

Alumina Supported Copper-Manganese Catalysts for Combustion of Exhaust Gases: Effect of Preparation Method

Krasimir I. Ivanov, Elitsa N. Kolentsova, Dimitar Y. Dimitrov

Abstract—The development of active and stable catalysts without noble metals for low temperature oxidation of exhaust gases remains a significant challenge. The purpose of this study is to determine the influence of the preparation method on the catalytic activity of the supported copper-manganese mixed oxides in terms of VOCs oxidation. The catalysts were prepared by impregnation of γ - Al_2O_3 with copper and manganese nitrates and acetates and the possibilities for CO, CH_3OH and dimethyl ether (DME) oxidation were evaluated using continuous flow equipment with a four-channel isothermal stainless steel reactor. Effect of the support, Cu/Mn mole ratio, heat treatment of the precursor and active component loading were investigated. Highly active alumina supported Cu-Mn catalysts for CO and VOCs oxidation were synthesized. The effect of preparation conditions on the activity behavior of the catalysts was discussed.

The synergetic interaction between copper and manganese species increases the activity for complete oxidation over mixed catalysts. Type of support, calcination temperature and active component loading along with catalyst composition are important factors, determining catalytic activity. Cu/Mn molar ratio of 1:5, heat treatment at 450°C and 20 % active component loading are the best compromise for production of active catalyst for simultaneous combustion of CO, CH_3OH and DME.

Keywords—Copper-manganese catalysts, Preparation methods, Exhaust gases oxidation.

I. INTRODUCTION

THE Volatile Organic Compounds (VOCs) are a broad class of chemicals and at this stage more than 300 compounds are classified as such by the United States Environmental Protection Agency [1]. Various technologies for eliminating VOCs have been developed, with catalytic oxidation being among the most effective ones [2]. The main advantages of this method are its relatively low cost and the possibility to remove very small amounts of VOCs (< 0.1%) in the waste gases. Usually this type of catalysts are synthesized by using a small amount of noble metals (0.05-2%), most commonly Au, Pt and Pd, highly dispersed on materials with highly developed surface such as SiO_2 or Al_2O_3 [3]-[6]. Satisfactory activity, however, occurs only in systems with nano-sized metal particles (0.5-5.0 nm) [5]. This

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).

significantly complicates the obtaining process and therefore further increases the cost of the final product. Another disadvantage of this type of catalysts is their relatively rapid deactivation [4]. These circumstances have encouraged the search for cheaper and more efficient materials based on metal oxides [7], [8]. The main advantage of these systems is their highly developed surface at high temperatures, which lengthens their operation time.

It is known that copper oxides show high catalytic activity in the oxidation of CO [7]-[9], related to the reduction of CuO to Cu_2O . According to some scientists [7], [8], [10], [11] this process can be slowed down by the presence of other transition metals such as Mn, Cr, etc. It is considered that the copper-manganese mixed oxides are promising because of their high thermal stability, chemical resistance and low cost [11]. The methods of synthesis, however, are essential for the obtaining of active catalysts.

One of the main factors that determine the activity of the oxides is the temperature, at which they are obtained [12], [13]. The studies [14] showed that the activity of the manganese oxides supported on γ - Al_2O_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. [15] showed that a hopcalite catalyst (80% MnO_2 and 20% CuO) was comparable to a $\text{Pt}/\text{Al}_2\text{O}_3$ 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, which is the most suitable for the oxidation of CO [16]. Many efforts are focused on CO oxidation because it is the dominating by-product of important industrial processes. Often 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.

The purpose of this study is to determine the influence of the preparation method on the catalytic activity of the supported copper-manganese mixed oxides in terms of simultaneous oxidation of CO, methanol and DME.

II. MATERIALS AND METHODS

All catalysts were prepared by the wet impregnation of

different supports with fraction of 0.6-1.0 mm. Prior to the impregnation, the carrier was calcined for 2 hours at 500°C in a ceramic furnace. After keeping it at room temperature, previously prepared solutions of copper and manganese nitrates or copper and manganese acetates with desired ratio were added. The support remained immersed for 12 hours in the salt solutions at 80°C. After this, 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 at 10°C/min to desired level, where it was held for 4 hours. Thermogravimetric analysis (TG), differential thermogravimetric analysis (DTG) and differential thermal analysis (DTA) 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. The texture characteristics were determined by low-temperature (77.4 K) nitrogen adsorption in a Quantachrome Instruments NOVA 1200e (USA) specific surface area & pore analyser.

The catalytic measurements 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. 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 stream 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 -Al₂O₃ in tubular pseudoisothermal reactor.

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, CO₂ and DME) and column MS-5A (for CO, oxygen 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.

III. RESULTS

A. Effect of Support on the Catalytic Activity of the Supported Cu-Mn Catalysts

As noted above, the activity of Cu/Mn catalyst regarding the complete CO oxidation is associated with the formation of CuMn₂O₄ spinel [16]. It can be expected that this also refers to the VOCs oxidation. This motivated us to start the selection of the support with such composition of the active component.

The hydrophobicity, acidity and pore characteristics of the catalyst support are very important for catalytic combustion. According to [17] the order of activity of a series of mixed oxide catalysts is in close agreement with the strong acidity of the samples. For the purpose of our investigation we chose

supports, which are widely used in practice, but differ significantly in their essential characteristics (Table I).

TABLE I
SPECIFIC SURFACE, PORE VOLUME AND AVERAGE PORE DIAMETER OF THE SUPPORTS

Support	S _{BET} m ² /g	V _{total} cm ³ /g	D _{average} nm
Al ₂ O ₃	219	0.40	7.40
Silicaalumogel SiO ₂ 87%, Al ₂ O ₃ 17%	500	0.40	25
Silicagel	450	1.0	10
Silicagel type A	720	0.4	2.5

The results for CO, methanol and DME oxidation on the catalysts with Cu/Mn molar ratio 1:2, prepared by using nitrate solutions, are presented in Figs. 1-3. In all cases the only product of oxidation processes is CO₂.

