Alumina Supported Cu-Mn-Cr Catalysts for CO and VOCs Oxidation

Krasimir I. Ivanov, Elitsa N. Kolentsova, Dimitar Y. Dimitrov, Petya Ts. Petrova, Tatyana T. Tabakova

Abstract—This work studies the effect of chemical composition on the activity and selectivity of γ–alumina supported CuO/MnO$_2$/Cr$_2$O$_3$ catalysts toward deep oxidation of CO, dimethyl ether (DME) and methanol. The catalysts were prepared by impregnation of the support with an aqueous solution of copper nitrate, manganese nitrate and CrO$_3$ under different conditions. Thermal, XRD and TPR analysis were performed. The catalytic measurements of single compounds oxidation were carried out on continuous flow equipment with a four-channel isothermal stainless steel reactor. Flow-line equipment with an adiabatic reactor for simultaneous oxidation of all compounds under the conditions that mimic closely the industrial ones was used. The reactant and product gases were analyzed by means of on-line gas chromatographs.

On the basis of XRD analysis it can be concluded that the active component of the mixed Cu-Mn-Cr/γ–alumina catalysts consists of at least six compounds – CuO, Cr$_2$O$_3$, MnO$_2$, Cu$_{1.5}$Mn$_{1.5}$O$_4$, Cu$_{1.5}$Cr$_{1.5}$O$_4$ and CuCr$_2$O$_4$, depending on the Cu/Mn/Cr molar ratio. Chemical composition strongly influences catalytic properties, this influence being quite variable with regards to the different processes. The rate of CO oxidation rapidly decrease with increasing of chromium content in the active component while for the DME was observed the reverse trend. It was concluded that the best compromise are the catalysts with Cu/(Mn + Cr) molar ratio 1:5 and Mn/Cr molar ratio from 1:3 to 1:4.

Keywords—Copper-manganese-chromium oxide catalysts, CO, deep oxidation, volatile organic compounds.

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. It is known that catalysts, based on copper-manganese mixed oxides are of considerable interest owing to their activity as oxidation catalysts [3], [4]. These materials

Krasimir Ivanov is with the Department of Chemistry, Agricultural University, 4000 Plovdiv, Bulgaria (corresponding author, phone: +359-887-745-734; fax: +359-32-633-157; e-mail: kivanov1@ abv.bg).

Elitsa Kolentsova and Dimitar Dimitrov are with the Department of Chemistry, Agricultural University, 4000 Plovdiv, Bulgaria (e-mail: elitsa_kolentsova@abv.bg, mitko_dme@abv.bg).

Petya Petrova and Tatyana Tabakova are with the Institute of Catalysis, Bulgarian Academy of Science, 1113 Sofia, Bulgaria (e-mail: petia@ic.bas.bg, tabakova@ic.bas.bg).

can catalyse the oxidation of CO at low temperatures and catalyse many organic compounds, often included in the composition of the waste gases, such as nitrogen-containing compounds, hydrocarbons and other organic compounds [5], [6]. Therefore monolithic and supported copper-manganese catalysts caused a great interest of fundamental work devoted to clarifying the role of each component and the nature of the active sites. This has been object of many scientific publications during the last years [7]-[9]. It is considered that the copper-manganese mixed oxides are promising because of their high thermal stability, chemical resistance and low cost [10]. The studies of Ferrandon [11] showed that the activity of the manganese oxides supported on γ-Al$_2$O$_3$ passes through a maximum with increasing of the heat treatment temperature. According to the author, this is partly due to the reduction of the specific surface area. The ratio of the two elements in the active component also plays a leading role regarding the activity in catalytic oxidation. McCabe et al. [12] showed that a hopcalite catalyst (80% MnO$_2$ and 20% CuO) was comparable to a Pt/Al$_2$O$_3$ catalyst for combustion of ethanol but was irreversibly deactivated at around 500°C. According to many other literature sources the formation of Cu-Mn spinels with atomic ratio Cu:Mn is 1:2, is the most suitable for the oxidation of CO [13].

It is known that one of the most effective catalyst systems for CO oxidation is based on a combination of copper and chromium oxides [14], [15]. 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 [16]. According to Laine and co-workers [17] 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 at al. suggested that Cu$^+$ is the active site responsible for CO chemisorption over this catalyst [18] More often the catalysts activity is associated with formation of different Cu-Cr species such as CuCr$_2$O$_4$ and Cu$_2$Cr$_2$O$_4$ [19], and the role of chromium is attributed to a limitation of the extent of copper reduction.

Many efforts of the scientists are focused on CO oxidation because it is dominating by-product of important industrial processes. Frequently the problems are more complex due to the diversity of the waste gases content. The catalytic oxidation of methanol to formaldehyde (object of our investigation) is an important industrial process in which the waste gas in addition to CO contains methanol and dimethyl ether (DME).

