 110 °C. The precursor thus dried was placed in a furnace, the temperature was gradually increased during 3 h to 500 °C and the catalyst was heated for 3 h at this temperature in air. Some samples were calcinated at different temperatures as follows: sample 1 - 300°C, sample 2 - 500 °C, sample 3 - 700 °C, sample 4 - 800 °C, sample 5 - 500 °C (triple impregnated). The content of the active component after calcination was 16 ± 0.2 wt. % and the copper – chromium molar ratio 3.8.

K. Ivanov is with Dept. of Chemistry, Agricultural University, 12 Mendeleev St., 4000 Plovdiv, Bulgaria (Mob. tel: +359 887745734; Fax: +359 32 633157; e-mail: kivanov1@abv.bg)

D. Dimitrov is with Dept. of Chemistry, Agricultural University, 12 Mendeleev St., 4000 Plovdiv, Bulgaria (e-mail: mitko_dme@abv.bg)

B. Boyanov is with Plovdiv University "Paisii Hilendarski", 24 Tsar Assen St., 4000 Plovdiv, Bulgaria (e-mail: boyanb@uni-plovdiv.bg)

X-Ray, XPS and SEM - EDS analysis were performed on the catalysts' bulk and surface composition.

The X-Ray phase analysis was performed by means of a TUR-M62 apparatus, having Breg-Brentano geometry and by means of computer-controlled goniometer HZG-3, Co-K α radiation, step of scanning of the spectrum 0.05° and increased time of collecting the impulses – 5 s. By means of the experimental diffraction spectra a profile analysis was made of the lines according to the “Fit” program [16] for determining their exact position and intensity. The phase identification has been made with help of the database of the JCPDS (International Center for Diffraction Data, Alphabetical Indexes, Pennsylvania 19073-3273, sets 1-86, 1997).

XPS was carried out using ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5. 10–10 mbar (during the measurement 1.10–8 mbar), using MgK α X-ray source (excitation energy $h\nu = 1253.6$ eV) (AlK α X-ray source excitation energy $h\nu = 1486.6$ eV)). The pass energy of the semispherical analyzer was 20 eV (because of its small signal for Cu2p and Cr2p 50 eV pass energy was used), 6 mm slit widths (entrance/exit). The instrumental resolution measured at the full width at a half maximum (FWHM) of the Ag3d5/2, photoelectron peak is 1 eV. The energy scale is corrected to the C1s peak maximum at 285 eV for electrostatic charging. The fitting of the recorded XPS spectra was performed, using a symmetrical Gaussian–Lorentzian curve fitting after Shirley type subtraction of the background.

2. Activity measurement

In order to resolve the problem two types of equipment were used (Fig.1): (i) flow-line equipment with isothermal reactor, allowing precise control on the methanol oxidation and amount of by-products (Section 1) and (ii) flow-line equipment with an adiabatic reactor for additional deep oxidation of the by-products (Section 2).

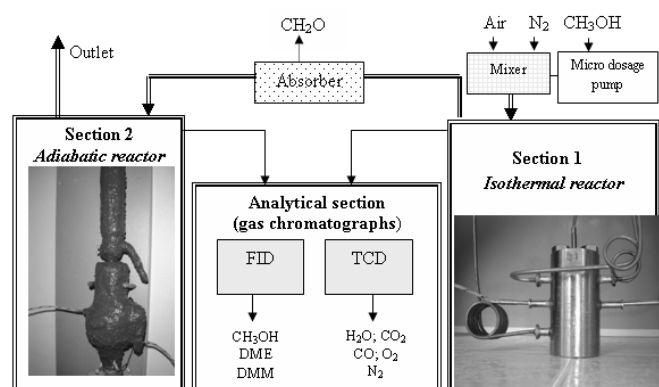


Fig. 1 Apparatus for estimation of oxide catalysts for methanol oxidation

An industrial catalyst produced by Neochim S.A. – Dimitrovgrad, Bulgaria [17] in the first reactor and alumina supported CuO-Cr $_2$ O $_3$ catalysts with 15 % active component in the second reactor were used. The content of the gas mixture entering the main reactor, space velocity and

temperature regime allow the experiment to be carried out at conditions closest to the industrial ones (Table 1).