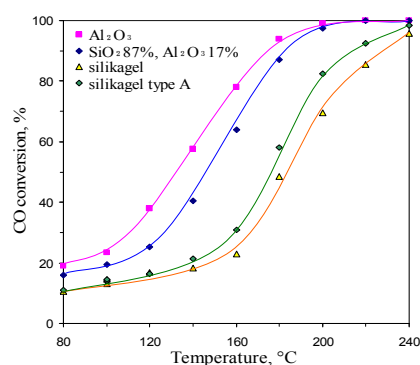


Fig. 1 Effect of support on CO oxidation activity of Cu-Mn catalyst with Cu/Mn molar ratio 1:2. Active component 10 ± 0.5 %, calcination temperature 450°C

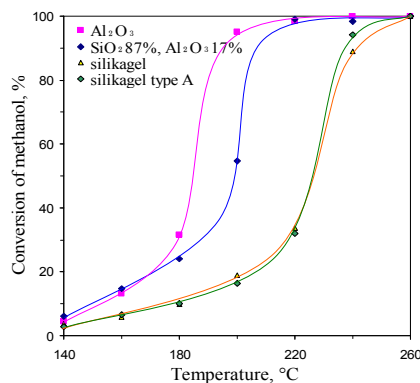


Fig. 2 Effect of support on CH₃OH oxidation activity of Cu-Mn catalyst with Cu/Mn molar ratio 1:2. Active component 10 ± 0.5 %, calcination temperature 450°C

The results show strong dependence of catalytic activity on the type of the support. The results of CO oxidation reaction (Fig. 1) reveal that catalysts differ substantially in their activity. The oxidation process started at temperatures lower than 80°C for all catalysts, but acceleration of reaction velocity depends strongly on the type of support. In terms of activity, we can distinguish two clearly formed groups: (i) catalysts, supported on pure silicagel and (ii) catalysts,

supported on alumina containing supports. It is remarkable that supports on the base of silica differ significantly in all main characteristics, but the activity of the supported catalysts is nearly the same. The situation is the same with alumina containing supports. This tendency is even more sharply expressed in the cases with methanol and DME oxidation (Figs. 2 and 3), although the activity of all the catalysts is significantly lower.

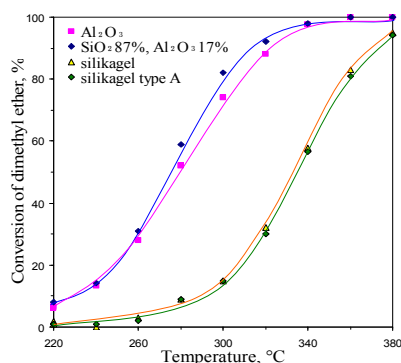


Fig. 3 Effect of support on DME oxidation activity of Cu-Mn catalyst with Cu/Mn molar ratio 1:2. Active component $10 \pm 0.5\%$, calcination temperature 450°C

Measurable oxidation of methanol begins at about 120°C and complete oxidation is achieved at 220°C for alumina containing supports and at 240°C for catalysts, deposited on silica. For DME these temperatures are much higher. The oxidation starts at about 200°C and complete oxidation is achieved at 340°C for alumina containing supports and at 400°C for catalysts, deposited on silica.

The experiments described above were repeated by using the same supports, but with copper and manganese acetate instead of nitrates. The same tendencies were observed with the only difference that in all cases the activity of the catalysts was little bit lower.

On the base of the results presented above it can be concluded that the type of support is a dominating requirement for preparation of active Cu/Mn catalysts for CO and VOCs oxidation. Modification of silicagel with alumina increases the activity for complete oxidation of all investigated compounds. This is in agreement with the results of [18]. Obviously the most appropriate support is pure alumina, therefore it was chosen as support for the preparation of Cu/Mn catalysts for our next investigations.

B. Effect of Cu/Mn Molar Ratio in the Active Component on the Catalytic Activity of the Supported Cu-Mn Catalysts

The results for CO, CH_3OH and DME oxidation on Cu-Mn/ $\gamma\text{-Al}_2\text{O}_3$ catalyst with atomic ratio Cu/Mn=1:2 presented in Figs. 1-3 confirm the high activity of this sample in CO oxidation. Regarding the methanol oxidation, the activity is also high, as complete oxidation is achieved at 200°C . A noticeable DME oxidation is observed, however, only at above 200°C and complete oxidation is achieved at temperatures above 340°C . Obviously, this composition of the catalyst is suitable for full CO and MeOH oxidation, but its

activity is comparatively low in relation to the complete DME oxidation. To find the optimal composition of Cu-Mn catalyst system for simultaneous oxidation of all toxic components in the waste gases in the production of formaldehyde we checked the effect of Cu/Mn molar ratio in the active component on the catalyst activity. Figs. 4-6 show the results for CO, methanol and DME oxidation on samples with a different Cu-Mn atomic ratio.

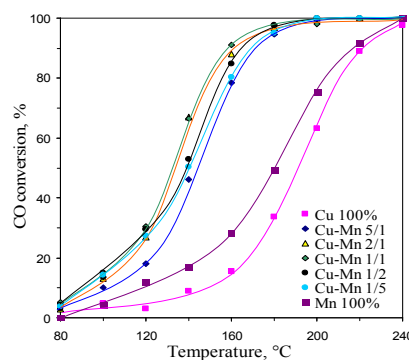


Fig. 4 Effect of Cu/Mn molar ratio in the active component on CO, oxidation. Active component $10 \pm 0.5\%$, calcination temperature 450°C

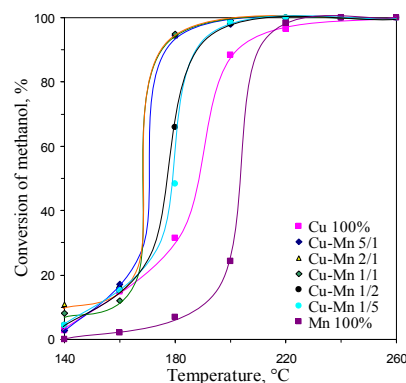


Fig. 5 Effect of Cu/Mn molar ratio in the active component on CH_3OH oxidation. Active component $10 \pm 0.5\%$, calcination temperature 450°C

