Alumina Supported Copper-Manganese Catalysts for Combustion of Exhaust Gases: Catalysts Characterization

Krasimir I. Ivanov, Elitsa N. Kolentsova, Dimitar Y. Dimitrov, Georgi V. Avdeev, Tatyana T. Tabakova

Abstract—In recent research copper and manganese systems were found to be the most active in CO and organic compounds oxidation among the base catalysts. The mixed copper manganese oxide has been widely studied in oxidation reactions because of their higher activity at low temperatures in comparison with single oxide catalysts. The results showed that the formation of spinel $Cu_xMn_{3-x}O_4$ in the oxidized catalyst is responsible for the activity even at room temperature. That is why the most of the investigations are focused on the hopcalite catalyst ($CuMn_2O_4$) as the best copper-manganese catalyst. Now it's known that this is true only for CO oxidation, but not for mixture of CO and VOCs. The purpose of this study is to investigate the alumina supported copper-manganese catalysts with different Cu/Mn molar ratio in terms of oxidation of CO, methanol and dimethyl ether.

The catalysts were prepared by impregnation of γ-Al_2O_3 with copper and manganese nitrates and the catalytic activity measurements were carried out in two stage continuous flow equipment with an adiabatic reactor for simultaneous oxidation of all compounds under the conditions closest possible to the industrial. Gas mixtures on the input and output of the reactor were analyzed with a gas chromatograph, equipped with FID and TCD detectors. The texture characteristics were determined by low-temperature (- 196°C) nitrogen adsorption in a Quantachrome Instruments NOVA 1200e (USA) specific surface area & pore analyzer. Thermal, XRD and TPR analyses were performed.

It was established that the active component of the mixed Cu-Mn/γ–alumina catalysts strongly depends on the Cu/Mn molar ratio. Highly active alumina supported Cu-Mn catalysts for CO, methanol and DME oxidation were synthesized. While the hopcalite is the best catalyst for CO oxidation, the best compromise for simultaneous oxidation of all components is the catalyst with Cu/Mn molar ratio 1:5.

Keywords—Supported copper-manganese catalysts, CO and VOCs oxidation.

I. INTRODUCTION

COPPER based catalysts are extensively studied during the last year due to their good catalytic performance in many industrially important reactions such as CO and VOCs oxidation, steam reforming, water gas shift reaction and other important hydrogenation and oxidation reactions [1]-[3]. It is considered that the copper-manganese mixed oxides are promising because of their high thermal stability, chemical resistance and low cost [4]. Morales et al. [5] have reported that total oxidation of VOCs over Mn-Cu mixed oxide was more efficient in comparison with Mn and Cu pure oxides. According to many literature sources the formation of Cu-Mn spinels with atomic ratio Cu:Mn 1:2 is the most suitable for the oxidation of CO [6]. Mixed copper manganese oxide catalyst $CuMn_2O_4$ (hopcalite) has been widely studied in oxidation reactions because of its high activity at low temperatures [7]. The results showed that the formation of the spinel $Cu_xMn_{3-x}O_4$ in the oxidized catalyst is responsible for its high activity [8, 9]. It is generally accepted that in the Cu–Mn catalysts the most active phase for low temperature CO oxidation is an amorphous $CuMn_2O_4$ spinel [2], [10].

The catalytic oxidation of methanol to formaldehyde is an important industrial process in which the waste gas, in addition to CO, contains methanol and dimethyl ether. Several patents are known, describing different oxide catalysts for purification of the exhaust gases from formaldehyde production. Cremona et al. [11] propose copper-manganese catalyst modified by rare-earth metals. According to the invention samples with 10 to 75% Mn (as MnO_2), 8 to 50% copper (as CuO) and 2 to 15% La_2O_3 are suitable for industrial application. Temperature of 250°C of the gas stream entering the bed is sufficient to ensure 100% yield in the combustion of CO (1.6%), methanol (700 ppm), formaldehyde (200 ppm) and DME (2300 ppm). The patent [12] reveals very high activity of the supported Cu-Cr oxides with 20-30% of copper (as CuO) at the same conditions.