TABLE I
MAIN PARAMETERS OF THE PROCESS IN THE FIRST AND SECOND EQUIPMENT

Parameter	Isothermal reactor	Adiabatic reactor
<i>Gas mixture:</i>		
Methanol	7.0 %	0.10 – 0.13 %
Oxygen	10.5 - 11.0 %	7.0 – 7.3 %
Carbon monoxide	0.0	0.9 – 1.0 %
DME	0.0	0.3 – 0.4 %
Water	0.0	3.0 – 3.2 %
Nitrogen and other	to 100 %	to 100 %
<i>Catalyst:</i>		
quantity	10,0 cm 3	10.0 cm 3
Space velocity	10000 h $^{-1}$	10000 h $^{-1}$
Contact time	0.36 s	0.36 s
<i>Temperature:</i>		
Inlet	300 – 320 °C	180 – 300 °C
Outlet	-	300 – 460 °C

The temperature in the first reactor was maintained in the range 300-320 °C, which ensured a practically complete methanol oxidation and a concentration of CO and DME in the outlet gas mixture commensurate with the one during the industrial realization of the process. After the formaldehyde absorption, the quantity of methanol necessary for maintaining its concentration in the range 0.12-0.13 % was added in. The gas mixture thus composed was heated to the desired temperature before entering the second apparatus with an adiabatic reactor. The temperature in the adiabatic reactor was maintained at the expense of the heat emitted during methanol oxidation.

The reactant and product gases were analyzed for methanol and DME by an on-line gas chromatograph, equipped with flame-ionization detector and Porapak Q column. A second gas chromatograph, equipped with a thermal conductivity detector and MS-5A and Porapak Q columns was employed for CO, CO $_2$, O $_2$ and N $_2$ determination. The formaldehyde content in the reaction products was determined by Spectroquant Pharo 100 spectrometer.

3. Industrial experiment

A three months industrial experiment was carried out. The industrial installation monitored consists of an adiabatic reactor with 600 kg catalyst and possibilities to maintain the space velocity in the range of 5000 to 15000 h $^{-1}$ and inlet gas temperature of 180-240 °C. Inlet concentration of the exhaust gases was as follows: CO – 1.4 to 1.6 %, DME – 0.4 to 0.5 %, CH $_3$ OH – 0.10 to 0.15 % and CH $_2$ O – 0.01 to 0.03 %.

III. RESULTS AND DISCUSSION

1. Catalyst composition

The distribution of the active component on the entire carrier surface was investigated by SEM - EDS analysis. For this purpose 10 catalyst grains were cut in two and then polished, after which we analyzed 3 points from each bead, as shown in Fig.2.

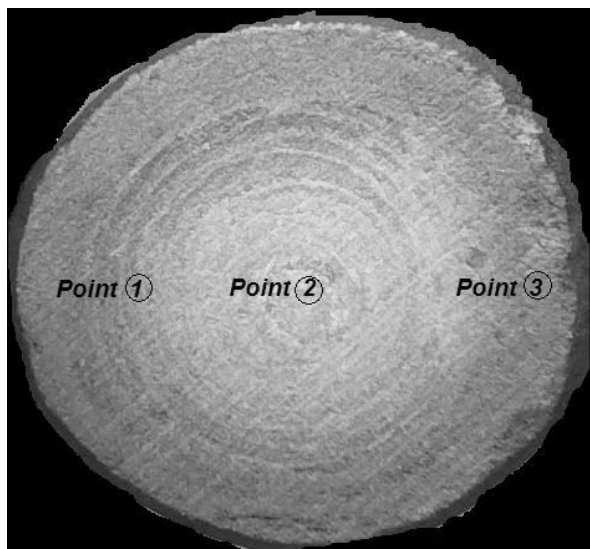


Fig. 2 Scheme for determination of the active component distribution on the carrier surface

It was found the distribution of the active component on the carrier surface to be nearly uniform, as can be seen from Fig.3.