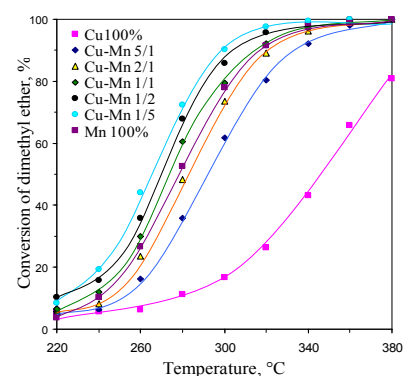


Fig. 6 Effect of Cu/Mn molar ratio in the active component on DME oxidation. Active component $10 \pm 0.5\%$, calcination temperature 450°C

In terms of CO oxidation the activity of the catalysts differs substantially and can be divided into two groups – pure copper and manganese oxides and mixed Cu-Mn oxides. The samples from the second group showed higher activity and reached full oxidation at temperature lower than 200°C. With respect to the oxidation of methanol pure manganese oxide catalyst shows the lowest activity, while with respect to the oxidation of DME pure copper oxide has the lowest activity. The differences in catalytic activity cannot be attributed to the difference in texture characteristics of the catalysts (Table II).

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

As it can be seen, the surface area, pore volume and average pore diameter of the catalysts are nearly identical.

In order to give a better understanding of the effect of Cu/Mn ratio in the active component on the activity of CO, CH₃OH and DME oxidation the results are summarized in Fig. 7.

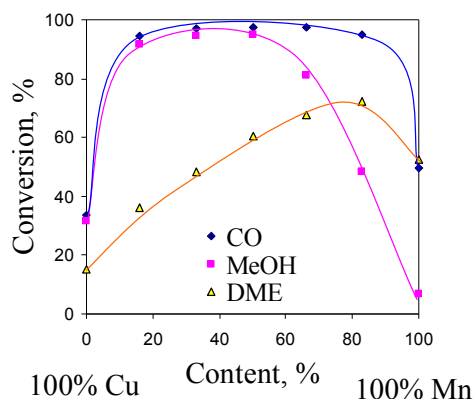


Fig. 7 Effect of Cu/Mn molar ratio on CO, CH₃OH and DME oxidation ($T_{CO}=180^{\circ}C$, $T_{MeOH}=180^{\circ}C$, $T_{DME}=280^{\circ}C$).

It is undisputed that single oxide catalysts are less active than mixed oxide 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 the oxidized compound. The addition of small amount of manganese oxide to the pure copper oxide leads to a sharp increase in activity in relation to CO oxidation. This high activity is retained for all mixed specimens and is greatly reduced only with the pure manganese oxide. Even more pronounced synergistic effect is observed in the methanol oxidation. In this case, the more active of the two pure oxides is the copper oxide. 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, in the DME oxidation the higher activity is shown by manganese-rich oxide specimens.

Our results are in agreement with the results of other authors. It has already been shown by [19] that the incorporation of small amounts of copper in MnO_x improve ethanol combustion to CO₂. These authors suggested that the addition of copper reduced the crystalline structure of manganese oxide, and thus increased the number of oxygen vacancies.

The results presented in Fig. 7 show that in the oxidation of the gas mixtures containing CO and MeOH, most suitable are catalysts containing Cu in the active component in the range of 50-80% where complete oxidation is achieved at temperatures below 200°C. However, for complete oxidation of a mixture containing all three components, the catalysts with such composition require substantially higher temperatures. In this case more suitable are specimens with low copper content (up to 20%) in which a complete oxidation of all the components is possible at temperatures below 350°C.

The results presented allow concluding that there are two regions of interest in respect to active component composition of the alumina supported Cu-Mn catalysts: copper-rich samples (Cu/Mn molar ratio about 2:1) for the oxidation of CO and methanol and manganese-rich samples (Cu/Mn molar ratio about 1:5) for the oxidation of DME. These samples are chosen for our next investigations.

C. Effect of Heat Treatment Temperature on the Catalytic Activity of the Supported Cu-Mn Catalysts

Along with the type of support and Cu/Mn molar ratio the active component loading during the catalyst preparation and the subsequent calcination step are important in controlling the activity of supported copper manganese mixed oxide catalysts.

The calcination temperature is an important factor, influencing the activity of catalysts. It is connected with the conduct of both phase transitions in materials and modification of the specific surface area [20].

According to [21] the heat treatment of mixed Cu-Mn oxides plays an essential role on the oxidation activity regarding CO. The results of the studies, carried out in the range of 300-800°C, show that the highest activity is displayed by the samples calcined at 500°C. The same authors showed that the increase of the activity from 300 to 400°C is associated with the decomposition of the inactive forms and the formation of stable oxides. Its reduction at temperatures above 500°C is due to the increase of the size of the oxide crystals, and the decrease of the specific surface. Data from [22] show that the most active in the CO oxidation are catalysts, calcined at 550°C. Other authors, however, obtain active samples at 300-400°C [23], [24]. Literature data analysis suggests that the results for the thermal decomposition of a mixture of Cu-Mn nitrates are controversial.

DTA, DTG and TG analysis of the samples with Cu/Mn molar ratio 2:1 and 1:5 were carried out, the results of which are presented in Figs. 8 and 9.

Both catalysts show four main weight losses, due to different decomposition steps. 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 MnO₂ and spinel (Cu/Mn molar ratio 1:5) formation. This is in agreement with our XRD results [25] and experimental results of [26] 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 MnO₂ to Mn₂O₃ 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 [3], [19].