Our previous investigations [20], [21] indicate that γ–

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alumina supported Cu-Mn and Cu-Cr oxide catalysts are effective for simultaneous oxidation of methanol, CO and DME. It was established that single Cu and Mn oxide catalysts are less active than mixed oxides ones with respect to all three compounds investigated. Obviously the synergetic effect between copper and manganese oxide increases the activity in all cases [20]. This effect strongly depends on the catalyst composition and on the nature of oxidized compound. The addition of small amounts of manganese oxide to the pure copper oxide leads to a sharp increase in activity in relation to CO oxidation. Even more pronounced synergistic effect is observed in the methanol oxidation. While in the first case, the influence of the atomic ratio of Cu-Mn is weakly expressed in almost the entire concentration range in the methanol oxidation the copper-rich oxide samples show significantly higher activity. Conversely, the higher activity in the DME oxidation is shown by manganese-rich oxide specimens.

The investigation of the Cu-Cr system [22] led to the conclusion that at least two types of active centers exist on the catalyst surface. The rate of DME oxidation increases continuously and reaches maximum at pure Cr_2O_3. Copper compounds seem to be inert diluents. Considerably different is the activity of the catalysts with respect to the CO. 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 in the Cu-Cr/γ–alumina catalysts.

The main idea of this study is to combine the advantages of both Cu-Mn and Cu-Cr catalytic systems by obtaining a new mixed Cu-Mn-Cr catalyst with high activity and selectivity in simultaneous oxidation of CO, methanol and DME. For the purpose of the investigation we selected two basic samples: (i) copper-rich Cu-Mn/γ-Al$_2$O$_3$ catalyst with Cu/Mn molar ratio 2:1, which was found to be the most active in oxidation of CO and methanol and (ii) manganese-rich Cu-Mn/γ–Al$_2$O$_3$ catalyst with Cu/Mn molar ratio 1:5, which was found to be the most active in the oxidation of DME. Manganese in these samples was replaced by chromium in the whole concentration region and catalytic properties were determined.

II. MATERIALS AND METHODS

A. Catalysts Preparation

All catalysts were prepared by the wet impregnation of γ–Al$_2$O$_3$ with fraction of 0,6-1.0 and 5.0-5.5 mm. Prior to the impregnation, the carrier was calcined for 2 hours at 450°C in a ceramic furnace. After keeping it at a room temperature, previously prepared solutions of copper and manganese nitrates and CrO_3 with desired ratio were added. The support remained immersed for 12 hours in the salt solutions at 80°C. After the impregnation samples were dried and calcined in the following sequence: 12 h drying at room temperature, followed by heating at 120°C for 10 h, after which the temperature was increased with 10°C/min to desired level,

where it was held for 4 hours.

B. Analytical Techniques for Sample Characterization

- *Thermal Analysis (TG, DTG and DTA)*

DTA, DTG and analysis were carried out using "Stanton Redcroft" (England) instrument under the following experimental conditions: heating temperature range – 20-650°C, heating rate 10°C/min, specimen mass 12.00 mg, gas environment 100 % air, pot-stabilized corundum.

- *Texture Measurements*

The texture characteristics were determined by low-temperature (-196°C) nitrogen adsorption in a Quantachrome Instruments NOVA 1200e (USA) specific surface area&pore analyser. The NOVAs are self-contained instruments with a powerful built-in microprocessor, using either the classical helium-void-volume method or a patented technique that eliminates the use of helium. Automatic coolant level control ensures constant, small void volume for accurate data throughout the measurement. A long-life (30 hr) dewar permits continuous operation over an extended time if necessary. The Nova 1000e is designed for routine analyses using nitrogen gas and liquid nitrogen and has the added flexibility of being able to use a variety of gases (e.g. argon, carbon dioxide) and coolants (e.g. liquid argon, ice/water) for advanced applications in addition to standard N$_2$ work.

- *Powder X-ray Diffraction (XRD)*

X-ray powder diffraction (XRD) patterns for phase identification were recorded on a Philips PW 1050 diffractometer, equipped with Cu Kα tube and scintillation detector. Data for cell refinements were collected in θ-2θ, step-scan mode in the angle interval from 10 to 90° (2θ), at steps of 0.03° (2θ) and counting time of 3 s/step. The cell refinements were obtained with the PowderCell program. The size-strain analysis was carried out using the BRASS-Bremen Rietveld Analysis and Structure Suite.

- *Temperature Programmed Reduction (TPR)*

TPR measurements were carried out in a flow system under the following conditions: gas mixture hydrogen-argon (10% H$_2$); flow rate 24 ml.min^{-1}; temperature rise 15°C min^{-1}; sample amount 0,05g.