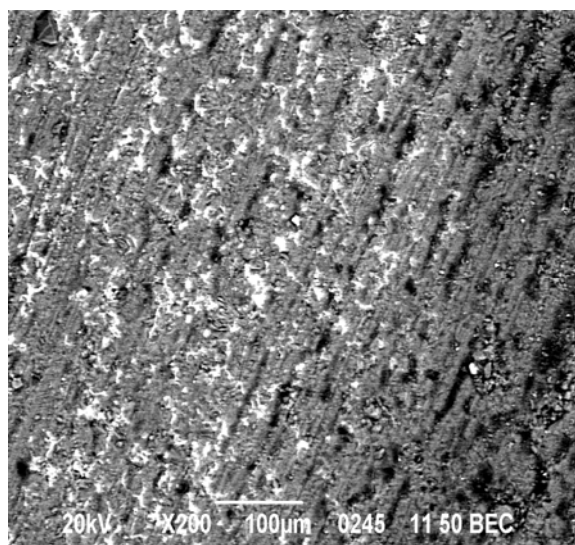


Fig. 3 Typical SEM image of “fresh” Cu-Cr/ γ -alumina catalyst

The total quantity of copper and chromium varied in narrow range – $13 \pm 1,5$ wt % (typical sample is presented on Table 2), while the atomic ratio Cu/Cr changed in a large range – from 2.4 to 3.8. This indicates a considerable difference in the chemical composition of the compounds building the active component in the different areas of the catalyst surface. In our SEM - EDS analysis we could establish the presence of only one phase with defined chemical composition – $\text{Cu}_2\text{Cr}_2\text{O}_4$ (Fig.4 and Table 3).

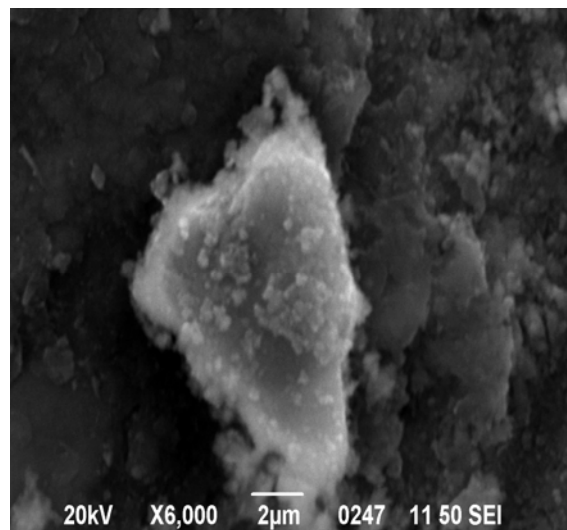


Fig. 4 Single crystal of $\text{Cu}_2\text{Cr}_2\text{O}_4$

We registered an aluminum hydroxide phase - α - AlOOH besides the main crystalline phase - γ - Al_2O_3 . The spectra of double oxide samples Cu-Cr-O supported on γ - Al_2O_3 (Fig. 5, samples 1, 4 and 5) include mainly the characteristic pattern of the support, as well as broadened lines of low intensity, belonging to highly dispersed supported phases. The reason for this is the small crystallite size, as well as the low crystallinity degree of supported phases, which complicates the exact analysis. The aluminum hydroxide phase was not registered in the XRD patterns after thermal treatment. The crystallinity of the supported phases slowly increased and mixed Cu-Cr oxide phases (as CuCr_2O_4 , CuCrO_2 and CuCrO_4) were obtained with an increase of thermal treatment (Fig.5, samples 4 and 5). There is no evidence of supported Cu-Cr oxides and alumina support interaction.

TABLE II
ENERGY DISPERSIVE X-RAY MICROANALYSIS OF THE CATALYST,
PRESENTED ON FIG.3 (INTEGRAL SPECTRUM)

