**Journal of International Scientific Publications: Ecology and Safety**

Volume 8, ISSN 1314-7234 (Online), Published at: http://www.scientific-publications.net

# INFLUENCE OF CATALYST COMPOSITION ON CO AND VOCs OXIDATION OVER $Cu\text{-}Mn/\gamma\text{-}Al_2O_3$

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**Abstract**

*Background: Emission of volatile organic compounds (VOCs) from industrial pollution sources is a major concern worldwide. Strict environmental requirements demand low emissions of these pollutants. The purpose of this study is to determine the influence of the composition of the active ingredient and the calcination temperature on the catalytic activity of the supported copper-manganese mixed oxides in terms of oxidation of CO, methanol and dimethyl ether. Methods: The catalysts were prepared by impregnation of $\gamma\text{-}Al_2O_3$ with copper and manganese nitrates and the possibilities for CO and VOCs oxidation were evaluated using continuous flow equipment with a four-channel isothermal stainless steel 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. Results: Highly active alumina supported Cu-Mn catalysts for CO and VOCs oxidation were synthesized. The effect of preparation conditions on the active component composition and activity behavior of the catalysts was discussed. Conclusions: The present study showed that the Cu-Mn/γ–alumina supported catalysts have enhanced activity toward CO, methanol and DME oxidation. The synergetic interaction among copper and manganese species would promote the catalytic activity of the catalysts.*

**Key words:** *copper-manganese catalysts, CO and VOCs oxidation*

## 1. INTRODUCTION

The concentration of efforts to protect the environment and the modern clinical trials on the negative effects of certain volatile organic compounds (VOCs) on human health, including carbon monoxide, lead to the application of more and more stringent preventive measures to reduce their emissions. The continuous increase of the consumption of raw materials, on the other hand, increases the amount of waste products, which requires the establishment of more effective methods for their reduction (Moretti E.C., 2001).

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. Various technologies for eliminating VOCs have been developed, with the catalytic oxidation being one of the most effective one (Yea Q., et al., 2011). The main advantages of this method is its relatively low cost and the ability of removal of 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 as $SiO_2$ or $Al_2O_3$ (An K., et al., 2013; Cortie M. B. and Lingen E., 2002; Ma Z .and Dai S.,2011; Kim J.Y., et al. 2012). Satisfactory activity, however, occurs only in systems with nano-sized metal particles (0.5-5.0 nm) (Ma Z. and Dai S., 2011). This 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 (Cortie M. B. and Lingen E., 2002). These circumstances have encouraged the search for cheaper and more efficient materials based on metal oxides (Larsson P. and Andersson A., 2000; Martınez-Arias A., et al, 2000). 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 (Larsson P. and Andersson A., 2000; Martınez-Arias A., et al, 2000; Zeng S., et al., 2012), related to the reduction of CuO to $Cu_2O$. According to some scientists (Borisov A. S., et al. 1988; Davydov A. A., 1984; Larsson P. and Andersson A.,2000; Martınez-Arias A., et al., 2000; Xanthopoulou1 G., Vekinis G., 1998), this process can be slowed 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 (Ren Y., et al., 2009). 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 (Jonesa C., et al., 2009; Zengjian Z., et al., 2011). The studies of Ferrandon and Megali (2001) showed that the activity of the manganese oxides supported on $\gamma\text{-}Al_2O_3$ 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. The ratio of the two elements in the active component also plays a leading role regarding the activity in catalytic

oxidation. According to many 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 (Hasegawa Y., et al., 2009). 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. The purpose of this study is to determine the influence of the composition of the active component and the calcination temperature on the catalytic activity of the supported copper-manganese mixed oxides in terms of oxidation of CO, methanol and dimethyl ether.

## 2. MATERIALS AND METHODS

The supported copper-manganese oxides are prepared by the wet impregnation method. $\gamma$-$Al_2O_3$ with fraction of 0,6-1.0 mm was used as support, impregnated with copper and manganese nitrates. For the purposes of the study, catalyst specimens were obtained with an active component content 30 ± 1 % and an atomic ratio Cu/Mn from 0 to 100 %. Prior to the impregnation, the carrier was calcined for 2 hours at $500^0$C in a ceramic furnace. After keeping it at a room temperature, a previously prepared solutions of copper and manganese nitrates were added. $\gamma$-$Al_2O_3$ stays in the salt solutions at 80 $^o$C for 12 hours. 10-hour drying follows at a temperature of 120 $^o$C, and calcining at 450 $^o$C for 4 hours. For the thermal analysis of the samples computerized thermal installation "Stanton Redcroft" (England) was used under the following experimental conditions: heating temperature range – 20-650 $^o$C, heating rate – 10 $^o$C/min, specimen mass - 12.00 mg, gas environment – 100 % air, pot - stabilized corundum.