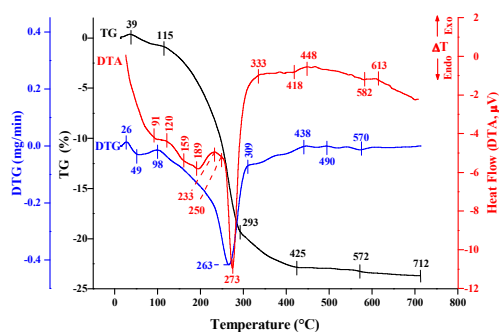


Fig. 8 Thermal analysis of catalyst with Cu/Mn molar ratio 2:1

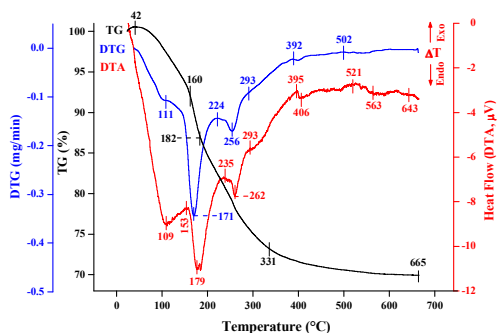


Fig. 9 Thermal analysis of catalyst with Cu/Mn molar ratio 1:5

The data obtained show that at temperatures above 300°C no considerable thermal effects occur. Studies of [27] show that with the increase of the calcination temperature the phase of the mixed oxides at Cu/Mn 1:5 pass from MnO₂ + spinel in Bixbyite + Spinel at 425°C. According to [28] at 430°C MnO₂ passes into Mn₂O₃.

In order to clarify the influence of thermal treatment on the catalytic activity samples with molar ratio Cu/Mn 1:5 and 2:1 have been investigated. Figs. 10-12 present the influence of

the heat treatment of Cu-Mn/ γ -Al₂O₃ catalysts with Cu/Mn molar ratio 1:5 on CO, CH₃OH and DME oxidation.

As it can be seen, the effect of the heat treatment is specific for each of the oxidized components. While in the oxidation of CO the sample calcined at 300°C is with the lowest activity, in the oxidation of methanol and DME such heat treatment yields the samples with the highest activity.

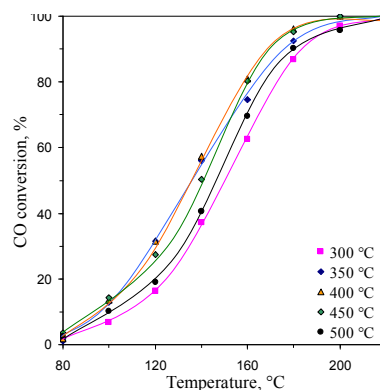


Fig. 10 Effect of heat treatment of Cu-Mn catalysts with Cu/Mn molar ratio 1:5 on CO oxidation activity

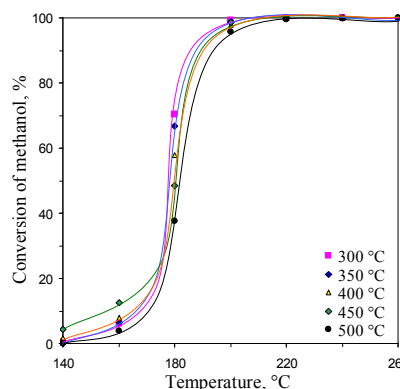


Fig. 11 Effect of heat treatment of Cu-Mn catalysts with Cu/Mn molar ratio 1:5 on CH₃OH oxidation activity

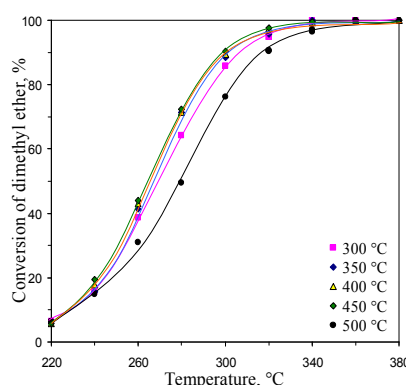


Fig. 12 Effect of heat treatment of Cu-Mn catalysts with Cu/Mn molar ratio 1:5 on DME oxidation activity

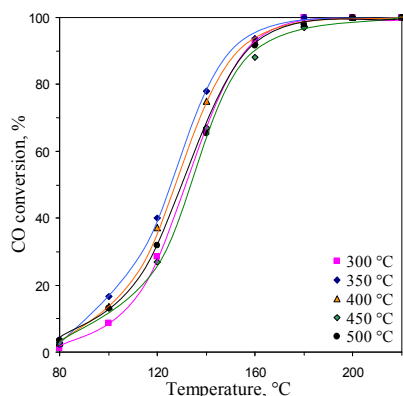


Fig. 13 Effect of heat treatment of Cu-Mn catalysts with Cu/Mn molar ratio 2:1 on CO oxidation activity

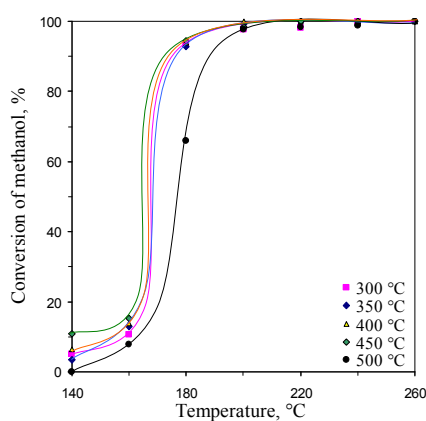


Fig. 14 Effect of heat treatment of Cu-Mn catalysts with Cu/Mn molar ratio 2:1 on CH₃OH oxidation activity

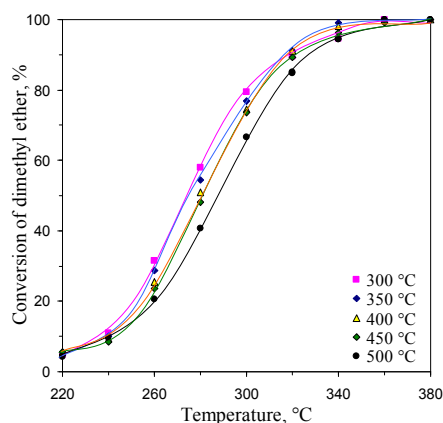


Fig. 15 Effect of heat treatment of Cu-Mn catalysts with Cu/Mn molar ratio 2:1 on DME oxidation activity

Figs. 13-15 present the influence of the heat treatment of Cu-Mn/ γ -Al₂O₃ catalysts with Cu/Mn molar ratio 2:1 on CO, CH₃OH and DME oxidation.