Element	Weight %	Atomic %
Al	40,1	32,1
Cr	2,5	1,0
Cu	10,5	3,6
O	46,9	63,3

TABLE III
SEM IMAGE AND ENERGY DISPERSIVE X-RAY MICROANALYSIS
OF THE CATALYST, PRESENTED ON FIG.4

Element	Weight %	Atomic %
Cr	45.8	50.8
Cu	54.2	49.2

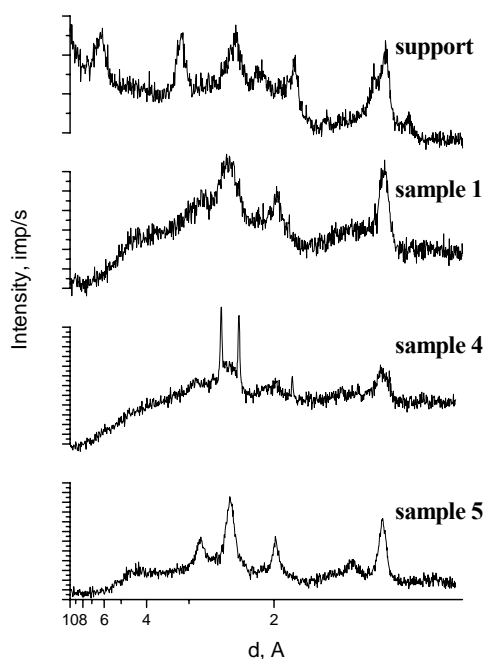


Fig. 5. Powder XRD patterns of the support, sample 1 (calcined at 500 °C), sample 4 (calcined at 800 °C) and sample 5 (calcined at 500 °C - triple impregnated)

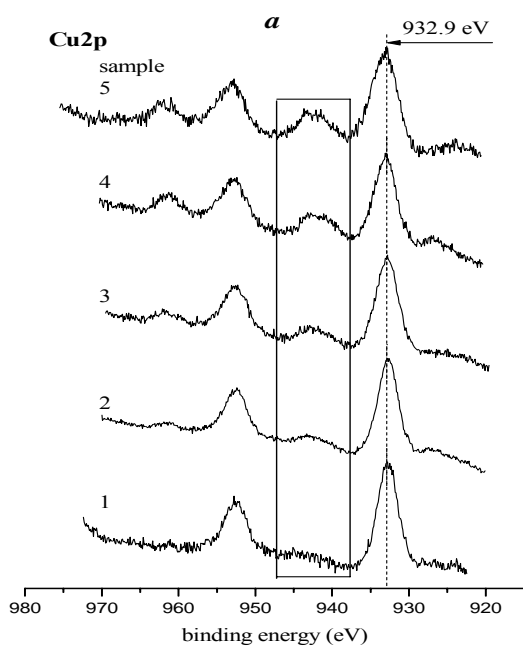


Fig. 6a. XPS spectra of Cu2p for investigated samples

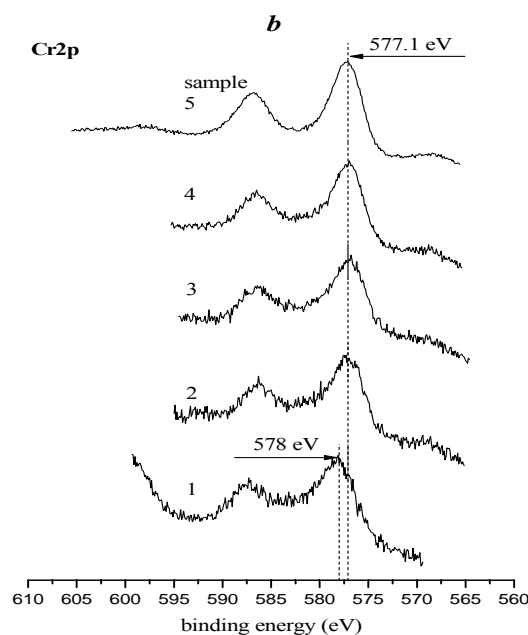


Fig. 6b. XPS spectra of Cr2p for investigated samples

The samples were characterized also by XPS. The obtained spectra (Fig.6a) show that the intensity of the satellite of the Cu2p peak increases from samples 1 to 5. This means that copper changed from Cu^+ to mixture of Cu^+ and Cu^{2+} . The established $\text{Cu}^+ / (\text{Cu}^+ + \text{Cu}^{2+})$ ratio is as follows: for sample 1 – 1.0; sample 2 – 0.85; sample 3 – 0.67; sample 4 – 0.25 and sample 5 – 0.47 (triple impregnated). The result of these values is in a very good agreement with the XRD analysis. The peak form and FWHM of Cr2p (Fig.6b) show that the chromium exists in two forms of different chromium oxides

2. Catalytic activity

The effect of preparation conditions on the chemical composition, activity and selectivity of the γ -alumina supported copper-chromium catalysts toward deep oxidation of CO, DME, formaldehyde and methanol oxidation was investigated. It was found that the optimal conditions for obtaining the catalyst are calcination at 500-550 °C and active component content in the range of 15-30 %. Chemical composition strongly influences catalytic properties, this influence being quite variable with regards to the different processes (Fig.7).