- *Catalyst Testing*

The catalytic measurements of single compounds oxidation were carried out on continuous flow equipment with a four-channel isothermal stainless steel reactor, containing 1.0 ml catalyst at atmospheric pressure and space velocity (GHSV) of 10000 h^{-1}, allowing simultaneous examination of four catalysts under the same conditions. The flow of ambient air (40 – 50% humidity) and CO (final concentration 2.0%) were fed using mass flow controllers (GFC Mass Controller AABORG, Germany). Liquid methanol was cooled to 0°C in evaporator through which the steam of air was passing and additional air was added before reaching the preheater to final concentration of methanol 2.0%. DME (1.0%) was obtained by dehydration of methanol on γ-Al$_2$O$_3$ in tubular isothermal

reactor.

Two stage equipment with an adiabatic reactor for simultaneous oxidation of all compounds under the conditions closest possibly to the industrial was used (inlet gas mixture: methanol 0.10-0.12%, CO 0.9-1.0%, DME 0.3-0.4% and water 3.0-3.2%). Details for both apparatus are given elsewhere [21].

Gas mixtures on the input and output of the reactor were analyzed with a gas chromatograph HP 5890 Series II, equipped with FID and TCD detectors, column Porapak Q (for methanol, CO_2 and DME) and column MS-5A (for CO, oxigen and nitrogen).

III. RESULTS

A. Catalyst Charachterisation.

- *Thermal Analysis (TG, DTG and DTA)*
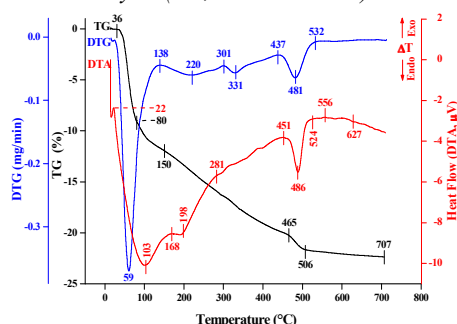
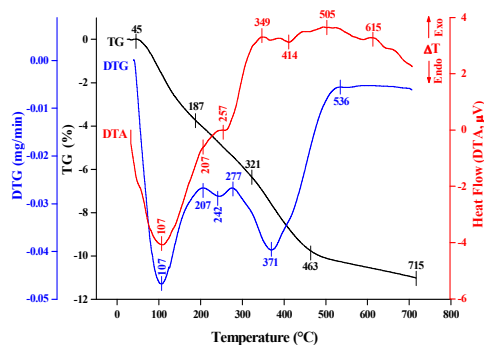Fig. 1 Thermal analysis of Cu-Cr/γ-Al$_2$O$_3$ catalyst with Cu/Cr molar ratio 2:1

Fig. 2 Thermal analysis of Cu-Cr/γ-Al$_2$O$_3$ catalyst with Cu/Cr molar ratio 1:5

TABLE I
THERMOGRAVIMETRIC RESULTS FOR DIFFERENT CU-MN-CR/Γ-AL$_2$O$_3$ CATALYSTS

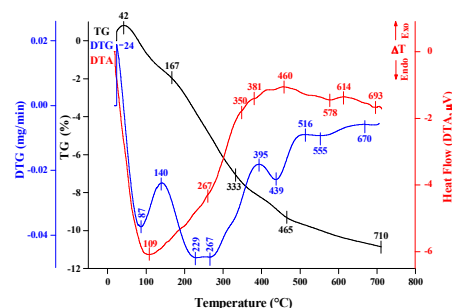| Sample	Weight loss, %			
	First	Second	Third	Forth
	Onset T, $^{\circ}$C (Weight loss)	Onset T, $^{\circ}$C (Weight loss)	Onset T, $^{\circ}$C (Weight loss)	Onset T, $^{\circ}$C (Weight loss)
Fig. 1	36 (11.7)	150 (8.1)	465 (1.8)	506 (0.2)
Fig. 2	45 (4.1)	187 (1.3)	321 (4.2)	463 (1.2)
Fig. 3	42 (2.4)	167 (6.5)	333 (1.6)	465 (1.0)

Fig. 3 Thermal analysis of Cu-Mn-Cr/γ-Al$_2$O$_3$ catalyst with Cu/(Mn+Cr) molar ratio 1:5 and Mn/Cr molar ratio 1.5 (40 % replacement of Mn by Cr)

DTA, DTG and TG analysis of the samples with Cu/Cr molar ratio 2:1 and 1:5 and mixed Cu-Mn-Cr catalyst were carried out, the results of which are presented in Figs. 1-3 and Table I.

