EFFECT OF THE NATURE OF THE PRECURSOR ON THE PERFORMANCE OF Cu-Mn CATALYSTS FOR CO AND VOCs OXIDATION

D. Dimitrov, E. Kolentsova, K. Ivanov

Department of Chemistry, Agricultural University, 4000 Plovdiv, Bulgaria

Abstract

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 (DME). Evaluation of the possibility for removing the harmful components from the exhaust gasses needs a more complex investigation. Our previous work indicates that supported Cu-Mn oxide catalysts are promising for effective deep oxidation of these compounds. This work relates to more detail investigation of the catalyst, comprising copper-manganese spinel, coated on carrier γ-Al_2O_3. The effect of preparation conditions on the active component composition and activity behaviour of the catalysts is discussed. Different organometallic compounds on the base of four natural amino acids (Glycine, Alanine, Valine, Leucine) as precursors were used for the preparation of catalysts with Cu/Mn molar ratio 1:5. X-Ray analyses were performed on the catalyst's bulk, and surface composition and the specific surface area was determined by BET method. The results obtained show that the activity of the catalysts increase up to 40% although there are some specific features, depending on the nature of the amino acid and the oxidized compound.

Keywords: *Cu-Mn/γ-Al_2O_3, CO and VOCs oxidation, amino acids*

1. INTRODUCTION

In recent decades, nanoscience and nanotechnology have played an important role in the development of new heterogeneous catalysts. In many cases, the physicochemical properties of the materials, and hence their catalytic properties, strongly depend on the particle size [1]. One of the effective methods for obtaining nanomaterials is Solution Combustion Synthesis (SCS), which is successfully applied in the production of powder oxides, materials for lithium-ion batteries [2-5], as well as for the production of heterogeneous catalysts [6-10]. It is well known that various salts, such as nitrates, metal sulphates and carbonates, may be used as oxidants, and as reducing agents – fuels such as glycine, urea, sucrose or other water-soluble carbohydrates [11]. It has been found that in this method particle morphology, cluster size and specific surface area are directly related to the amount of gases emitted during combustion. [11-13]. The rapid generation of large volumes of gases during the reaction dissipates the heat from the process and limits the temperature rise. This process reduces the possibility of premature agglomeration of primary crystals by limiting the contact between them [11]. Combustion of different compounds occurs at different rates and reaches different temperatures, in many cases exceeding 1000°C [14]. In this way, two reactions compete - on the one hand, the crystallites agglomerate as a result of the high temperature and on the other hand, the large amount of exhaust gases does not allow this agglomeration.

The method is relatively new in its use for the production of heterogeneous catalysts and is therefore insufficiently studied. A study by Hosseini et al. [15] shows that by applying the SCS method, the synthesis of mixed Co-Mn-O oxides using citric acid as fuel is obtained by active oxidation catalysts of VOCs compared to the standard co-precipitation method. According to the authors, this is due to the formation of a larger amount of spinal phase in the SCS samples at ignition temperatures lower than those in the coagulation method. The increase in temperature during the thermal treatment is associated with the increase in the size of the crystals and hence the decrease in activity. Morphological measurements indicate that the specific surface area in the more active SCS samples is higher, although the degree of agglomeration of the crystals is greater. According to other authors, the urea combustion method leads to a decrease in activity compared to methods such as the citric acid sol-gel method (SG), Co-impregnation method (CI) and Urea gelation co-precipitation method (UG)

due to agglomeration of particles in the violent processes of combustion [16]. Robert Ianoş et al. [12] claim that the phase composition of the final oxides obtained by the SCS method strongly depends on the type of fuel used and the type of flame produced. The work of V.D. Zhuravlev et al. [17] shows that the formation of stable chelate complexes in the crystal structure of the fuel-nitrate mixture strongly influences the formation of certain intermediate products during combustion, which in its turn can influence the final phase composition of the oxides obtained.