Noticeable difference can be seen in the activity of both groups of catalysts. It is evident that the manganese-rich samples are more active in DME oxidation and nearly 100% conversion is possible at temperatures at about 320°C. The copper-rich catalysts are more active with respect to CO and

methanol oxidation. This trend remains unchanged in the whole interval of calcination temperatures.

The results of the effect of heat treatment of Cu-Mn/ γ -Al₂O₃ catalysts with Cu/Mn molar ratio 1:5 and 2:1 on the activity of CO, CH₃OH and DME oxidation are summarized in Figs. 16 and 17.

The results show a general trend of decreasing the activity with the increase of the thermal treatment temperature. 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 manganese (Cu/Mn molar ratio 1:5) the degree of DME oxidation remains constant up to 450°C, while in the MeOH oxidation there is a trend of activity decrease. In the catalysts consisting predominantly of copper (Cu/Mn molar ratio 2:1) the opposite picture has been observed - the temperature of the heat treatment in the range of 300 - 450°C practically has no effect on the MeOH oxidation, while in the DME oxidation there is a trend of slight decrease. It can be concluded that in this temperature range the catalyst composition takes a predominant role.

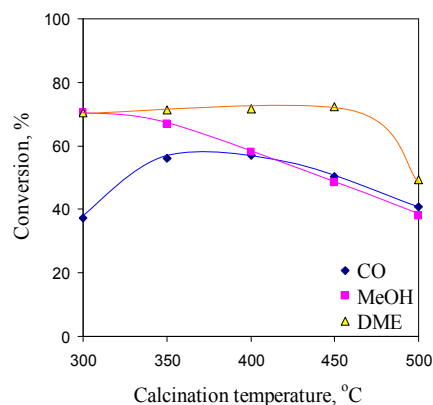


Fig. 16 Effect of heat treatment of Cu-Mn catalysts with Cu/Mn molar ratio 1:5 on CO, CH₃OH and DME oxidation activity. ($T_{CO}=140^{\circ}C$, $T_{MeOH}=180^{\circ}C$, $T_{DME}=280^{\circ}C$)

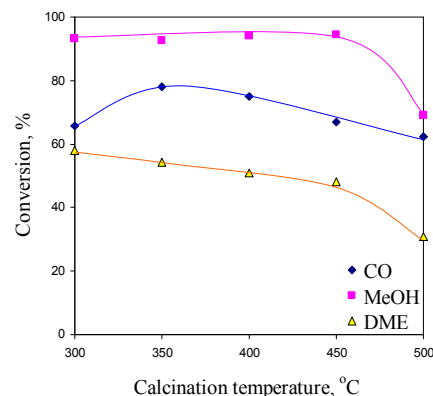


Fig. 17 Effect of heat treatment of Cu-Mn catalyst with Cu/Mn molar ratio 2:1 on CO, CH₃OH and DME oxidation activity. ($T_{CO}=140^{\circ}C$, $T_{MeOH}=180^{\circ}C$, $T_{DME}=280^{\circ}C$)

At calcination temperature above 450°C, however, the oxidation degree of both gases decreases greatly. Obviously, a predominant role here takes agglomeration of the particles, reduction of the specific surface area and partial crystallization of Cu-Mn spinel.

In CO oxidation in both catalyst samples we observe the same trend - increase in activity with the increase of the calcination temperature from 300 to 400°C, followed by its gradual decrease. Obviously in this case the heat treatment of the catalyst, leading to change in the catalyst composition takes a predominant role. The increase in activity with the increase of the calcination temperature from 300°C to 400°C is probably due to the formation of an active amorphous spinel structure, active in CO oxidation. This suggestion is in agreement with the results of [20] and [21].

D. Effect of the Active Component Content on the Catalytic Activity of the Supported Cu-Mn Catalysts

Figs. 18-20 present the effect of the active component content on the catalytic activity in oxidation of CO, CH₃OH and DME on Cu-Mn/ γ -Al₂O₃ with Cu/Mn molar ratio 1:5.

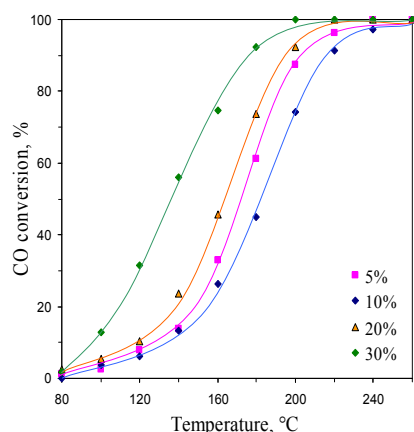


Fig. 18 Effect of active component content in Cu-Mn catalyst with Cu/Mn molar ratio 1:5 on CO oxidation activity

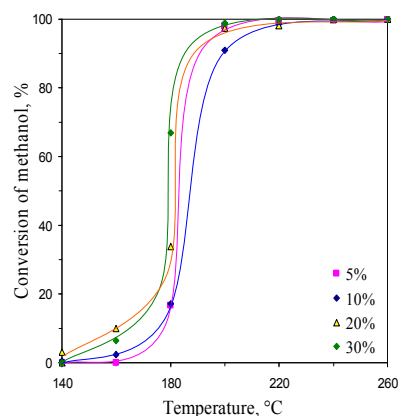


Fig. 19 Effect of active component content in Cu-Mn catalyst with Cu/Mn molar ratio 1:5 on CH₃OH oxidation activity

The results show strong dependence of the active component content on the catalytic activity. The results of CO

oxidation reaction (Fig. 18) reveal that catalysts differ substantially in their activity. The oxidation process started at temperatures lower than 80°C and reached 100% conversion at 240°C for all catalysts. The catalyst with 30% active component is the most active while the catalyst with 5% active component is the least active in the whole temperature region.