Our previous investigation [13] indicates that γ–alumina supported Cu-Mn oxide catalysts are effective for simultaneous oxidation of methanol, CO and DME (Fig. 1). The influence of the preparation methods (type of support, calcination temperature, Cu/Mn molar ratio and active component loading) were studied in details. It was established that single Cu and Mn oxide catalysts are less active than mixed ones with respect to all three compounds investigated. Obviously the synergetic effect between copper and manganese oxide increases the activity in all cases. This effect strongly depends on the catalyst composition and on the nature of oxidized compound.

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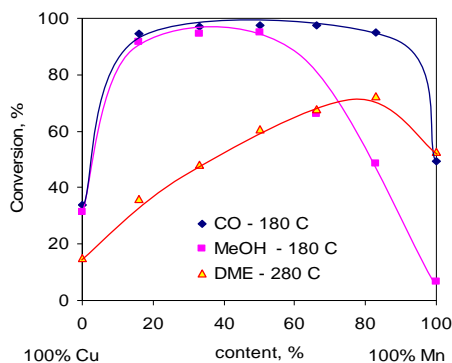
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Fig. 1 Effect of Cu/Mn molar ratio on CO, CH_3OH and DME oxidation ($T_{CO}=180^{o}C$, $T_{MeOH}=180^{o}C$, $T_{DME}=280^{o}C$).

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 molar 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, in DME oxidation the higher activity is shown by manganese-rich oxide specimens.

The main idea of this study is to obtain more information about γ-Al$_2$O$_3$ supported Cu-Mn catalysts and to evaluate the possibility for their practical application in simultaneous oxidation of CO, CH_3OH 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.

Our results are in agreement with the results of other autors. It has already been shown by [5] that the incorporation of small amounts of copper in MnO_x improve ethanol combustion to CO_2. These authors suggested that the adition of copper reduced the crystalline structure of manganese oxide, and thus increased the number of oxygen vacancies.

II. EXPERIMENTAL

A. Catalysts Preparation

All catalysts were prepared by the wet impregnation method. Commercial γ-Al$_2$O$_3$ with fraction of 0.6-1.0 and 5.0–5.5 mm was used as support impregnated with copper and manganese nitrates. Prior to the impregnation, the carrier was calcined for 2 hours at $500^{o}C$ in a ceramic furnace. After keeping it at a room temperature, previously prepared solutions of copper and manganese nitrates were added. γ-Al$_2$O$_3$ stays in the salt solutions at $80^{o}C$ for 12 hours. 10-hour drying follows at a temperature of $120^{o}C$, and calcination at $450^{o}C$ for 4 hours.

B. Catalyst Charachterisation

Thermal Analysis (TG, DTG and DTA)

Computerized thermal installation "Stanton Redcroft" (England) was used for thermal analysis of the samples under the following experimental conditions: heating temperature range - 20-650°C, heating rate - 10°C.min^{-1}, 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.

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^{o} (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 0.05 g.

Activity Measurements

Two stage equipment with an adiabatic reactor for simultaneous oxidation of all compounds under the conditions closest possible 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 [14].

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).

The activity of the catalysts was evaluated according to the oxidation degree of gases which have passed through the catalyst layer, in percentages.

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III. RESULTS

Thermal Analysis (TG, DTG and DTA)

DTA, DTG and TG analysis of copper and manganese nitrates and samples with Cu/Mn molar ratio 2:1 and 1:5 were carried out. The results are presented in Figs. 2–5 and Table I.
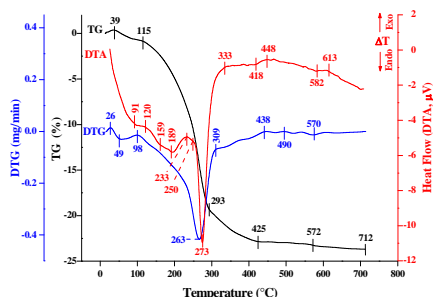
Fig. 2 Thermal analysis of $Cu(NO_3)_2.xH_2O/\gamma-Al_2O_3$. Active component content 22.0%
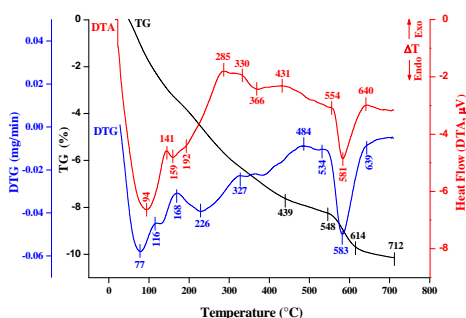
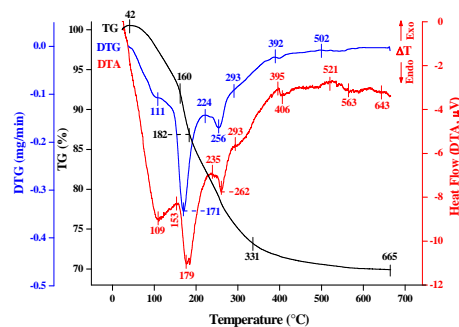Fig. 3 Thermal analysis of $Mn(NO_3)_3.xH_2O/\gamma-Al_2O_3$. Active component content 22.0%