A. Sharma et al. [18] conclude from their experiments that the combination of oxidant and fuel is essential for generating a violent reaction. According to the data obtained, the use of urea leads to a high reaction rate, whereas the combination with alanine has a smouldering character. According to various authors [14, 19, 20], combustion usually starts between gas products when metal nitrate and fuel are decomposed. Therefore, the reaction starts when the nitrate decomposition temperature overlaps with the interval at which the fuel decomposes. According to P. Erri et al. [20], the separated amino groups in the decomposition of the compounds used by them are relatively higher than the hydroxyl and carboxyl groups. This means that the number and type of chemical groups in the compounds-reducers used will be of importance to how the burning process will take place. Natural amino acids, for example, have a different decomposition temperature, therefore, gas phase reactive groups will be separated at different temperature intervals that may or may not coincide with the interval of thermal decomposition of the nitrates used. Thus, with some amino acids, more combustible gases will be produced than others at the time of nitric oxide release from nitrates, which will likely influence the speed of the process. On the other hand, amino acids differ in both the length and type of the carbon chain as well as the number and types of their functional groups. For this reason, we consider that the use of different agents in SCS catalyst synthesis will probably result in varying intensity of the combustion process and correspondingly obtaining different temperatures in the reaction zone, which can affect the phase composition and crystallite size [18]. The control of the morphological indicators in its turn will lead to possibilities for a positive influence on the catalytic activity of already known catalyst systems.

The aim of this work is to determine the influence of fuel used on the morphological characteristics and catalytic activity of proven systems for catalytic oxidation of CO and VOC as Cu-Mn-O catalysts. The activity of samples obtained by impregnation of a carrier with a mixture of nitrates (Standard Impregnation Method - SIM) and the SCS method using four natural amino acids - glycine, alanine, valine and leucine are compared.

2. MATERIALS AND METHODS

2.1. Materials

All catalysts were prepared by wet impregnation method. The samples are impregnated with solutions of copper and manganese nitrates with a Cu/Mn = 1/5 molar ratio. In the standard impregnation method - SIM, the carrier is impregnated only with the copper and manganese nitrates solution. In catalysts obtained by SCS method, Glycine, Alanine, Valine and Leucine are dissolved in the Cu-Mn nitrate solution, to obtain the SCS_{Gly}, SCS_{Ala}, SCS_{Val} and SCS_{Leu} samples, respectively. Impregnation is followed by drying at 100°C for 2 hours and calcination at 450°C for 4 hours in an air atmosphere. The speed for reaching the final temperature is 0.57°C/min.

2.2. Methods

2.2.1. Texture Measurements

The texture characteristics were determined by low-temperature (-196 ^{o}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.

2.2.2. 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 90º (2θ), at steps of 0.03º (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.

2.2.3. Activity Measurements

The catalytic measurements were carried out in continuous flow equipment with a four-channel isothermal stainless steel reactor. 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 10 L/h, amount of the catalyst 1 ml, space velocity 10 000 h^{-1}, tested temperature range 40-380 ºC, the flow of ambient air (40-50% humidity) and CO (final concentration 2.0%), methanol (2.0%), DME (1.0%).

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, oxygen and nitrogen).

3. RESULTS AND DISCUSSION

Preliminary studies have shown that the catalyst activity fluctuates smoothly over long periods of time in isothermal mode. This required all samples to be subjected to a pre-heat treatment to stabilize the catalyst surface including heating up to 300°C for 2 hours in reactor nests with an air flow rate of 10 l/h.

Figures 1, 2 and 3 present the results of the catalytic measurements of the oxidation of carbon monoxide (CO), methanol (MeOH) and dimethyl ether (DME) on Cu-Mn/γ-Al_2O_3 catalysts, prepared with and without amino acids. It can be noticed from the three graphs that, regardless of the amino acid used, the application of the SCS method leads to better results in terms of catalytic activity. CO oxidation reaction begins in the range of 60-70°C for all samples. Increasing the temperature of the catalyst nests above 80°C leads to activity differences. The greatest difference is at 140°C, where between the sample obtained by the SIM method and the most active sample obtained by the SCS Leucine (SCS_{Leu}) method, it is about 40%. The least difference is the activity of the catalysts obtained by the standard impregnation method and the SCS_{Gly} sample, where it reaches about 10%. At temperatures above 220°C, complete elimination of CO in all samples is achieved.