Methanol oxidation process (Fig. 19) started at 140°C and increased rapidly with temperature rising to 100% for all catalysts at 220°C. In terms of this process the activity of the catalysts differs substantially at 180°C and passes into diffusion region and full conversion at 200°C.

Measurable oxidation of DME started at 220°C for all catalysts and rose to 100% at 340°C for catalyst with 30% active component and at 360°C for all other samples (Fig. 20). The same order of activity as in the CO and CH₃OH oxidation can be observed.

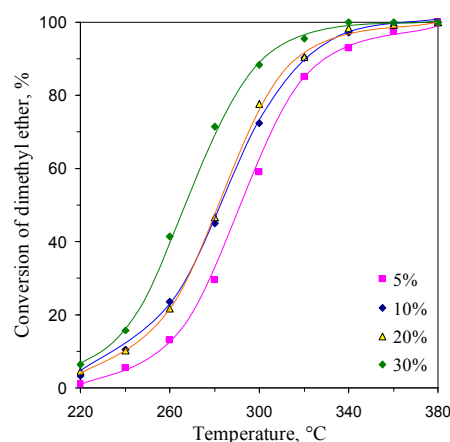


Fig. 20 Effect of active component content in Cu-Mn catalyst with Cu/Mn molar ratio 1:5 on DME oxidation activity

The results for the effect of active component content in Cu-Mn/ γ -Al₂O₃ with Cu/Mn molar ratio 1:5 on the CO, CH₃OH and DME oxidation activity are summarized in Fig. 21.

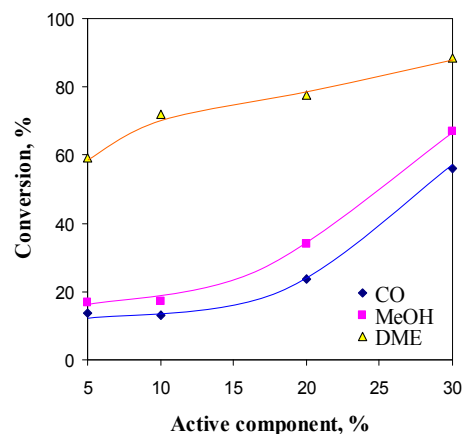


Fig. 21 Effect of active component content in Cu-Mn catalyst with Cu/Mn molar ratio 1:5 on CO, CH₃OH and DME oxidation activity (T_{CO} = 140°C, T_{MeOH} = 180°C, T_{DME} = 300°C)

Clear tendency for moderate increase in CO, methanol and DME oxidation with active component enlargement can be observed. These results are not in consent with the expectation for a lower activity due to reduction of the specific surface area of the catalysts with increasing amount of the active component loading. This was confirmed by the result for BET specific surface area of the catalysts.

Table III shows the specific surface area of the samples with different active component loading. It is seen that the specific surface area decreases down to 37% with increased loading, but this can be attributed mainly to the increased weight of the catalysts. Date in the brackets presents surface area in m^2/g of support instead of m^2/g catalyst. The slightly increased surface area for the catalysts with active component 10 and 10% as compared to the support indicates some pore structure in the material deposited. Obviously dominating factors for catalyst activity are active component content and active component composition.

TABLE III
SPECIFIC SURFACE AREA OF CATALYSTS WITH DIFFERENT ACTIVE COMPONENT LOADING

Composition	Active component, %	S_{BET}^* m^2/g
Al_2O_3	-	219 (219)
Cu/Mn 1:5	10.0	206 (197)
Cu/Mn 1:5	15.0	199 (186)
Cu/Mn 1:5	20.0	152 (175)
Cu/Mn 1:5	30.0	137 (153)

*The BET surface area of catalysts (m^2/g) and within brackets of support (m^2/g).

Figs. 22-24 present the effect of the active component content on the catalytic activity in oxidation of CO, CH_3OH and DME on Cu-Mn/ $\gamma\text{-Al}_2\text{O}_3$ with Cu/Mn molar ratio 2:1.

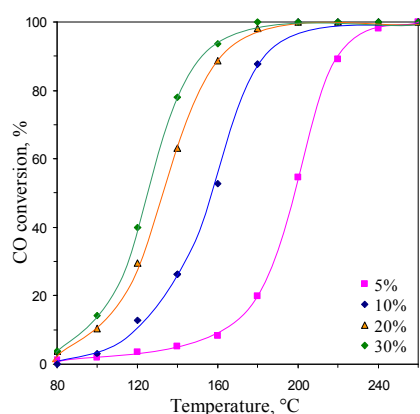


Fig. 22 Effect of active component content in Cu-Mn catalyst with Cu/Mn molar ratio 2:1 on CO oxidation activity

The difference in the catalytic activity of the samples in the oxidation of CO in this case is expressed significantly stronger (Fig. 22). Full oxidation over catalyst with 30% active component was reached at 180°C , while for catalyst with 5% active component it was at 240°C . With respect to DME oxidation this difference is less pronounced (Fig. 24), while in methanol oxidation this difference is almost invisible (except

for a sample with 5% active component content).