Earlier works showed that two or three step reduction pathway of unsupported CrO_3 is accompanied by simultaneous decomposition of intermediate CrOx phases (Cr_3O_8 and Cr_5O_{12}) into crystalline Cr_2O_3 at about 500°C. [22]. Our experiment showed onset temperature of CrO_3 decomposition 32°C and end of the process at 480°C.

TG, DTG and DTA curves of copper nitrate showed four distinct weight loss regions with total weight loss of 60.8% (recalculated on the base of supported substance) [23]. Analyzing the results of thermal analysis it can conclude that decomposition of the supported copper nitrate is stepwise process. The largest weight loss 19.4% (49.6 % on the base of supported substance) centered on 260°C shows that water and nitric oxide are lost simultaneously. Only CuO was observed by X-ray analysis after calcination at 450°C.

TG, DTG and DTA curves of manganese nitrate showed total weight loss of 41.0% (recalculated on the base of supported substance) [24] and this is very close to the theoretical value of 44,1%, calculated from the formulas of $Mn(NO_3)_2$ and Mn_2O_3. Obviously dehydration and partial decomposition of manganese nitrate occur during drying at 120°C. The stepwise decomposition of the manganese nitrate to MnO_2 takes place in a large temperature region up to 530°C. The last weight loss at 530-614°C amounts to a 1.9% (7.5 % on the base of supported substance) weight loss and could be assigned to the decomposition of MnO_2 to Mn_2O_3, in which the weight loss is estimated to be 9.2 %.

TG curves of the mixed Cu-Cr/γ-Al$_2$O$_3$ catalyst with Cu/Cr molar ratio 2:1 (Fig. 1) shows 56.8% total weight loss, recalculated on the base of supported substance, which is very close to the theoretical value of 54,7%. Four well expressed weight losses, due to different decomposition steps can be seen. The first weight loss of 30.5% below 150°C (recalculated on the base of supported substance) can be attributed to the loss of hydrated water and first stage of copper nitrate and CrO_3 decomposition. The second weight loss occurs at 150 - 465°C and amount of weight loss of 21.1% (recalculated on the base of supported substance) is associated with complete copper nitrate decomposition, CrO_3 to Cr_2O_3

transformation and $Cu_{1.5}Cr_{1.5}O_4$ formation. The third weight loss at 465 – 506°C (4.7 % weight loss) can be attributed to formation of $CuCr_2O_4$ spinel. These suggestions were confirmed by XRD results (Fig. 7). The forth weight loss (0.5% weight loss) is due to spinel transformation, which is visible more clear in Fig. 2.

TG curves of the mixed Cu-Cr/γ-Al$_2$O$_3$ catalyst with Cu/Cr molar ratio 1:5 (Fig. 2) shows four main weight losses connected with the same decomposition processes in different proportion. The first weight loss of 13.8% below 180°C (recalculated on the base of supported substance) is considerably smaller obviously due to low amount of copper nitrate and a major amount of CrO$_3$. The second weight loss (4.4%), centered at 242 ^{o}C is due to complete copper nitrate decomposition. The third weight loss (14.1%) can be attributed to CrO$_3$ to Cr$_2$O$_3$ transformation and spinel formation. The last weight loss of 4.0 % (recalculated on the base of supported substance) at temperatures higher than 460°C probably is due to the successive transformation of $Cu_{1.5}Cr_{1.5}O_4$ to $CuCr_2O_4$. This suggestion is in agreement with our XRD analysis (Fig. 7) and with the results of Monnier et al. [25].

Fig. 3 shows TG, DTG and DTA curves of the mixed Cu-Mn-Cr/γ-Al$_2$O$_3$ catalyst with Cu/(Mn+Cr) molar ratio 1:5 and Mn/Cr molar ratio 1.5 (40% replacement of Mn by Cr). The total weight loss of 43.3% (recalculated on the base of supported substance) (47.0% theoretical) can be divided to four clear expressed steps of decomposition. The first one (9.8%) is due mainly to copper and manganese nitrate decomposition. The second (26.6%) and third (6.5%) weight losses can be attributed to complete decomposition of nitrates and CrO$_3$, formation of MnO$_2$ and different spinel structures. This suggestion is in agreement with our XRD analysis (Fig. 8). The fourth weight loss (4.1%) is associated with Mn$_2$O$_3$ formation and spinels transformation.

- *Texture Measurements*

Table II shows the specific surface area, pore volume and average pore diameter of the support, basic samples and mixed Cu-Mn-Cr sample, used for carrying out the process under the conditions closed possibly to industrial.

TABLE II
SPECIFIC SURFACE, PORE VOLUME AND AVERAGE PORE DIAMETER OF SUPPORT AND SELECTED CATALYSTS.