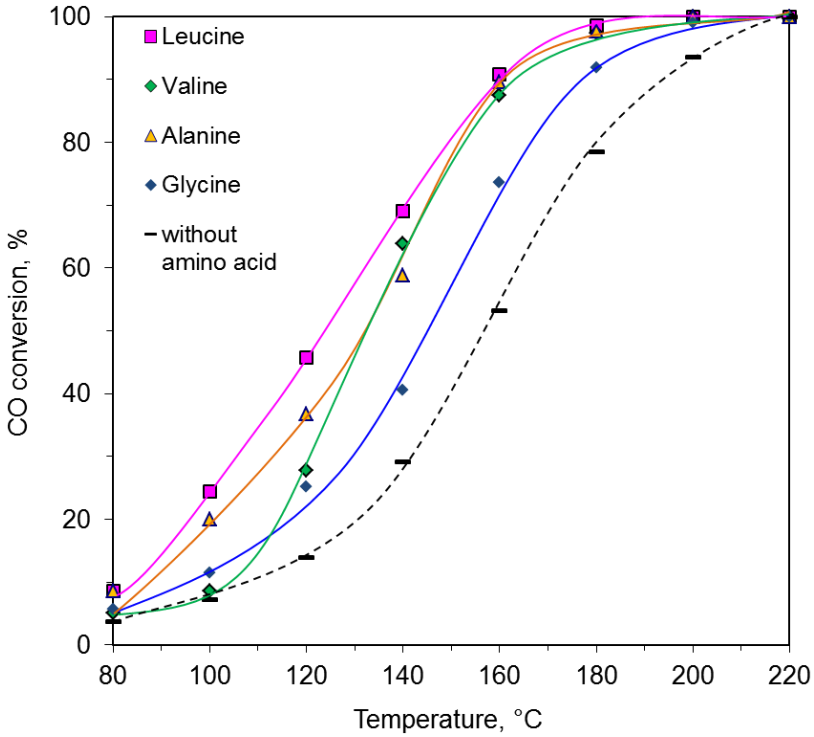


Fig. 1. Conversion of CO over sample with and without amino acids

As for the structure of the amino acids used, they are not very different. They contain one carboxyl and one amino group in the alpha position. The difference is mainly in the length of the carbon chain and the branching of valine and leucine. The isoelectric points of the four amino acids are about pH=6. G. Gorboletova et al. [21] studied the acid-base equilibrium between Cu^{+2} and glutamine. According to them, at pH~1, complexes between Cu^{+2} ions and amino acids in the solution are practically not formed, since both ions are positively charged in this area. The pH values measured in the present work, after a dissolution of the amino acids in the nitrate solutions, are about pH=1. This means that, under these conditions, complexes between copper, manganese and amino acid ions will also not be formed in the impregnation solutions.

The MeOH oxidation proceeds a little more specifically (Fig. 2). A noticeable process of oxidation is observed at temperatures above 140 °C.