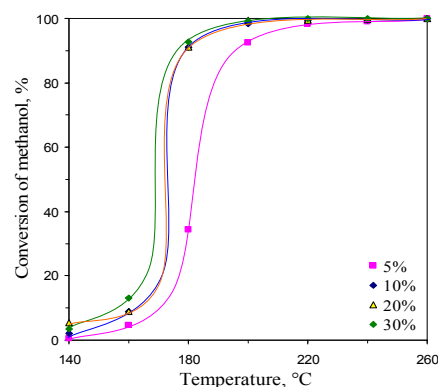


Fig. 23 Effect of active component content in Cu-Mn catalyst with Cu/Mn molar ratio 2:1 on CH_3OH oxidation activity

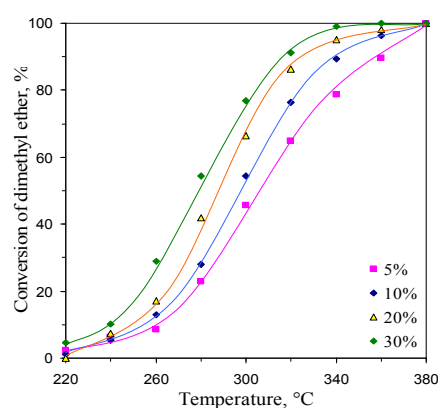


Fig. 24 Effect of active component content in Cu-Mn catalyst with Cu/Mn molar ratio 2:1 on DME oxidation activity

The results for the effect of active component content in Cu-Mn/ $\gamma\text{-Al}_2\text{O}_3$ with Cu/Mn molar ratio 2:1 on CO, CH_3OH and DME oxidation activity are summarized in Fig. 25.

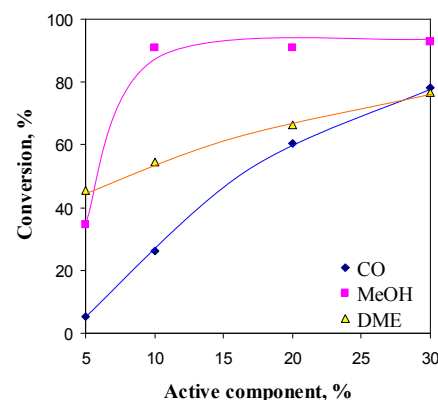


Fig. 25 Effect of active component content in Cu-Mn catalyst with Cu/Mn molar ratio 2:1 on CO, CH_3OH and DME oxidation activity ($T_{\text{CO}} = 140^\circ\text{C}$, $T_{\text{MeOH}} = 180^\circ\text{C}$, $T_{\text{DME}} = 300^\circ\text{C}$)

It is seen that increasing the active component dramatically enhanced the activity for carbon monoxide oxidation, while the activity in the oxidation of DME increased marginally. Methanol oxidation activity increases sharply with active component rise to 10%, after which remains unchanged. Since

the tendency in BET specific surface area is the same as described for the catalysts with Cu/Mn ratio 1:5, the results can be assumed as confirmation of the conclusion 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 Cu-Mn/ γ -alumina supported catalysts have enhanced activity toward CO, methanol and DME oxidation. The synergetic interaction among copper and manganese species increases the activity for complete oxidation over mixed catalysts compared with activity over $\text{CuO}_x/\gamma\text{-Al}_2\text{O}_3$ and $\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts.

Cu/Mn molar ratio from 2:1 to 1:1 in the active component can ensure successful oxidation of CO and CH_3OH . Reduction of copper content to Cu/Mn molar ratio to 1:5 is the best compromise for production of catalyst for simultaneous combustion of CO, CH_3OH and DME.

Type of support, calcination temperature and active component loading along with catalyst composition are important factors determining catalytic activity. For the alumina supported Cu-Mn catalysts heat treatment at 450°C and 20% active component can ensure preparation of active catalyst for combustion of waste gases from formaldehyde production.

ACKNOWLEDGMENT

Authors gratefully acknowledge the financial support by the National Science Fund (Project DFNI T 02/4).

REFERENCES

- [1] E. C. Moretti, "Practical Solutions for Reducing Volatile Organic Compounds and Hazardous Air Pollutants", *Center for Waste Reduction Technologies of the American Institute of Chemical Engineers*, New York, 2001.
- [2] Q. Yea, J. Zhao, F. Huo, J. Wang, S. Cheng, T. Kanga, H. Daib, "Nanosized Ag/ α - MnO_2 catalysts highly active for the low-temperature oxidation of carbon monoxide and benzene", *Catalysis Today*, Vol. 175, pp. 603-609, 2011.
- [3] J. Y. Kim, M. Jin, K. J. Lee, J. Y. Cheon, S. H. Joo, J. M. Kim, H. R. Moon, "In situ-generated metal oxide catalyst during CO oxidation reaction transformed from redox-active metal-organic framework-supported palladium nanoparticles", *Nanoscale Research Letters*, 7:461, August 2012.
- [4] Z. Ma, S. Dai, "Development of Novel Supported Gold Catalysts: A Materials Perspective", *Nano Res.*, Vol. 4(1), pp. 3-32, ISSN 1998-0124, DOI 10.1007/s12274-010-0025-5, 2011.
- [5] K. An, S. Alayoglu, N. Musselwhite, S. Plamthottam, G. Melae, A. E. Lindeman, G. A. Somorjai, "Enhanced CO Oxidation Rates at the Interface of Mesoporous Oxides and Pt Nanoparticles", *J. Am. Chem. Soc.*, Vol. 135 (44), pp. 16689-16696, 2013.
- [6] M. B. Cortie, Lingen E. "Catalytic gold nanoparticles", *Materials Forum*, Vol. 26, pp. 1-14, 2002.
- [7] P. Larsson, A. Andersson, "Oxides of copper, ceria promoted copper, manganese and copper manganese on Al_2O_3 for the combustion of CO, ethyl acetate and ethanol", *Applied Catalysis B: Environmental*, Vol. 24, pp. 175-192, 2000.
- [8] S. Zeng, Y. Wang, K. Liu, H. Su, "Study on Inverse CeO_2/CuO Catalysts for CO Preferential Oxidation", in *Proc. 3rd International Conference on Chemistry and Chemical Engineering, IPCBEE* vol. 38, 2012, pp. 63-65.