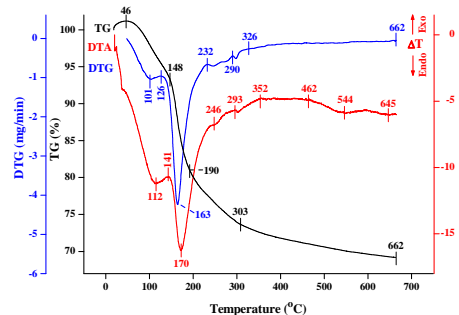Fig. 4 Thermal analysis of $Cu-Mn/\gamma-Al_2O_3$ (1:5). Active component content 21.0%

Fig. 5 Thermal analysis of $Cu-Mn/\gamma-Al_2O_3$ (2:1). Active component content 21.0%

TABLE I
THERMOGRAVIMETRIC RESULTS FOR DIFFERENT Cu-Mn/γ-Al$_2$O$_3$ CATALYSTS

Sample	Weight loss			
	First	Second	Third	Forth
	Onset temp.,^{o}C (Weight loss,%)	Onset temp.,^{o}C (Weight loss,%)	Onset temp.,^{o}C (Weight loss,%)	Onset temp.,^{o}C (Weight loss,%)
Fig. 3	39 (0.8)	115 (19.4)	293 (2.8)	425 (0.8)
Fig. 4	23 (3.8)	168 (2.9)	439 (1.9)	548 (1.9)
Fig. 5	54 (5.3)	160 (12.9)	182 (5.9)	303 (6.4)
Fig. 6	46 (5.8)	148 (17.6)	190 (2.2)	331 (2.3)

TG, DTG and DTA curves of copper nitrate over ambient to 800°C temperature range are shown in Fig. 2. Four distinct weight loss regions are observed with total weight of 60.8% (recalculated on the base of supported substance). This value is a little bit lower than the theoretical value of 67.1% calculated from the formulas of copper nitrate trihydrate and copper oxide. It is due to the loss of part of hydrated water during drying at 120°C before thermal analysis. Analyzing the results of thermal analysis we 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 263°C shows that water and nitric oxide are lost simultaneously. This is in agreement with the results of [15], which investigated decomposition of

unsupported copper nitrate. Only CuO was observed by X-ray analysis after calcination at 450°C.

TG, DTG and DTA curves of manganese nitrate are shown in Fig. 3. The total weight loss in this case is 41.0% (recalculated on the base of supported substance) and it 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%.

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Both catalysts with Cu/Mn molar ratio 1:5 (Fig. 4) and 2:1 (Fig. 5) show four weight losses, due to different decomposition steps and differ significantly from the results, presented in Figs. 3 and 4. Obviously the decomposition of nitrates mixture proceeds through significantly different pathway than that of single copper nitrate and manganese nitrate. The first weight loss below 150°C can be attributed to the loss of hydrated water and partial nitrate decomposition. The second and third weight losses occur at 150-330°C and amount of weight loss of 61.3% and 52.7% respectively (calculated on the base of supported substance) are associated mainly with copper nitrates decomposition. The last weight loss is associated with highly dispersed mixture of CuO and spinel (Cu/Mn molar ratio 2:1) or MnO_2 and spinel (Cu/Mn molar ratio 1:5) formation. This is in agreement with our XRD results (Fig. 10) and experimental results of [16] according to which at temperatures above 300°C in the active phase included only oxides. The absence of well-expressed endothermic effect in the temperature range 500-600°C connected with decomposition of MnO_2 to Mn_2O_3 suggests formation of stable spinel phase. The gradual reduction of the specimen weight is likely due to the loss of oxygen from the crystal structure of the resulting oxides, and the progress of oxide transformations [10].