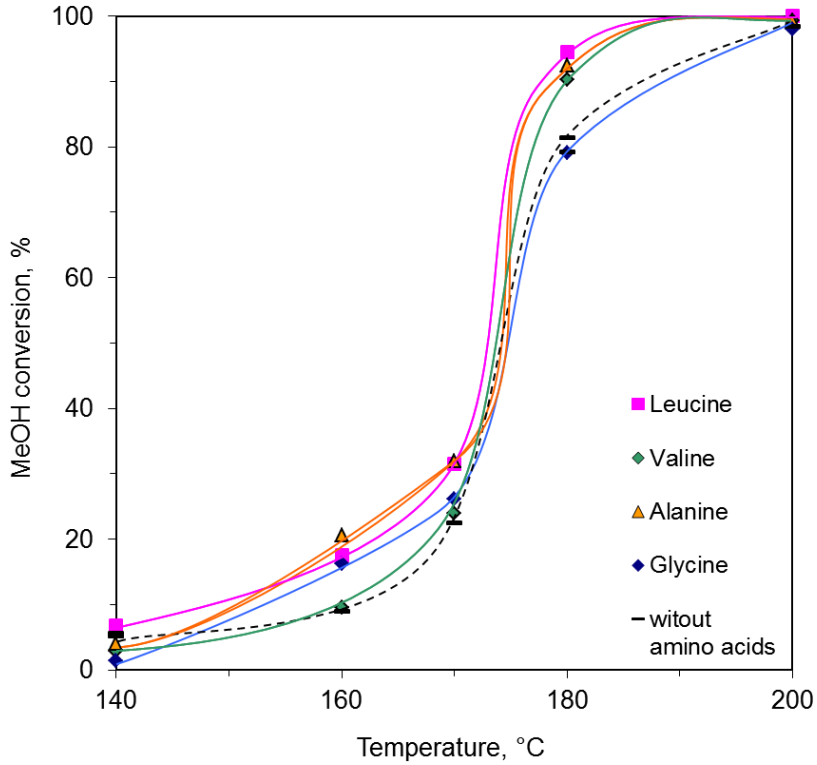


Fig. 2. Conversion of MeOH over sample with and without amino acids

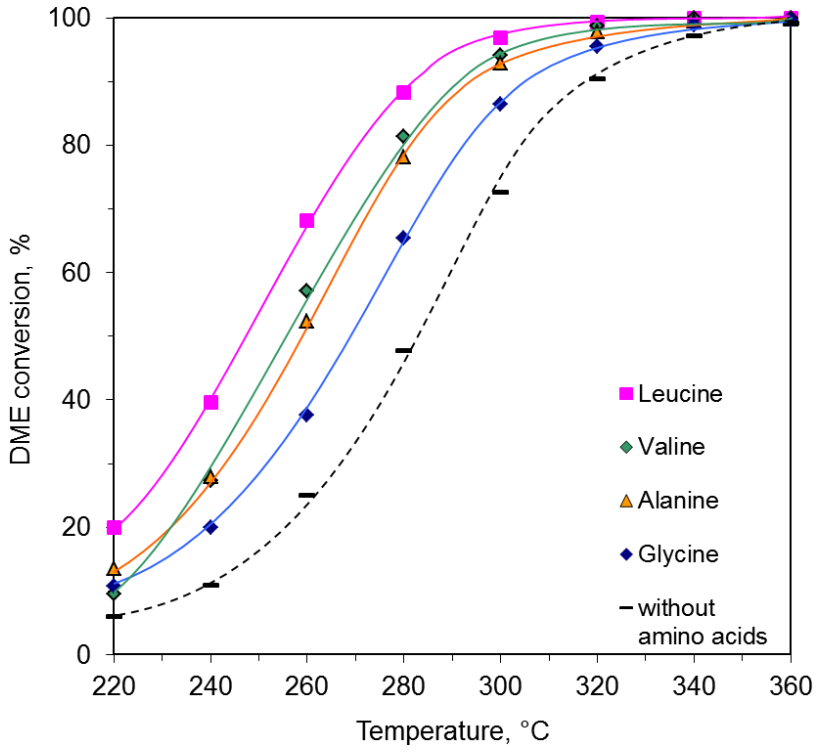


Fig. 3. Conversion of DME over sample with and without amino acids

There is little difference in the catalytic activity of the compared catalysts. The reason for this is the rapid reaction transfer into diffusion area with an increase in the reactor temperature. Despite the slight differences, it can be seen from Fig. 2 that at 180°C most active is the SCS_{Leu} sample. Its activity is about 12% higher than that of the base catalyst. In the analysis of the results, it can be stated that the activity of SIM and SCSGly samples are commensurable in the temperature range studied.

Fig. 3 shows the results of the catalytic measurements of DME oxidation. The reaction starts in the 170-190°C range depending on the catalyst studied. At high temperatures the difference in activity between catalysts is substantial, at 260°C it reaches its highest value. Here, as in the MeOH oxidation, the samples are arranged in the same order in terms of their activity. The SCS_{Leu} sample is about 44% more active than the base catalyst. The difference with the least active, in this case, SCS_{Gly}, is about 14%.