- [9] A. Martinez-Arias, M. Fernandez-Garcia, O. Galvez, J. M. Coronado, J. A. Anderson, J. C. Conesa, J. Soria, G. Munuera, "Comparative Study on Redox Properties and Catalytic Behaviour for CO Oxidation of CuO/CeO_2 and $\text{CuO}/\text{ZrCeO}_4$ Catalysts", *Journal of Catalysis*, Vol. 195, pp. 207-216, 2000.
- [10] G. Xanthopoulos, G. Vekinis, "Investigation of catalytic oxidation of carbon monoxide over a Cu-Cr-oxide catalyst made by self-propagating high-temperature synthesis", *Applied Catalysis B: Environmental*, Vol. 19, pp. 37-44, 1998.
- [11] Y. Ren, Z. Ma, L. Qian, S. Dai, H. He, P.G. Bruce, "Ordered Crystalline Mesoporous Oxides as Catalysts for CO Oxidation", *Catal. Lett.*, Vol. 131, pp. 146-154, 2009.
- [12] Z. Zengjian, W. Hui, G. Guofeng, "Catalytic Combustion of Methyl Acetate over Cu-Mn Mixed Oxide Catalyst", *International Conference, Computer Distributed Control and Intelligent Environmental Monitoring (CDCIEM)*, 19-20 Feb. 2011, pp. 1994-1997, Digital Object Identifier: 10.1109/CDCIEM.2011.107.
- [13] C. Jonesa, K. J. Colea, S. H. Taylora, M. J. Crudaceb, and G. J. Hutchings, "Copper manganese oxide catalysts for ambient temperature carbon monoxide oxidation: Effect of calcination on activity", *Journal of Molecular Catalysis A: Chemical*, Vol. 305, Issues 1-2, pp. 121-124, June 2009.
- [14] M. Ferrandon, "Mixed Metal Oxide-Noble Metal Catalyst for Total Oxidation of Volatile Organic Compounds and Carbon Oxide," *PhD Thesis*, Department of Chemical Engineering and Technology, Chemical Reaction Engineering, Royal Institute of Technology, Stockholm, 2011.
- [15] R. McCabe and P. J. Mitchell, "Reactions of ethanol and acetaldehyde over noble metal and metal oxide catalysts", *Ind. Eng. Chem. Prod. Res. Dev.*, Vol. 23 (2), pp. 196-202, 1984.
- [16] Y. Hasegawa, K. Fukumoto, T. Ishima, H. Yamamoto, M. Sano, T. Miyake, "Preparation of copper-containing mesoporous manganese oxides and their catalytic performance for CO oxidation", *Appl. Catal. B: Environ.* Vol. 89, pp. 420-424, 2009.
- [17] S. Imamura, H. Tarumoto, S. Ishida, "Decomposition of 1,2-dichloroethane on titanium dioxide/silica", *Ind. Eng. Chem. Res.*, Vol. 28 (10), pp 1449-1452, 1989.
- [18] J. Oi-Uchisawa, S. Wang, T. Nanba, A. Ohi, and A. Obuchi, "Improvement of Pt catalyst for soot oxidation using oxide as a support", *Applied Catalysis B: Environ.*, Vol. 44, pp. 207-215, 2003.
- [19] M. Morales, L. Barbero, L. Cadús, "Combustion of volatile organic compounds on manganese iron or nickel mixed oxide catalysts", *Applied Catalysis B: Environmental*, Vol. 67, Issues 3-4, pp. 229-236, 2006.
- [20] S. Kanungo, "Physicochemical properties of MnO_2 and $\text{MnO}_2\text{-CuO}$ and their relationship with the catalytic activity for H_2O_2 decomposition and CO oxidation", *J. Catal.*, Vol. 58, pp. 419-435, 1979.
- [21] G. J. Hutchings, A. A. Mirzaei, R. W. Joynerb, M. Siddiqui, S. H. Taylor, "Effect of preparation conditions on the catalytic performance of copper manganese oxide catalysts for CO oxidation", *Applied Catalysis A: General*, Vol. 166, pp. 143-152, 1998.
- [22] M. Wojciechowska, W. Przystajko, M. Zielin'ski, "CO oxidation catalysts based on copper and manganese or cobalt oxides supported on MgF_2 and Al_2O_3 ", *Catalysis Today*, Vol. 119, pp. 338-341, 2007.
- [23] L. N. Cai, Y. Guo, A. H. Lu, P. Branton, W. C. Li, "The choice of precipitant and precursor in the co-precipitation synthesis of copper manganese oxide for maximizing carbon monoxide oxidation", *Journal of Molecular Catalysis A: Chemical*, Vol. 360, pp. 35-41, 2012.
- [24] K. Ivanov, E. Kolentsova, D. Dimitrov, Georgi, Avdeev, Tatyana Tabakova, "Alumina Supported Copper-Manganese Catalysts for Combustion of Exhaust Gases: Catalysts Characterization", *XIII International Conference on Chemical Engineering and Applications*, Venice, Italy, 2015 (accepted for publication).
- [25] M. Kramer, T. Schmidt, K. Stowe, W. F. Maier, "Structural and catalytic aspects of sol-gel derived copper manganese oxides as low-temperature CO oxidation catalyst", *Applied Catalysis A: General*, Vol. 302, pp. 257-263, 2006.
- [26] S. A. Kondrat, T. E. Davies, Z. Zu, P. Boldrin, J. K. Bartley, A. F. Carley, S. H. Taylor, M. J. Rosseinsky, and G. J. Hutchings, "The effect of heat treatment on phase formation of copper manganese oxide: Influence on catalytic activity for ambient temperature carbon monoxide oxidation", *Journal of Catalysis*, Vol. 281, pp. 279-289, 2011.
- [27] P. Wei, M. Bieringer, L. Cranswick, A. Petric, "In situ high-temperature X-ray and neutron diffraction of Cu-Mn oxide phases", *Journal of Materials Science*, Vol. 45, Issue 4, pp. 1056-1064, 2010.

- [28] K. Qian, Z. Qian, Q. Hua, Z. Jiang, W. Huang, "Structure-activity relationship of CuO/MnO₂ catalysts in CO oxidation", *Applied Surface Science*, Vol. 273, pp. 357– 363, 2013.