The results for the thermal decomposition of a mixture of Cu-Mn nitrates in the scientific papers are incomplete. This required a study connected with the optimization of the heat treatment in order to obtain catalysts with a constant phase composition and the greatest possible specific surface area. Taking into account that the most active phase for low temperature CO oxidation is an amorphous $CuMn_2O_4$ spinel we can conclude that calcination of the precursor at about 450°C would be the most appropriate for preparation of active catalysts for CO and VOCs oxidation. This assumption was confirmed by the activity measurements, presented below.

Texture Measurements

Table II shows the specific surface area, pore volume and average pore diameter of the support, basic samples and Cu-Mn samples, used for carrying out the process under conditions that mimic closely the industrial ones. It is seen that the specific surface of the basic samples decreases to 30% compared to the support. The pore volume and average pore diameter of the support and all catalysts are nearly identical.

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

Composition	S_{BET} $m^2.g^{-1}$	V_{total} $cm^3.g^{-1}$	$D_{average}$ nm
Al_2O_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 2:1	188	0.32	6.8
**Cu/Mn 1:5	181	0.33	7.4

*Active component loading 22 %, calcination temperature 450°C, fraction 0.6-1.0 mm.
**Active component loading 21%, calcination temperature 450°C, γ-Al_2O_3 with particle size of 5.0-5.5 mm.

The adsorption-desorption isotherm for the samples, presented in Table II and their corresponding pore size distributions, are shown in Figs. 6, 7, 8, and 9, respectively. As can be seen all catalysts show a type-H1 hysteresis loop with capillary condensation at a relative pressure of P/Po= 0.4. The adsorption increases gradually with an increase of P/Po 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.
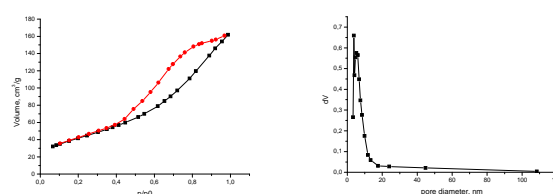

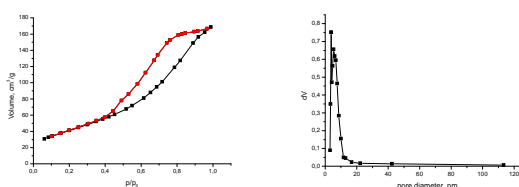Fig. 6 Adsorption-desorption isotherm and pore size distribution of Cu-Mn 2:1(S_{BET}=153 $m^2.g^{-1}$)

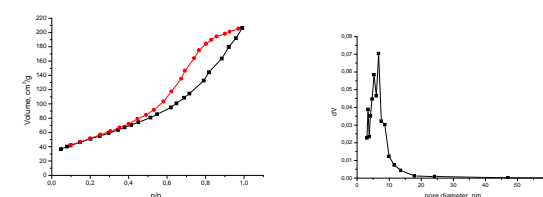Fig. 7 Adsorption-desorption isotherm and pore size distribution of Cu-Mn 1:5 (S_{BET}=152 $m^2.g^{-1}$)

Fig. 8 Adsorption-desorption isotherm and pore size distribution of Cu-Mn 2:1(S_{BET}=188 $m^2.g^{-1}$)
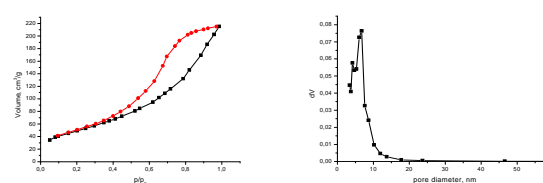

Fig. 9 Adsorption-desorption isotherm and pore size distribution of Cu-Mn 1:5 (S_{BET}=181 $m^2.g^{-1}$)

Powder X-ray Diffraction (XRD).