Sample	S, m^2/g	V_{total}, cm^3/g	$D_{average}$, nm
SIM	152	0,26	5.8
SCS_{Leu}	191	0.30	6.4
SCS_{Gly}	210	0.31	5.8

Table 1. Specific surface, pore volume and average pore diameter of selected catalysts

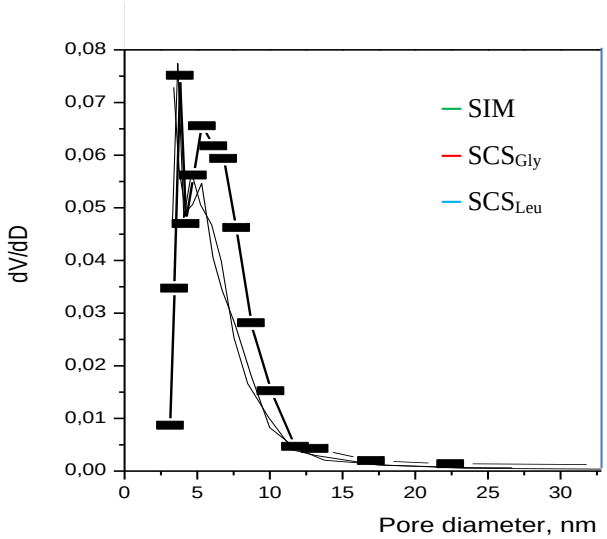


Fig. 4. Pore distribution of SIM, SCS_{Gly} and SCS_{Leu}

Table 1 shows the results of measurement of the specific surface area, the pore volume and average pore diameter of some of the samples tested. It is evident that by applying the SCS method, the specific surface is increased by 20-27%, depending on the modified sample compared to the SIM method. Fig. 4 show that the pore distribution by diameter for the SCS_{Leu} and SCS_{Gly} samples is identical. Pores with a diameter of about 3 nm predominate. Data from the absorption measurements show that there is not much difference in the specific surface and pore volume between SCS_{Leu} and SCS_{Gly}. At the same time, the difference in activity of the two samples is significant - about 30% in the CO and DME oxidation. This means that the activity does not substantially depend on the increase of the specific surface and the variations in pore diameter. Similar results have been obtained in our other studies [22].

According to the XRD analysis shown in Fig. 5, the catalysts obtained by the SCS process has a higher degree of amorphousity compared to that synthesised using the SIM method.

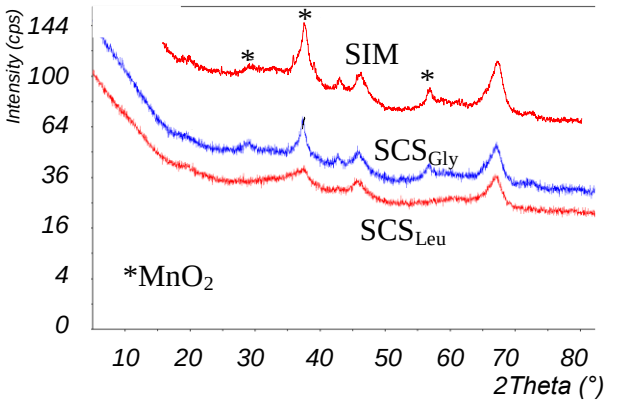


Fig. 5. XRD analysis of catalysts SIM, SCS_{Gly} and SCS_{Leu}

In the SCS_{Gly} sample, MnO_2 reflexes of lower intensity than the SIM catalyst are observed. Low-intensity reflexes in the SCS_{Leu} sample indicate that it is completely amorphous. The resulting copper-manganese oxide crystallites are much smaller than the other two catalysts. The formation of an amorphous phase, according to Amit Sharma et al. [18] is due to a relatively weak exothermic process in the interaction of reducing compounds with metallic nitrates.

According to some authors [14,19,20], an important factor in the interaction of amino acids with nitrates in the combustion process is the overlapping of temperature decomposition intervals of the compounds in the thermal treatment. Comparing literature data for Glycine-nitrate combustion synthesis [11, 14] indicates that ignition, in most cases, starts at lower heating temperatures than the glycine decomposition. This means that the oxidation of amino acids probably starts in a solid phase.