Composition	S_{BET} m^2/g	V_{total} cm^3/g	$D_{average}$ nm
Al$_2$O$_3$	219	0.40	7.40
*Cu/Mn 2:1	153	0.25	6.5
*Cu/Mn 1:5	152	0.26	5.8
**Cu/(Mn+Cr) 1:5	210	0.27	5.3

*Active component loading 20 %
**Active component loading 15.0 %, Mn/Cr molar ratio 0.25 (80% replacement of Mn by Cr).

It is seen that the specific surface area of the basic samples decreases up to 30 % compared to the support. The surface area of the mixed catalyst is significantly larger because of less active component loading and calcination at lower temperature. The pore volume and average pore diameter of the support and all catalysts are nearly identical.

The adsorption-desorption isotherm for the samples, presented in Table II and their corresponding pore size distributions are shown in Figs. 4, 5 and 6, respectively. As can be seen all catalysts show a type-H1 hysteresis loop with capillary condensation at a relative pressure of P/P_0= 0.4. The adsorption increases gradually with an increase of P/P_0 without a steep jump in the hysteresis loop. The slope and the height of the step are clear indications of very well defined mesopores with narrow pore size distribution.
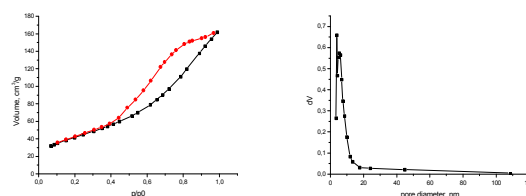

Fig. 4 Adsorption-desorption isotherm and pore size distributions of Cu-Mn 2:1
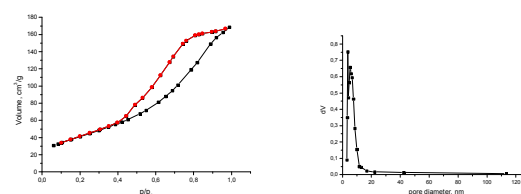

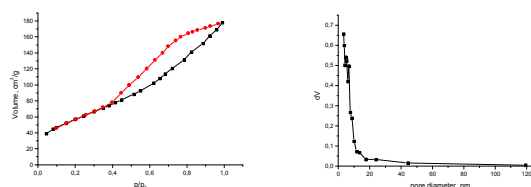Fig. 5 Adsorption-desorption isotherm and pore size distributions of Cu-Mn 1:5

Fig. 6 Adsorption-desorption isotherm and pore size distributions of Cu/(Mn+Cr) 1:5 and Mn/Cr molar ratio 0.25 (80 % replacement of Mn by Cr)

- *Powder X-ray Diffraction (XRD)*

The phase composition of the samples is analyzed on the basis of powder X-ray diffraction data presented in Figs. 7 and 8.

In Fig. 7 are presented the XRD patterns of mixed copper-chromium samples with Cu/Cr molar ratio 2:1 after thermal treatment at 450°C and 500°C. The diffractogram of alumina supported CrO$_x$ is shown for comparison. The analysis of the XRD data agrees well with thermogravimetric results regarding formation of CuCr$_2$O$_4$ spinel in temperature range 450-500°C (Fig. 1). The well discernible reflections at 2Θ = 24.4, 33.2 and 36.2 indicate the presence of Cr$_2$O$_3$ (marked with *, JCPDS 38-1479) in the sample calcined at 450°C. These reflections almost disappear and new ones at 2Θ = 18.4, 30, 4, 35.6, 43.5, 53.8, 57.5 and 63.2 (marked with o, JCPDS

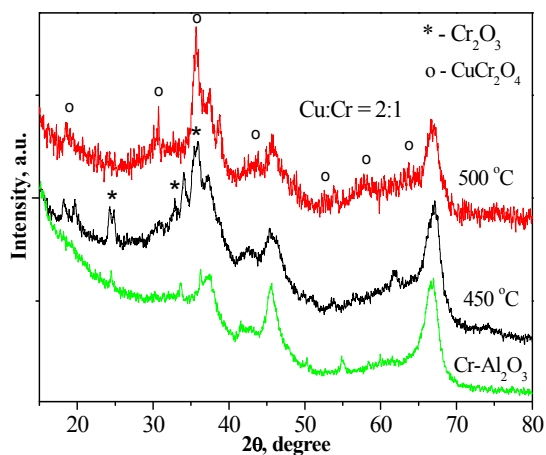26-509) are observed. These peaks are typical for $CuCr_2O_4$ spinel structure.