The powder X-ray diffraction patterns of the catalysts and support are presented in Fig. 10. The diffraction lines of γ-Al_2O_3 were clearly identified in the XRD patterns of all samples. Significant differences between diffractograms of both Cu-Mn samples were observed. The typical reflections of CuO at 2Θ = 35.6, 38.8, 48.6 and 61.8 (marked with *, JCPDS 02-1040) were observed in the X-ray difractogram of the catalyst with Cu-Mn ratio 2:1. The sharpness of the peaks indicated that the CuO particles are highly crystalline. The average size of about 30 nm was calculated on the basis of

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XRD (111) and (002) reflexions. In the Cu-Mn 1:5 sample, beside the dominant alumina pattern, some reflections of MnO_2 (marked with o, JCPDS 24-0735) were visible. The broadness of the peaks indicated poor crystallization of MnO_2 and presence of defects in the crystal structure. The average particles size was about 10 nm. This poor crystalline structure of manganese oxide may contain structural defects, in particular oxygen vacancies giving a best performance in VOCs oxidation. 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 [17]. The weak lines at $2\Theta =$ 35.9 and 43.0 belong to $Cu_{1.5}Mn_{1.5}O_4$ phase (JCPDS 35-1172). The other lines overlapped those of MnO_2. Our suggestion is consistent with the finding of Li et. al. [18] that have prepared copper manganese oxides catalysts with molar ratio Cu:Mn from 5:1 to 1:2 by co-precipitation method. The authors have observed by XRD formation of $Cu_{1.5}Mn_{1.5}O_4$ phase in all catalysts and the addition of higher amount copper or manganese resulted in the formation of CuO or Mn_2O_3 phase, respectively.
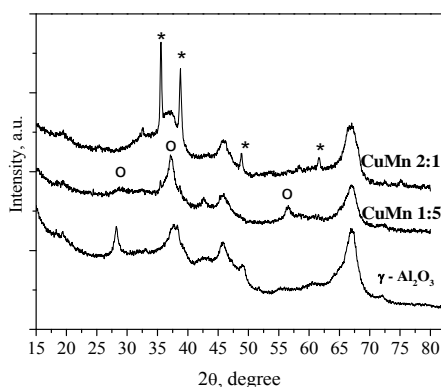

Fig. 10 XRD patterns of studied samples

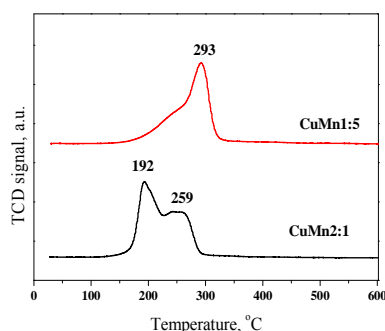*Temperature Programmed Reduction (TPR)*

Fig. 11 TPR profiles of studied samples

The reduction behavior of the samples was studied by means of H_2-TPR measurements. The TPR profiles of both samples are shown in Fig. 11. According to the literature data, the reduction of bulk CuO proceeds in a single step process with peak maximum about 300^oC [3].

The reduction peak of Cu-Mn with ratio 2:1 is complex with two components (T_{max} at 192 and 259^oC). The component at lower temperature may be assigned to the reduction of separate CuO phase, observed by XRD. The significant shift of T_{max} to lower temperature in comparison with that, reported for bulk CuO is a clear indication for presence of CuO particles with high dispersion. The component at higher temperature should be related to the reduction of manganese species. However, a separate MnO_x phase was not registered in XRD pattern. The presence of a highly dispersed Cu-Mn spinel phase with a relatively small crystallite size was suggested. In this case the component with T_{max} 259^oC could be related to the reduction of this phase. The reduction profile of Cu-Mn with ratio 1:5 exhibits peak with well-defined maximum at 293^oC that should be ascribed to reduction of MnO_2. The comparison with the data reported for bulk MnO_x catalysts revealed that the reduction of Cu-Mn 1:5 sample was completed at lower temperatures compared with that of pure MnO_x. The promoting effect of copper on the reduction of manganese ions can be the reason for this behavior [19]. Another explanation was proposed by [5] The easier reduction of mixed Mn-Cu catalysts in comparison with bulk Mn_2O_3 can be associated to the presence of structural defects, in particular oxygen vacancies, or a high dispersion of MnO_x in the mixed phase. A broad shoulder in the low-temperature side of the profile could be related to the reduction of copper species.