Compounds	Temperature decomposition, °C
$Mn(NO_3)_2$+$Cu(NO_3)_2$	170 [23]
Glycine	212-240 [24]
Alanine	241-309 [24]
Valine	298 [25]
Leucine	293-295 [26]

Table 2. Temperature decomposition intervals of the compounds

A significant factor in the course of a violent reaction, in this case, will be the oxidant quantity in the gas phase, since in this state its reactivity is higher. According to the results of the thermal analysis in our other experiments [23], the decomposition peak of Al_2O_3- applied copper-manganese nitrates is about 170°C, indicating that the decomposition of all used amino acids (Table 2) already has free nitrogen oxides. However, in the decomposition range of leucine and valine, there will be less nitrogen oxides than in glycine and alanine as the nitrate decomposition will be in its final phase. This will create conditions for a more violent reaction for low-temperature decomposition amino acids since the peak of reactive gas formation will be in this interval [14, 20]. Similar results are seen in the work of A. Sharma et al. [18] where glycine and urea are used. Urea decomposes at about 135°C and the glycine at approximately 233°C. The glycine-derived samples are more amorphous than those

obtained with urea. From the reflection made so far, it can be concluded that in a stoichiometric fuel/oxidant ratio = 1/1 in the catalysts with glycine and alanine, the exothermic process will be higher than that in leucine and valine.

Fig. 6 shows the dependence of the CO conversion at 140°C on the decomposition temperature of the relevant amino acids. There is a certain tendency in increasing the activity with increasing the decomposition temperature of the amino acid used. However, the difference in activity of SCS_{Gly} and SCS_{Ala} is significant, whereas the difference in decomposition temperatures is only 25°C. A similar trend was observed in the samples obtained with valine and leucine. The decomposition temperature of leucine is several degrees lower than that of valine, however, SCS_{Leu} activity is higher than that of SCS_{Val}.

The number of carbon atoms in the chain of the relevant amino acids is also shown in the figure. It is noticeable that activity increases with increasing the number of carbon atoms. According to A. Mukasyan et al. [27], the ratio between the oxidant and the fuel in the amino nitrate mixture influences the overall morphology of the oxides obtained. The small amount of fuel (fuel/oxidant <1) results in a relatively slow smouldering reaction, relatively low T in the reaction zone leaving unreacted carbon. During calcination, the resulting samples lose a significant part of their weight, and their surface becomes relatively small. Higher fuel in the mixture (fuel/oxidant ≥1) leads to a more violent reaction, combustion spreads as a wave throughout the entire volume of the mixture, the temperature increases considerably, as the heat released is sufficient to self-sustain the process, the carbon from the amino acid burns without residue if the reaction occurs in an oxygen medium. The time for the process decreases, thus the time for crystal agglomeration becomes insufficient.

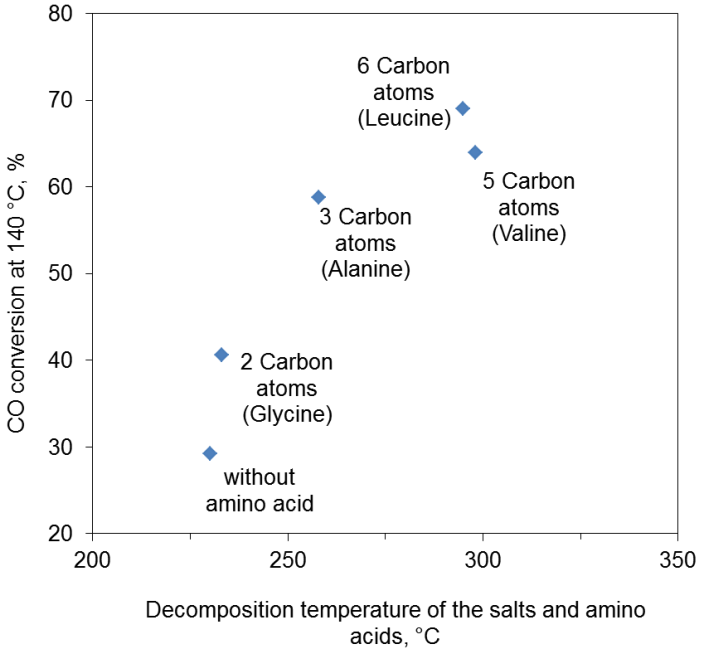


Fig. 6. Catalysts activity v/s decomposition temperatures of the salts and aminoacids