The catalytic measurements were carried out on continuous flow equipment with a four-channel isothermal stainless steel reactor (Fig. 1, section 3).

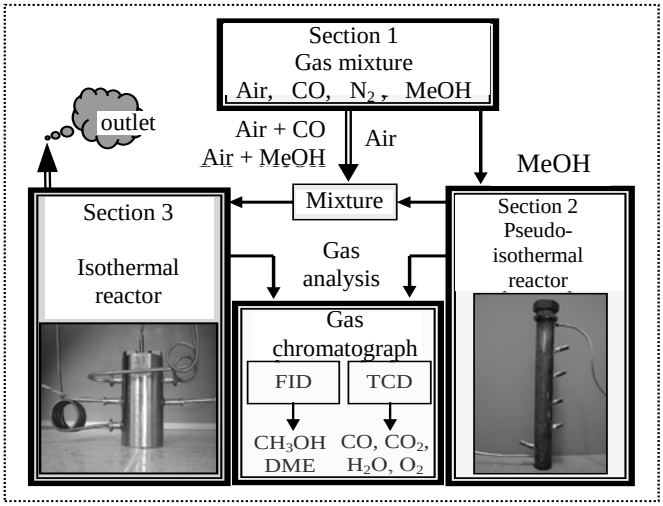



Fig. 1. Apparatus for estimation of oxide catalysts.

Conditions of the analysis are as follows: operating at atmospheric pressure, size of catalyst grains 0,6-1.0 mm, gas mixture rate through the catalyst layer 10 L/ h, amount of the catalyst layer 1 ml, space velocity 10 000 $h^{-1}$, tested temperature range 40-380 $^o$C, gas mixture concentration - $CH_3OH$ andair CO 2.0 %, DME – 1.0 % and to 100 %. For the purposes of the analyses DME was obtained by dehydration of methanol on $\gamma$-$Al_2O_3$ in tubular isothermal reactor (section 2) .

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.

## 3. RESULTS

The activity of Cu/Mn catalyst regarding the complete CO oxidation are associated with the formation of $CuMn_2O_4$ spinel (Hasegawa Y., et al., 2009). It can be expected that this also refers to the VOCs oxidation. Our

results, however, have not justified this expectation. The results for CO, MeOH and DME oxidation on Cu-Mn/γ-$Al_2O_3$ catalyst with atomic ratio Cu/Mn = 1:2, presented in Fig. 2, 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 320 °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 formalin we examined catalysts specimens with different atomic ratio Cu/Mn, obtained after different heat treatment.

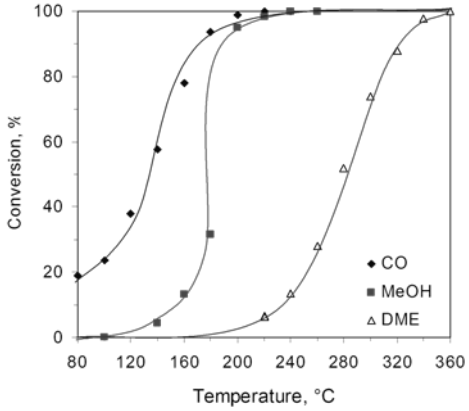



Fig. 2. Influence of reaction temperature on CO,MeOH and DME conversion for *Cu-Mn/ γ-$Al_2O_3$ catalyst.*

*3.1. Effect of the Cu/Mn ratio in the active component on the catalytic activity of the supported Cu-Mn oxides.*

Fig. 3-5 show the results from the CO, MeOH, DME oxidation on specimens with a different atomic ratio Cu-Mn in the active component. The obtained data show that the activity of the catalysts with respect to the three gases examined varies greatly, by passing through clearly defined maxima. In all cases, the activity of the pure copper and manganese oxides is significantly lower than that of the mixtures.