Fig. 7 XRD patterns of mixed copper-chromium catalysts with Cu/Cr molar ratio 2:1, calcined at 450 and 500 ^{o}C.
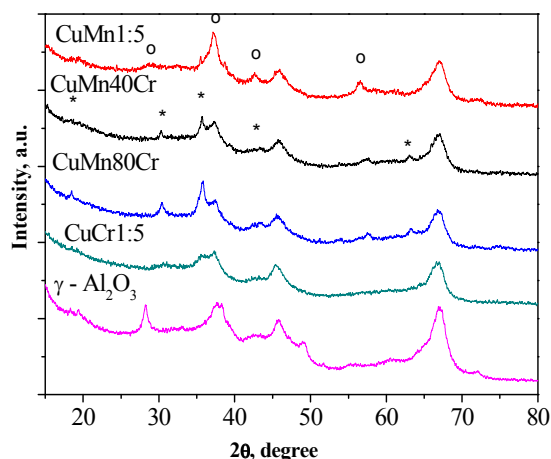

Fig. 8 XRD patterns of mixed copper-manganese catalysts with Cu/Mn molar ratio ratio1:5 after partial or total replacement of Mn with Cr

In Fig. 8 are shown the XRD patterns of copper-manganese catalysts with Cu/Mn molar ratio1:5 after partial or total replacement of Mn with Cr. The diffraction lines of γ-Al_2O_3 support are clearly identified in the XRD patterns of all samples. The typical reflections of MnO_2 at 2Θ = 28.6, 37.2, 42.8 and 56.5 (marked with o, JCPDS 24-0735) are observed in the X-ray diffractograms of the catalyst with Cu-Mn ratio 1:5. The broadness of the peaks indicates poor crystallization of MnO_2 and presence of defects in the crystal structure. The average particles size is about 10 nm. Additionally, the presence of a highly dispersed Cu-Mn spinel phase with a relatively small crystallite size could be suggested on the base of Cu-Mn-O phase diagram recently published [26]. The weak reflection at 2Θ = 35.9 could be related to the most intense peak, corresponding to (311) plane of $Cu_{1.5}Mn_{1.5}O_4$ spinel phase (JCPDS 35-1172). The other characteristic peaks

overlap those of MnO_2. The replacement of Mn with 40 wt.% Cr causes broadening and decreased intensity of the peaks at 2Θ = 42.8 and 56.5 that belonged to MnO_2. New weak peaks at 2Θ = 18.4, 30.2, 35.6 and 63.0, related to $Mn_{1.5}Cr_{1.5}O_4$ (marked with *, JCPDS 33-0892), appear in the XRD pattern of Cu-Mn (40% Cr). All these peaks became more visible in XRD pattern of Cu-Mn (80 wt.% Cr) due to the increased amount of chromium. However, it should be stressed that all these peaks are difficult distinguishable and the reason should be the high dispersion of spinel particles.

In the XRD pattern of sample Cu-Cr 1:5 (Mn is totally replaced with Cr) are observed weak and broad reflections at 2Θ = 30.6 35.6 and 43.4, related to poorly crystallized $CuCr_2O_4$ (JCPDS 26-0509).

- *Temperature Programmed Reduction (TPR)*

The reduction behavior of the samples is studied by means of H_2-TPR measurements. The TPR profiles of the samples are shown in Fig. 9.

The reduction profile of Cu-Mn with ratio 1:5 exhibits peak with well-defined maximum at 293 ^{o}C that should be ascribed to reduction of MnO_2. The comparison with the data reported for bulk MnOx catalysts reveals that the reduction of Cu-Mn 1:5 sample is completed at lower temperatures compared with that of pure MnOx. The promoting effect of copper on the reduction of manganese ions can be the reason for this behavior [27]. Another explanation is proposed by [28]. The structural defects associated to oxygen vacancies or a high dispersion of MnOx in the mixed phase probably play role for easier reduction of mixed Mn-Cu catalysts in comparison with bulk Mn_2O_3. A broad shoulder in the low-temperature side of the profile could be related to the reduction of copper species. The replacement of manganese with 40 wt.% Cr changes the shape of reduction peak and shifts T_{max} to lower temperature. The increased amount of Cr in the sample Cu-Mn80Cr facilitates additionally the reducibility. However, the complete replacement of Mn with Cr hampered slightly the reducibility in comparison with that of CuMn80Cr. The shift of T_{max} to higher temperatures could be due to formation of $CuCr_xO_y$ spinel structures in agreement with observations of [29]. The TPR profile of sample with Cu/Cr molar ratio 2:1 is with almost the same shape and position as those of Cu/Cr molar ratio 1:5. Significantly larger hydrogen consumption is due to the reduction of higher amount of copper in this sample.

The reduction behavior correlates well with catalytic activity toward CO, methanol and DME oxidation over the sample Cu/(Mn+Cr) with molar ratio 1:5 and Mn/Cr molar ratio 0.25 in the active component. The presence of copper species with improved reducibility (T_{max} = 220 ^{o}C) contributes to enhanced activity toward oxidation of all components of waste gases from formaldehyde production.