The fuel/oxidant ratio for all samples obtained in this work is 0.11. Table 3 presents model reactions between $Mn(NO_3)_2$ and the amino acids used, showing the optimal stoichiometric ratios to allow the reaction to proceed without residue from the starting materials. It can be observed that the ratio in the catalysts considered is closest to that of the model reaction with leucine. This means that the amount of fuel in SCS_{Gly} is much less than the stoichiometric compared, for example, with SCS_{Leu}, i.e. order to have total combustion at the same amount of oxidant, about four times less fuel is needed if leucine is used compared to the amount of glycine.

Oxidation reactions	The fuel/oxidant ratio
Catalyst obtained in this work	**0,11**
Model reaction with glycine	
$9\ Mn(NO_3)_2 + 8\ C_2H_5NO_2 = 9\ MnO_2 + 16\ CO_2 + 20\ H_2O + 13\ N_2$	0,88
Model reaction with alanine	
$15\ Mn(NO_3)_2 + 8\ C_3H_7NO_2 = 15\ MnO_2 + 24\ CO_2 + 28\ H_2O + 19\ N_2$	0,53
Model reaction with valine	
$27\ Mn(NO_3)_2 + 8\ C_5H_{11}NO_2 = 27\ MnO_2 + 40\ CO_2 + 44\ H_2O + 31\ N_2$	0,29
Model reaction with leucine	
$33\ Mn(NO_3)_2 + 8\ C_6H_{13}NO_2 = 33\ MnO_2 + 48\ CO_2 + 52\ H_2O + 37\ N_2$	**0,24**

Table 3. Stoichiometric ratios of nitrates and amino acids in model mixtures and present samples

It can be concluded that less fuel than it is necessary in the stoichiometric ratio leads to a weak exothermic process, and low-temperature decomposing fuels lead to an increase in combustion rate and possibly an increase in the heat released in the reaction. That means, in the present work there is competition in both processes, as in SCS_{Gly} and SCS_{Ala} the combustion rate is likely to be high, but the insufficient quantity of fuel has resulted in the release of a small amount of heat insufficient to eliminate the resulting carbon as a result of decomposition of amino acids. For SCS_{Val} and SCS_{Leu}, the combustion rate was probably slowed down due to the insufficient amount of nitrogen oxides at the time of decomposition of the amino acids. But the amount of fuel was probably enough to create a highly exothermic process, releasing a large amount of gas in a very short time, due to which the crystallites did not have agglomeration possibilities.

4. CONCLUSIONS

The synthesis of Cu-Mn/γ–alumina supported oxide materials by SGS method is an appropriate approach for the development of catalysts with enhanced activity toward CO, methanol and DME oxidation. The thermal decomposition of the supported copper and manganese nitrates in the presence of amino acids results in a high surface area material with a very well defined mesopores and narrow pore size distribution. The XRD analysis indicated the formation of highly dispersed Cu - Mn spinel phase and obvious amorphisation of MnO_2. This poor crystalline structure may favour structural defects formation, in particular, oxygen vacancies giving the best performance in the oxidation process. The results obtained show that a significant factor influencing the morphological characteristics of the catalytic surface in SGS synthesis is the ratio between the amount of oxidant and that of the fuel used. The use of different amino acids in the synthesis makes it possible to influence the properties of the catalysts by the fuel/oxidant ratio.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support by the Agricultural University - Plovdiv (Project 06/16).

REFERENCES

[1] Ma, Z & Dai, S 2011, "Development of Novel Supported Gold Catalysts: A Materials Perspective", *Nano Res.*,4(1), pp.3–32.