Notwithstanding the low concentration of methanol and formaldehyde, their measurable oxidation begins at temperatures, significantly inferior than 180 °C and reaches 100 % at about 190 °C for all catalysts investigated. Considerably different is the activity of the catalysts with respect to the CO and DME. Their oxidation increases rapidly with increasing of chromium content in the active component. The rate of CO oxidation passes through maximum at 15-30 % chromium content (expressed as Cr_2O_3) after which rapidly decreases. Obviously the association of copper species with chromium species leads to a higher CO conversion because of

the strong synergistic effect over the Cu-Cr/ γ -alumina catalysts. On the basis of X-ray and XPS analysis it can be concluded that the active component of the mixed copper-chromium catalysts consists of at least four compounds – CuO, Cr₂O₃, Cu₂Cr₂O₄ and CuCr₂O₄.

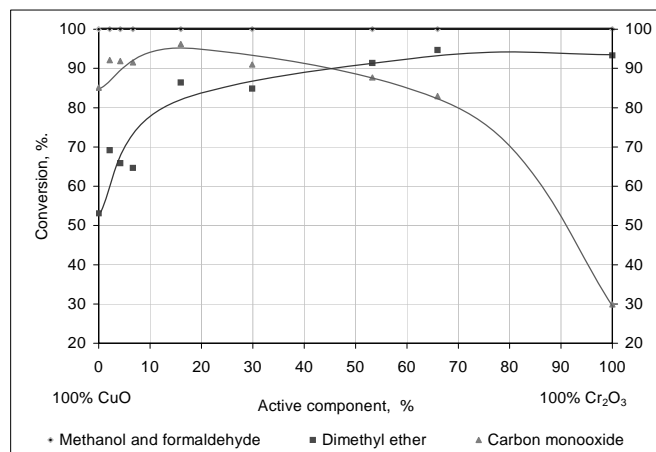


Fig. 7. Conversion of CO, DME, formaldehyde and methanol on alumina supported copper – chromium catalysts

At least two types of active centers exist on the catalyst surface. Obviously the ratio Cu⁺/Cu²⁺ is responsible for the catalysts activity toward CO oxidation. The rate of DME oxidation increases continuously and reaches maximum at pure Cr₂O₃. Copper compounds seem to be inert diluents.

Summarizing the results presented on Fig. 7, we can conclude that the interaction between copper and chromium ions and the formation of Cu⁺ and Cr⁶⁺ centers create active components of the mixed Cu–Cr oxide supported catalysts. The intimate contact of such phases and possibility of charge transfer in the course of the catalytic reaction, as well as the higher dispersion of supported phases are probably responsible for the higher catalytic activity of the catalysts. The presence of a number of compounds (CuO, CrO₃, Cr₂O₃, Cu₂Cr₂O₄, and CuCr₂O₄) in all studied samples leads to a synergistic effect and enhanced CO, DME, and methanol conversion compared with the sum of conversions on each oxide supported on the carrier separately [4, 5].

3. Industrial experiment

The industrial experiment was carried out in the formalin production department at Neochim S.A. One ton of catalyst with particle size of 4.8 mm was prepared by the impregnation method described above. The atomic ratio Cu/Cr in the initial solution was 3.8 and the amount of the active component after calcination at 500 °C was 16.0 ± 0.5 wt. %. The space velocity was 8800 h⁻¹ in the beginning and 12500 h⁻¹ at the end of the experiment (Table 4).

Outlet gas composition was in the range of the EU ecological norms for CO (100 ppm), (DME 200 mg/m³), CH₃OH (200 ppm) and CH₂O (20 ppm) (Table 5).