- *Catalyst Testing*

Catalytic activity of the supported Cu-Mn catalysts with Cu/(Mn+Cr) 2:1 and Cu/(Mn+Cr) 1:5 molar ratio were investigated in order to clarify the effect of Mn replacement by Cr in the active component (Figs. 10 and 11).
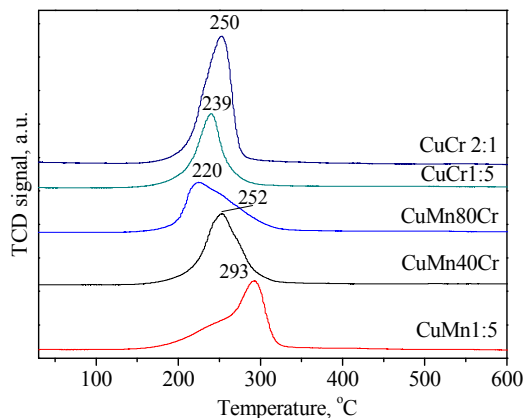
Fig. 9 TPR profiles of studied catalysts

The results show a general trend of decreasing the activity toward CO and methanol oxidation and increasing the activity toward DME oxidation with the increase of chromium for both groups of catalyst. This general trend, however, contains specific features, depending on the composition of the catalyst and the nature of the oxidized gas. In the sample consisting predominantly of copper (Cu/Mn molar ratio 2:1) the degree of CO oxidation decreases sharply in the whole concentration region (from 100% for pure Cu-Mn to 68 % for pure Cu-Cr catalyst), while in the sample consisting predominantly of manganese (Cu/Mn molar ratio 1:5) the slope of the curve is different. The replacement of small amount of manganese with chromium (to 20% Cr) leads to a sharp decrease in activity in relation to CO oxidation, after which the decrease is significantly less pronounced. In general, the activity of the samples from the second group is lower than that of the samples from the first group. This is in agreement with our previous results [21], [24] showing low activity of chromium oxides compared with copper and manganese oxides.

With respect to methanol oxidation the trends are more difficult to explain. In this case the replacement of Mn with Cr in the copper-rich oxide samples does not affect the catalytic activity up to 80% chromium. It is in agreement with the higher activity of the copper containing catalysts. Replacement of Mn with Cr in the manganese-rich oxide samples leads to a sharp decrease in activity to 40% Cr content, after which the trend reverses.

DME oxidation increases with Mn replacement for both groups of catalysts and this is more pronounced over the manganese-rich samples. In general the activity of the samples from the second group is much higher than that of the samples from the first group. This is due to the substantial difference in the individual activity of copper, manganese and chromium oxides and it is in consent with our previous results [21].

Table III shows the specific surface area of the samples with Cu/(Mn+Cr) molar ratio 1:5 and different Mn/Cr molar ratio and active component loading. Clear tendency for reduction of specific surface area with chromium content increase can be seen. The results obtained cannot be explained by substantial influence of the surface area. Obviously the

catalyst composition plays a dominant role in the oxidation processes.
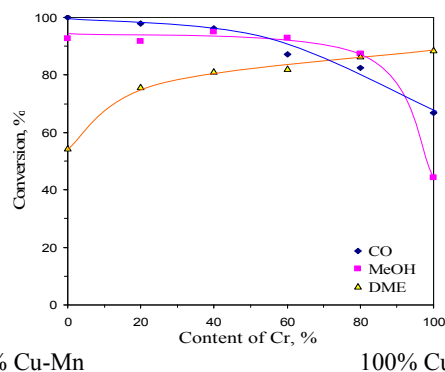

Fig. 10 Effect of manganese replacement by chromium in active component of Cu-Mn-Cr/γ-Al$_2$O$_3$ catalyst on CO, CH$_3$OH and DME oxidation (T$_{CO}$=180 ^{o}C, T$_{MeOH}$=180 ^{o}C, T$_{DME}$=280 ^{o}C); Cu/(Mn+Cr) molar ratio 2:1
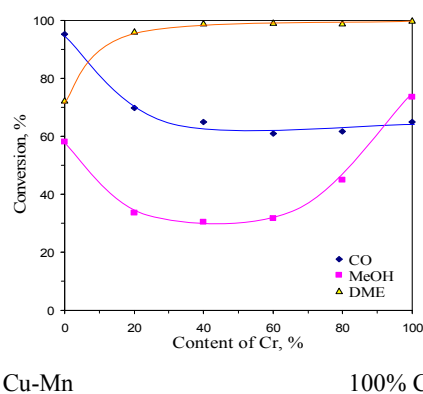