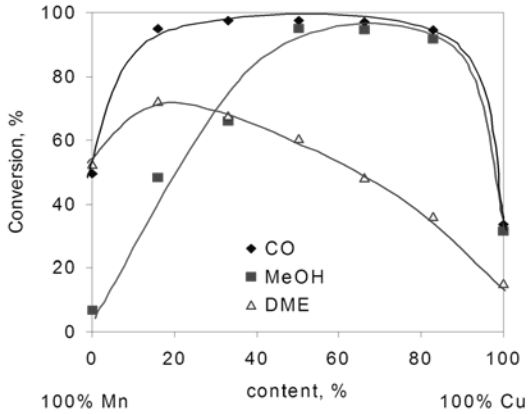



Fig. 3. Catalytic performance for CO, MeOH and DME oxidation versus active component content.

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. 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 that of the copper. 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.

Fig. 4 shows the oxidation degree of the gases at 300 °C. At this temperature, the CO and MeOH oxidation is 100 % in the entire concentration range, and the DME oxidation reaches 90.4 % on the sample with a composition of $Cu_{17\%}Mn_{83\%}$.

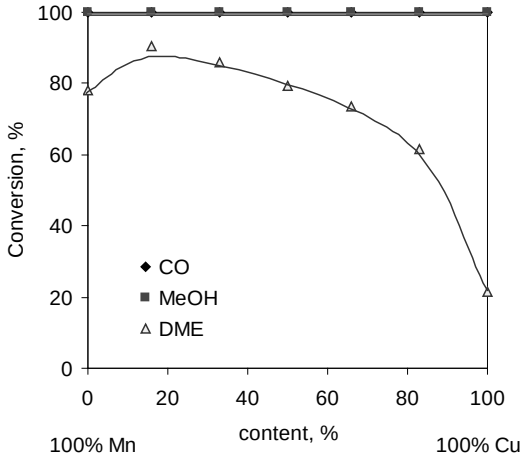



Fig. 4. Catalytic performance for CO, MeOH and DME oxidation at 300 °C versus active component content.

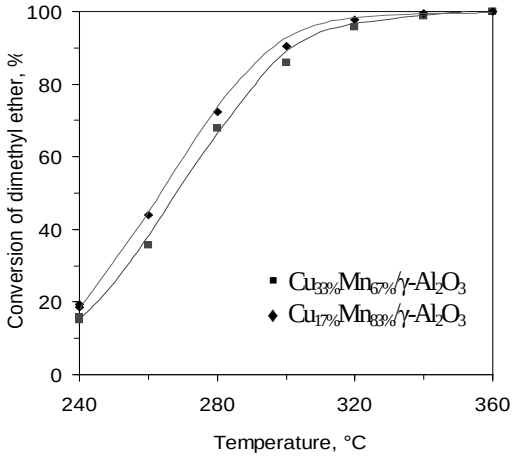



Fig. 5. Influence of reaction temperature on DME oxidation.

To achieve complete oxidation at this temperature it is necessary to reduce the volume rate less below 10000 $h^{-1}$ or to increase the temperature in the catalyst layer. Fig. 5 shows the temperature dependence of the DME oxidation on the two most active samples with a composition of $Cu_{17\%}Mn_{83\%}$ and $Cu_{33\%}Mn_{67\%}$. As can be seen, complete oxidation at a volume rate of 10000 $h^{-1}$ is achieved at temperatures above 340°C.

The results presented in Fig. 3 allow to conclude that in the oxidation of the gas mixtures containing CO and MeOH most suitable are catalysts containing the Cu active component in the range of 50-83 % 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 requires substantially higher temperatures. In this case more suitable are secimens with low copper content (up to 20 %) in which a complete oxidation of all the components is possible at temperatures below 350 °C.

*3.2. Effect of the heat treatment temperature on the catalytic activity of the applied Cu-Mn oxides.*

The calcination temperature is an important factor influencing the activity of catalysts in the heterogeneous catalysis. It is connected with the conduct of both phase transitions in materials and modification of the specific surface area. According to a research by G.J. Hutchings et al. (1998) 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. According to them, 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. It 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 the studies of Maria Wojciechowska et al. (2007) show that the most active in the CO oxidation are catalysts calcined at 550 °C. Other authors, however, obtain active samples at 300 °C – 400 °C (Cai L. N., et al., 2012; Kra¨mer M., et al., 2006). Literature data analysis suggests that the choice of heat treatment depends on the type of the used starting salts. In all described cases, the lower limit of the temperature range is associated with obtaining specimens of relatively constant composition. Studies of Ž. D. Živkovič et al. (Živković Ž. D., et al., 1998) show that the thermal decomposition of pure $Cu(NO_3)_2$ after 300 °C leads to obtaining specimens with a relatively constant composition. In the present studies, nitrates have been used in the synthesis of the catalysts. 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.