DME content in the outlet gases was in the range of 180-370 mg/m³ which exceeds slightly the norms established by the EU (200 ppm). The solution to this problem necessitates increasing the quantity of catalyst and reducing the space velocity of the gas flow through the adiabatic reactor.

TABLE IV

EXPERIMENTAL CONDITIONS OF THE INDUSTRIAL EXPERIMENT

Days	Temperature, °C		W _{vol} , h ⁻¹ × 10 ⁻³	Loading
	Inlet	Outlet		
2	173	328	8.8	70 %
5	205	376	10.0	80 %
30	220	420	11.3	90 %
50	235	458	12.5	100 %
60	235	465	12.5	100 %
90	230	461	12.5	100 %

TABLE V

RESULTS FROM THE INDUSTRIAL EXPERIMENT

Days	CH ₂ O		CO		DME		CH ₃ OH	
	C _{inlet} mg/m ³	C _{outlet} mg/m ³	C _{inlet} mg/m ³	C _{outlet} mg/m ³	C _{inlet} mg/m ³	C _{outlet} mg/m ³	C _{inlet} mg/m ³	C _{outlet} mg/m ³
2	220	<20	15200	<100	4600	<200	<100	n.d.*
5	225	<20	15400	<100	4500	<200	<100	n.d.
30	250	34.6	16400	290	4750	370	<100	n.d.
50	240	25.9	15900	380	4600	230	<100	10
60	235	<20	15100	<100	4500	<200	<100	n.d.
90	230	<20	14800	<100	4600	270	<100	n.d.

n.d.* - not detectable

4. Spent catalyst

SEM – EDS analysis showed significant change in the catalyst composition during the industrial exploitation. Iron and molybdenum, obviously coming from the oxide catalyst in the main reactor for methanol oxidation, appear on the active component surface.

TABLE VI

CATALYST COMPOSITION OF THE SURFACE LAYER (FIG 2, POSITION 1) AND OF THE BULK (FIG 2, POSITION 2) DETERMINED BY ENERGY DISPERSIVE X-RAY MICROANALYSIS (INTEGRAL SPECTRUM)

Element	Fig. 2, position 1		Fig. 2, position 2	
	Weight %	Atomic %	Weight %	Atomic %
Al	37.4	30.4	38.8	31.3
Cr	2.30	0.97	1.40	0.60
Cu	9.74	3.37	10.2	3.50
Fe	0.65	0.26	0.39	0.15
Mo	3.05	0.70	2.05	0.46
O	46.84	64.27	47.1	64.0

Table 6 presents catalyst composition of the surface layer (Fig.2, position 1) and of the bulk (Fig.2, position 2). As the table shows, the iron and molybdenum are precipitated in the entire volume of the catalyst grain, their quantity being highest on the surface. Iron content varies in the range 0.3-0.7 and molybdenum content varies from 2.0 to 3.0 wt. %. The average content of Fe and Mo in the catalyst grains defined after grinding and homogenization by ICP (“Spectro” – Germany) is considerably lower – respectively 150 ± 30 and

1100 ± 200 ppm. The extraction was performed by aqua regia. It seems that iron and molybdenum are deposited mainly on the active component of the catalyst (up to 2.5 wt. % Fe and 7.0 wt. % Mo) which leads to the aggregation of the Cu-Cr spaces (Fig.8 and Table 7). No coke deposition was found.

TABLE VII
ENERGY DISPERSIVE X-RAY MICROANALYSIS OF "SPENT"
Cu-Cr/ γ -ALUMINA CATALYST

Element	Weight %	Atomic %
Al	30.02	24.42
Cr	3.03	1.28
Cu	7.09	2.45
Fe	2.52	0.99
Mo	6.82	1.56
O	50.52	69.30