Fig. 11 Effect of replacement of manganese with chromium in active component of Cu-Mn-Cr/γ-Al$_2$O$_3$ catalyst on CO, CH$_3$OH and DME oxidation (T$_{CO}$=160 ^{o}C, T$_{MeOH}$=180 ^{o}C, T$_{DME}$=280 ^{o}C); Cu/(Mn+Cr) molar ratio 1:5

TABLE III
SPECIFIC SURFACE, PORE VOLUME AND AVERAGE PORE DIAMETER OF SUPPORT AND SELECTED CATALYSTS

Cu/(Mn+Cr) molar ratio	Mn/Cr molar ratio	Active component, %	S$_{BET}$ m^2/g
1:5	100 % Mn	15.0	199
1:5	4.0	15.0	186
1:5	1.5	15.0	180
1:5	0.6	10.0	180
1:5	100 % Cr	10.0	165
Al$_2$O$_3$	-	-	219

Two samples with Cu/(Mn+Cr) molar ratio 2:1 and 1:5 and Mn/Cr molar ratio 0.25 were studied in order to evaluate the possibility for practical application of the mixed Cu-Mn-Cr/γ-Al$_2$O$_3$ catalysts in simultaneous oxidation of CO, CH$_3$OH and DME. Commercial γ-Al$_2$O$_3$ with fraction of 5.0–5.5 mm as a carrier was used. The results are presented in Figs. 12 and 13.
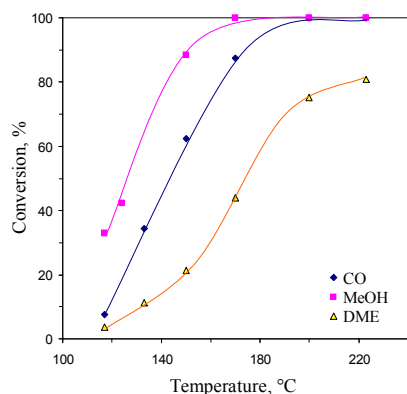
Fig. 12 Temperature dependence of CO, CH$_3$OH and DME oxidation over Cu-Mn-Cr/γ-Al$_2$O$_3$ catalyst with Cu/(Mn+Cr) molar ratio 2:1 and Mn/Cr molar ratio 0.25 (80% replacement of Mn by Cr)
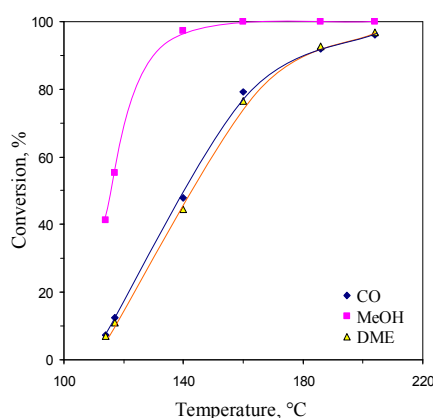

Fig. 13 Temperature dependence of CO, CH$_3$OH and DME conversion over Cu-Mn-Cr/γ-Al$_2$O$_3$ catalyst with Cu/(Mn+Cr) molar ratio 1:5 and Mn/Cr molar ratio 0.25 (80% replacement of Mn by Cr)

The results obtained confirm expectations for high activity of the mixed samples in CO and methanol oxidation. The oxidation process started at temperatures lower than 120°C for both catalysts and complete oxidation was achieved at temperatures about 160°C for methanol oxidation and 200°C for CO oxidation. The results of DME oxidation reveal that catalysts differ substantially in their activity. A noticeable oxidation was observed, however, at about 120°C for both catalysts, but acceleration of reaction velocity depends strongly on the catalyst composition. Obviously the catalyst with Cu/(Mn+Cr) molar ratio 1:5 and Mn/Cr molar ratio 0.25 shows much higher activity and complete oxidation can be achieve at 220°C.

IV. CONCLUSIONS

The present study demonstrates that the Cu-Mn-Cr/γ–alumina supported catalysts have enhanced activity toward CO, methanol and DME oxidation. Cu/(Mn+Cr) molar ratio 1:5 and Mn/Cr molar ratio 0.25 in the active component can ensure successful oxidation of CO CH$_3$OH and DME and could be a good base for preparation of industrial catalyst for combustion of waste gases from formaldehyde production.

The active component of the mixed Cu-Mn-Cr/γ–alumina catalysts consists of at least six compounds - CuO, Cr$_2$O$_3$, MnO$_2$, Cu$_{1.5}$Mn$_{1.5}$O$_4$, Cu$_{1.5}$Cr$_{1.5}$O$_4$ and CuCr$_2$O$_4$, depending on the Cu/Mn/Cr molar ratio. Chemical composition strongly influences catalytic properties, this effect being quite variable with regards to the different processes.

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