DTA, DTG and TG analysis of the specimens has been made, the results of which are presented in Fig. 6 and Fig. 7. The data obtained show that at temperatures above 300 $^{o}$C no considerable phase transitions occur. According to the experimental results of Simon A. Kondrat et al. (2011) at temperatures above 300$^{o}$C in the active phase there are only oxides.

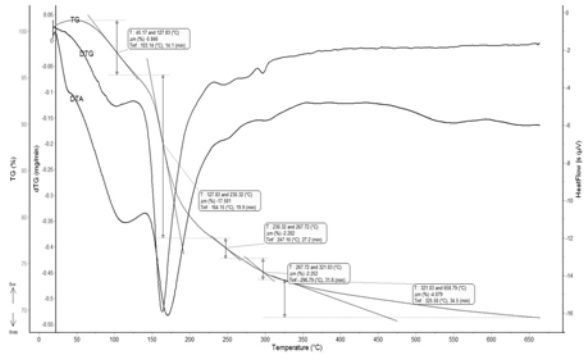



Fig. 6. Thermal analysis of $Cu_{67\%}Mn_{33\%}/\gamma\text{-}Al_2O_3$

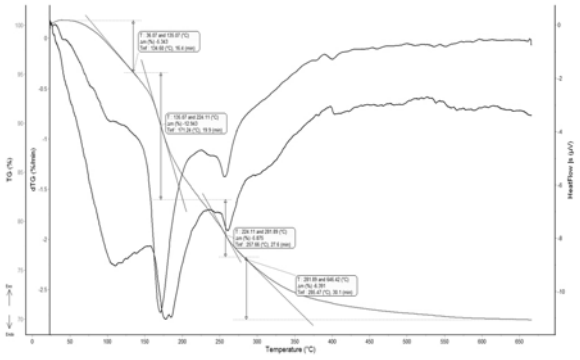



Fig. 7. Thermal analysis $Cu_{17\%}Mn_{83\%}/\gamma\text{-}Al_2O_3$

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 (An K., et al., 2013; Cai L. N., et al., 2012). Studies of Ping Wei et al. (Wei P., et al., 2010) show that with the increase of the ignition temperature the phase of the mixed oxides $Cu_{17\%}Mn_{83\%}$ pass from $MnO_2$ + spinel in Bixbyite + Spinel at 425 $^{o}$C. According to other authors (Qian K., et al., 2013) at 430 $^{o}$C $MnO_2$ passes into $Mn_2O_3$.

In order to clarify the influence of thermal treatment on the catalytic activity specimens an atomic ratio Cu/Mn 2:1 ($Cu_{67\%}Mn_{33\%}$) and 1:5 ($Cu_{17\%}Mn_{83\%}$) have been used. Fig. 8 and 9 present the dependence of the catalytic activity in oxidation of CO (140 $^{o}$C), methanol (180 $^{o}$C) and DME (280 $^{o}$C) from the calcination temperature.

The results show a general trend of decreasing the activity with the increase of the thermal treatment

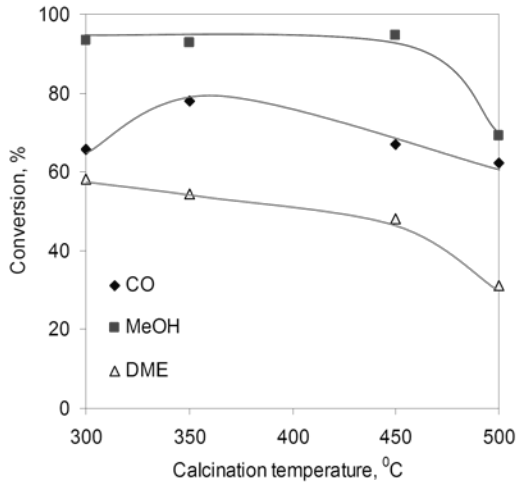



Fig.8. Influence of calcination temperature of $Cu_{67\%}Mn_{33\%}/\gamma\text{-}Al_2O_3$ catalyst on CO, MeOH