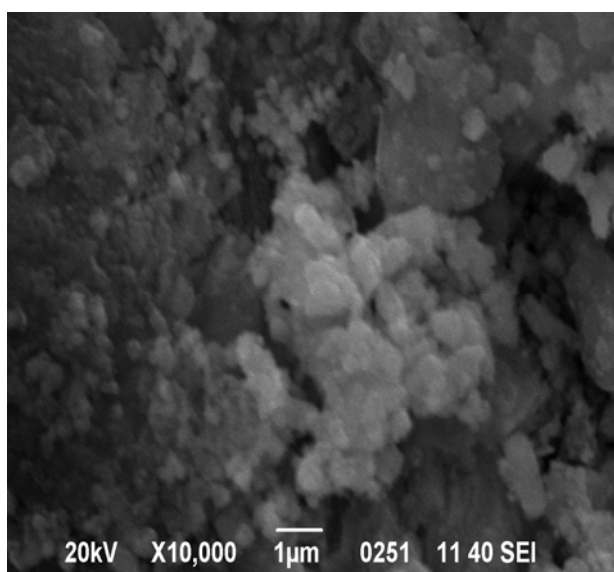


Fig. 8. Typical SEM image of the active component of the "spent" catalyst

Cu2p and Cr2p X-ray photoelectron spectra obtained for fresh sample at the surface, used sample at the surface, the bulk of the fresh sample and the bulk of the used sample are shown in Fig.9. From the linear shape of the Cu2p spectrum and the shake up satellite structure, one could conclude that the bulk consists of Cu²⁺ only. Looking at a used sample, we observe similar behavior of the dispersion of the Cu⁺ and Cu²⁺. However the amount of Cu²⁺ is less present in comparison with the bulk of the fresh sample. Therefore, we conclude that catalytic reaction changes the oxidation state of the elements. Looking at the Cr2p spectra, we obtained a similar change of ion oxidation state. The bulk of the fresh and the used samples, as well as the fresh sample surface, contain a mixture of Cr³⁺ and Cr⁶⁺, whereas the spectrum of the used sample surface is typical for the presence of Cr³⁺ only. Therefore, one can conclude the coexistence of various copper and chromium species CuO/Cu₂O and CrO₃/Cr₂O₃ or CuCr₂O₄/Cu₂Cr₂O₄ on the surface. According to Wojciechowska et al. [18] the presence of Cu²⁺ facilitates the redox processes. On the other hand, the presence of Cr₂O₃ stabilizes at the surface the Cr³⁺ ions. Since the redox potential

of the copper ions system is much higher than that of chromium ions system, there is a tendency for transfer electrons to form Cr⁶⁺ and Cu⁺ ions, playing the role of active sites in catalytic reaction.

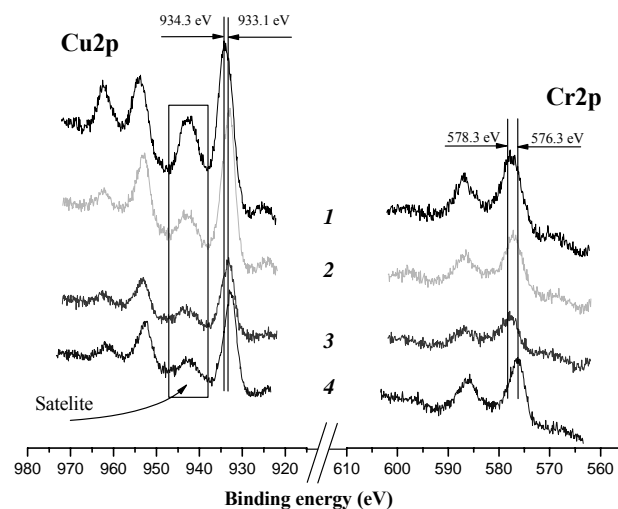


Fig. 9. XPS spectra of Cu2p and Cr2p for investigated samples: (1) – fresh bulk, (2) – used bulk, (3) – fresh surface and (4) – used surface.

IV. CONCLUSIONS

1. The CuO-Cr₂O₃/ γ -alumina supported catalysts have enhanced activity toward CO, DME, formaldehyde and methanol oxidation. We established that 15–30 % Cr₂O₃ content in the active component is the best compromise for production of industrial catalyst for successful combustion of all the components.
2. The main reason for catalyst deactivation seems to be the location of iron and molybdenum, coming from the main reactor, on the active component surface.