Higher CO and MeOH oxidation activity of Cu-Mn 2:1 can be reasonably correlated with its better reducibility.

Activity Measurements

Two samples with Cu/Mn molar ratio 2:1 and 1:5 were studied in order to evaluate the possibility for practical application of mixed Cu-Mn/γ-Al_2O_3 catalysts in simultaneous oxidation of CO, CH_3OH and DME. Commercial γ-Al_2O_3 with fraction of 5.0–5.5 mm as a carrier was used. The results are presented in Figs. 12 and 13.
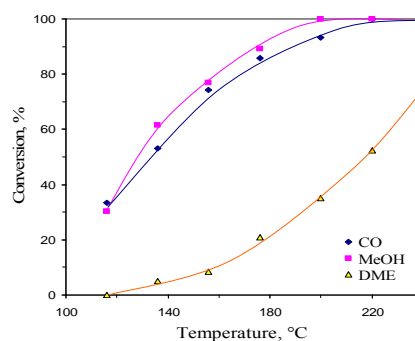

Fig. 12 Temperature dependence of CO, CH_3OH and DME conversion over Cu-Mn/γ-Al_2O_3 catalyst with Cu/Mn molar ratio 2:1

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 100^oC for both catalysts and complete oxidation was achieved at temperatures about 160^oC for methanol oxidation and 220^oC for CO oxidation. The results of DME oxidation reveal that

catalysts differ substantially in their activity. A noticeable oxidation was observed, however, at about 100°C for the catalyst with Cu/Mn molar ratio 1:5 and at about 140°C for the catalyst with Cu/Mn molar ratio 2:1. The acceleration of the reaction velocity strongly depends on the catalyst composition. Obviously the catalyst with Cu/Mn molar ratio 1:5 shows much higher activity and complete oxidation can be achieve at about 240°C.
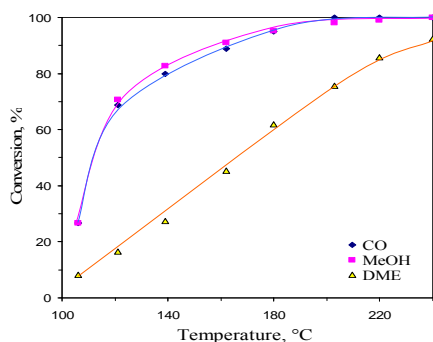

Fig. 13 Temperature dependence of CO, CH$_3$OH and DME conversion over Cu-Mn/γ-Al$_2$O$_3$ catalyst with Cu/Mn molar ratio 1:5

Considering close similarity of the values of BET specific surface area, pore volume and average pore diameter for both catalysts, the results can be interpreted as confirmation that the specific surface area of the catalysts is not the dominant factor in the oxidation of CO, methanol and DME on γ-alumina supported copper-manganese catalysts, especially in the frame of our experiments.

IV. CONCLUSIONS

The synthesis of Cu-Mn/γ–alumina supported oxide materials by wet impregnation method is an appropriate approach for development of catalysts with enhanced activity toward CO, methanol and DME oxidation. The thermal decomposition of the supported copper and manganese nitrates results in a high surface area material with a very well defined mesopores and narrow pore size distribution.

It was established that the phase composition and reduction properties of mixed Cu-Mn/γ–alumina catalysts depends on the Cu/Mn molar ratio. The XRD analysis indicated formation of highly dispersed Cu$_{1.5}$Mn$_{1.5}$O$_4$ phase in all catalysts. The presence of additional phase of CuO or MnO$_2$ was observed in the copper-rich or manganese-rich samples, respectively.

A lower amount of copper in the catalyst with Cu/Mn molar ratio 1:5 inhibits the crystallization of manganese oxide. This poor crystalline structure of manganese oxide may favor structural defects formation, in particular oxygen vacancies giving a best performance in DME combustion to CO$_2$. Additionally, the availability of structural defects agrees well with reduction behavior of this catalyst.

ACKNOWLEDGMENT

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