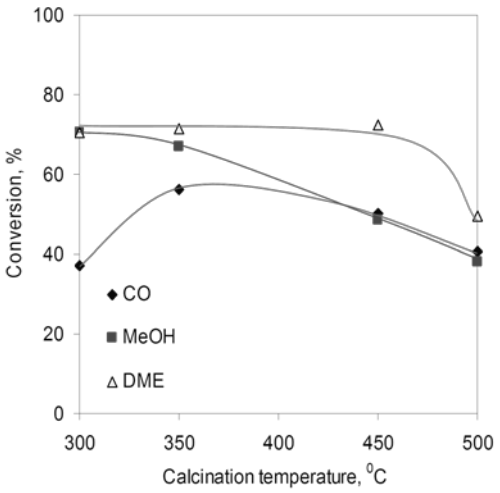



Fig. 9. Influence of calcination temperature of $Cu_{17\%}Mn_{83\%}/\gamma\text{-}Al_2O_3$ catalyst on CO, MeOH and

temperature.

This general trend, however, contains specific features, depending on the composition of the catalyst and the nature of the oxidation gas. In catalyst consisting predominantly of copper ($Cu_{67\%}Mn_{33\%}/\gamma\text{-}Al_2O_3$) the temperature of the heat treatment in the range of 300 – 450 $^oC$ practically has no effect on the MeOH oxidation, while in the DME oxidation there is a trend of a slight decrease. In the sample consisting predominantly of manganese ($Cu_{17\%}Mn_{83\%}/\gamma\text{-}Al_2O_3$) the opposite picture has been observed - the degree of DME oxidation remains constant, while in the MeOH oxidation there is a trend of activity decrease. This is due to the difference in the individual activity of copper and manganese oxides in respect of the two gases, which plays a dominant role in this heat treatment temperature range. At calcination temperature above 450 $^oC$, however, the oxidation degree of both gases reduces greatly, regardless of the catalyst composition. Obviously, a predominant role here takes the heat treatment the catalyst, leading to agglomeration of the particles and a reduction of the specific surface area. In CO oxidation in both catalyst samples we observe the same trend - increase in activity with the increase of the ignition temperature from 300 to 400 $^oC$, followed by its gradual decrease. Obviously in this case the heat treatment temperature takes a predominant role. The increase in activity with the increase of the calcination temperature from 300 to 400 $^oC$ is probably due to the formation of a spinel structure at a higher temperature.

## 4. 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 would promote the catalytic activity of the catalysts. The activity of the mixed catalyst significantly exceeds that of the pure copper and manganese oxides under the same conditions of conducting the oxidation.

We established that 50-80 % Cu content in the active component can ensure successful oxidation of CO and MeOH. Reduction of copper content to 20-30 % is the best compromise for production of catalyst for combustion of all components.

The calcination temperature along with catalyst composition is important factor, determining catalytic activity. For the mixed Cu-Mn catalysts it has to be lower than 450 $^oC$.

## REFERENCES

An K., Alayoglu S., Musselwhite N., Plamthottam S., Melaet G., Lindeman A. E., and Somorjai G. A., 2013. Enhanced CO Oxidation Rates at the Interface of Mesoporous Oxides and Pt Nanoparticles. J. Am. Chem. Soc., 2013, 135 (44), pp 16689–16696

Borisov A. S., Morozov L. N., Kostrov V. V., 1988. J. Appl. Chem. 61 (1988) 1972.

Cai L. N., Guo Y., Lu A. H., Branton P., Li W. C., 2012. 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 360 (2012) 35– 41

Cortie M. B., Lingen E., 2002. Ctatalytic gold nano-particles. Institute of Meterials Engineering Australasia Ltd, Materials Forum 2002, 26. 1-14.

Davydov A. A., 1984. IR-Spectroscopy in the Chemistry of Oxides Surface, Nauka, Moscow, 1984 (in Russian).

Ferrandon, Magali, 2001, (KTH, Tidigare Institutioner, Kemiteknik). Mixed metal oxide - noble metal catalysts for total oxidation of volatile organic compounds and carbon monoxide. Organisation: KTH, Tidigare Institutioner, Kemiteknik, book Serie: Trita-KET, ISSN 1104-3466; 137, 2001 Permanent länk: http://urn.kb.se/resolve?urn=urn:nbn:se:kth:diva-3156

Hasegawa Y., Fukumoto K., Ishima T., Yamamoto H., Sano M., Miyake T., 2009. Appl. Catal. B: Environ. 89 (2009) 420–424.