ACKNOWLEDGEMENT

This work is supported by Bulgarian Ministry of Education, Project VU- X-305/07.

REFERENCES

- [1] Xiaolan Tang, Baocai Zhang, Yong Li, Yide Xu, Qin Xin and Wenjie Shen, Carbon monoxide oxidation over CuO/CeO₂ catalysts, Catal. Today, 93-95 (2004) 191-198.
- [2] D. R. Mechandjiev, P. G. Dimitrova, I. A. Tzolovski, A. B. Raevski, Cu/CO spinel containing exhaust gas catalyst and method of its preparation (2003) WO Patent 03061821
- [3] Y. F. Yo-Yao, J. T. Kummer, A study of high temperature treated supported metal oxide catalysts, J. Catal., 46 (1977) 388-401.
- [4] F. Severino, J. Brito, O. Carias, J. Laine, Comparative study of Alumina-Supported CuO and CuCr₂O₄ as catalysts for CO Oxidation, J. Catal., 102 (1986) 172-179.
- [5] Chin-Cheng Chien, Wen-Po Chuang and Ta-Jen Huang, Effect of heat-treatment conditions on Cu-Cr/ γ -alumina catalyst for carbon monoxide and propene oxidation, Applied Catalysis A: General, 131 (1995) 73-87.

- [6] J. Laine, J. Brito and F. Severino, Germán Castro, Patricia Tacconi, Simón Yunes and José Cruz, Surface copper enrichment by reduction of copper chromite catalyst employed for carbon monoxide oxidation Catal. Lett., 5 (1990) 45-54.
- [7] J. R. Monnier, M. J. Hanrahan and G. Apai, A study of the Catalytically Active Copper Species in the Synthesis of Methanol Over Cu-Cr Oxide, J. Catal., 92 (1985) 119-126.
- [8] C. A. Leech, and L. E. Campbell, Spinel Solid Solution Catalysts for Automotive Applications, Adv. Chem. Ser., 143 (1975) 161-177.
- [9] T. V. Mulina, T. V. Borisova, V. A. Ljubushkin and V. A. Chumachenko, Catalyst for extensive oxidation of organics and carbon monoxide in gas emissions and method of preparation there (Versions), (2003) RU Patent 2 199 388 C₂.
- [10] P. W. Park and J. S. Ledford, The influence of surface structure on the catalytic activity of alumina supported copper oxide catalysts. Oxidation of carbon monoxide and methane, Appl. Catalysis, B-Environmental, 15 (3-4) (1998) 221-131.
- [11] A. P. Vieira Soares, M. Farinha Portela, A. Kiennemann, Iron molybdates for selective oxidation of methanol: Mo excess effects on the deactivation behavior, Cat. Commun., 2 (2001) 159-164.
- [12] J. M. Tatibouët, Methanol oxidation as a catalytic surface probe, Appl. Cat. A: General, 148 (1997) 213-252.
- [13] M. C. Alvarez-Galvan, B. Pawelec, V. A. de la Pena O'Shea, J. L. G. Fierro and P. L. Arias, Formaldehyde/methanol combustion on alumina-supported manganese-palladium oxide catalyst, Appl. Catalysis B: Environmental, 51 (2004) 83-91.
- [14] Cremona Alberto, Rubini Carlo, Vogna Edoardo, Oxidation catalyst, (2004) US Patent 2004121904.
- [15] K. Ivanov, D. Dimitrov, Alumina supported CuO – MnO₂ catalysts for deep oxidation of carbon oxide and organic compounds, Scientific articles, Ecology 2006, Part 1 (2006) 228-238.
- [16] V. Petkov, N. Bakaltchev, FIT, a computer program for decomposition of powder diffraction patterns and profile analysis of pair correlation functions, Appl. Crystallography, 23 (1990) 138-140.
- [17] K. Ivanov, Method for the preparation of oxide catalyst for the oxidation of methanol to formaldehyde, (1993) BG patent No 60779 B₁.
- [18] M. Wojciechowska, J. Haber, S. Łomnicki, J. Stoch, Structure and catalytic activity of double oxide system: Cu–Cr–O supported on MgF₂ Journal of Molecular Catalysis A: Chemical, 141 (1999) 155-170.