Hutchings G. J., Mirzaei A. A., Joynerb R. W., Siddiqui M., Taylor S. H., 1998. Effect of preparation conditions on the catalytic performance of copper manganese oxide catalysts for CO oxidation, Applied Catalysis A: General 166 (1998) 143-152

Jonesa C., Colea K. J., Taylora S. H., Crudaceb M. J., Hutchings G. J., 2009. Copper manganese oxide catalysts for ambient temperature carbon monoxide oxidation: Effect of calcination on activity. Journal of Molecular Catalysis A: Chemical , Volume 305, Issues 1–2, 15 June 2009, Pages 121–124

Kim J. Y., Jin M., Lee K. J., Cheon J. Y., Joo S. H., Kim J. M., Moon H. R., 2012. In situ-generated metal oxide catalyst during CO oxidation reaction transformed from redox-active metal-organic framework-supported palladium nanoparticles. Nanoscale Research Letters 2012, 7:461

Kondrat S. A., Davies T. E., Zu Z., Boldrin P., Bartley J. K., Carley A. F., Taylor S. H., Rosseinsky M. J., Hutchings G. J., 2011. 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 281 (2011) 279–289

Kra¨mer M., Schmidt T., Sto¨we K., Maier W. F., 2006. Structural and catalytic aspects of sol–gel derived copper manganese oxides as low-temperature CO oxidation catalyst, Applied Catalysis A: General 302 (2006) 257–263

Larsson P., Andersson A., 2000. 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 24 (2000) 175–192

Ma Z., Dai S., 2011. Development of Novel Supported Gold Catalysts: A Materials Perspective. Nano Res. 2011, 4(1): 3–32 ISSN 1998-0124 DOI 10.1007/s12274-010-0025-5

Martınez-Arias A., Fernandez-Garcıa M., Galvez O., Coronado J. M., Anderson J. A., Conesa J. C., Soria J., and Munueraz G.,2000. Comparative Study on Redox Properties and Catalytic Behavior for CO Oxidation of $CuO/CeO_2$ and $CuO/ZrCeO_4$ Catalysts. Journal of Catalysis 195, 207–216 (2000)

Moretti E. C., 2001. 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.

Qian K., Qian Z., Hua Q., Jiang Z., Huang W.,2013. Structure–activity relationship of CuO/MnO2 catalysts in CO oxidation, Applied Surface Science 273 (2013) 357– 363

Ren Y., Ma Z., Qian L., Dai S., He H., Bruce P.G.,2009. Ordered Crystalline Mesoporous Oxides as Catalysts for CO Oxidation. Catal Lett (2009) 131:146–154

Wei P., Bieringer M., Cranswick L., Petric A., 2010. In situ high-temperature X-ray and neutron diffraction of Cu–Mn oxide phases. Journal of Materials Science, February 2010, Volume 45, Issue 4, pp 1056-1064

Wojciechowska M. , Przystajko W., Zielin´ski M., 2007. CO oxidation catalysts based on copper and manganese or cobalt oxides supported on $MgF_2$ and $Al_2O_3$, Catalysis Today 119 (2007) 338–341

Xanthopoulou1 G., Vekinis G., 1998. Investigation of catalytic oxidation of carbon monoxide over a Cu-Cr-oxide catalyst made by self-propagating high-temperature synthesis. Applied Catalysis B: Environmental 19 (1998) 37-44

Yea Q., Zhaoa J., Huoa F., Wanga J., Chenga S., Kanga T., Daib H.,2011. Catalysis Today 175 (2011) 603– 609

Zeng S., Wang Y., Liu K., Su H., 2012. Study on Inverse $CeO_2$/CuO Catalysts for CO Preferential Oxidation. 2012 3rd International Conference on Chemistry and Chemical Engineering, IPCBEE vol.38 (2012)

Zengjian Z., Hui W., Guofeng G., 2011. Catalytic Combustion of Methyl Acetate over Cu-Mn Mixed Oxide Catalyst. Computer Distributed Control and Intelligent Environmental Monitoring (CDCIEM), 2011 International Conference on 19-20 Feb. 2011, pp. 1994 – 1997, Digital Object Identifier: 10.1109/CDCIEM.2011.107

Živković Ž. D., Živković D.T., Grujičić D. B., 1998. Kinetics and Mechanism of the Thermal Decomposition of $M(NO_3)_2 \cdot nH_2O$ (M=Cu, Co, Ni). Journal of Thermal Analysis and Calorimetry 07-1998, Volume 53, Issue 2, pp 617-623