[2] Aruna, ST & Patil, KC 1998, "Combustion synthesis and properties of nanostructured ceria–zirconiasolid solutions", *Nanostruct. Mater.*, 10, pp. 955–964.

[3] Julien, C, Camacho-Lopez, MA, Mohan, T, Chitra, S & Kalayani, P 2001, "Combustion synthesisand characterization of substituted lithium cobalt oxides in lithium batteries", *Solid StateIonics*, pp. 549–557.

[4] Patil, KC & Mimani, T 2000, "Preparation and properties of nanocrystalline magnetic oxides", *Mag. Soc. India Bull.*, 22, pp. 21–26.

[5] Anuradha, TV, Ranganathan, S, Mimani, T & Patil, KC 2001, "Combustion synthesis of nanostructured barium titanate", *Scripta Mater.* 44, pp. 2237–2241.

[6] Lamas, DG, Juarez, RE, Lascalea, GE & Walsoe, NE 2001, "Synthesis of compositionally homogeneous, nanocrystalline ZrO_2-35 mol% CeO_2 powders by gel combustion", *J. Mater.Sci. Lett.* 20, pp. 1447–1449.

[7] Bera, P, Patil, KC, Jayaram, V, Subbanna, GN & Hegde, MS 2000, "Ionic dispersion of Pt and Pd on CeO_2 by combustion method: effect of metal–ceria interaction on catalytic activities for NO reduction, CO and hydrocarbon oxidation", *J. Catal.* 196, pp. 293–301.

[8] Bera, P, Patil, KC, Jayaram, V, Hegde, MS & Subbanna, GN 1999, "Combustion synthesis of nano metal particles supported on α-Al_2O_3: CO oxidation and NO reduction catalysts", *J.Mater. Chem.*, 9, pp. 1801–1805.

[9] Bera, P, Patil, KC, & Hegde, MS 2000, "Oxidation of CH_4 and C_3H_8 over combustion synthesized nanosize metal particles supported on α-Al_2O_3", *Chem. Phys.*, 2, pp. 373–378.

[10] Quenard, O, Grave, E, Laurent, C & Rousset, A 1997, "Synthesis, characterization and thermalbehaviour of $Fe_{0.65}Co_{0.35}MgAl_2O_4$ and $Fe_{0.65}Ni_{0.35}MgAl_2O_4$ nanocomposite powders", *J. Mater. Chem.*, **7**, pp. 2457–2467.

[11] Alves, A, Bergmann, C & Beruttiet, F 2013, *"Novel Synthesis and Characterization of Nanostructured Materials"*, Engineering Materials, Springer-Verlag Berlin Heidelberg.

[12] Ianoş, R, Lazău, I, Păcurariu, C & Barvinschi, P 2009, "Fuel mixture approach for solution combustion synthesis of $Ca_3Al_2O_6$ powders", *Cement and Concrete Research.*, 39, pp. 566–572.

[13] Castano, MH, Molina, R & Moreno, S 2015, "Catalytic oxidation of VOCs on MnMgAlOx mixed oxides obtained by auto-combustion", *Journal of Molecular Catalysis A: Chemical*, 398, pp. 358–367.

[14] Hwang, C, Tsai, J & Huang, T 2005, "Combustion synthesis of Ni–Zn ferrite by using glycine and metal nitrates—investigations of precursor homogeneity, product reproducibility, and reaction mechanism", Materials Chemistry and Physics, 93, pp. 330–336.

[15] Hosseini, SA, Salari, D, Niaei, A, Deganello, F, Pantaleo, G & Pejmanhojati, H 2011, "Chemical-physical properties of spinel $CoMn_2O_4$ nano-powders and catalytic activity in the 2-propanol and toluene combustion: Effect of the preparation method", J. Envir. Sci. Health, Part A, 46, pp. 291–297.

[16] Rattan, G, Prasad, R & Katyal, RC 2011, "Comparison of Different Preparation Methods on Al_2O_3 Supported CuO-CeO_2-ZrO_2 Catalysts for CO Oxidation", TIChE International Conference 2011 November 10 – 11, Hatyai, Songkhla Thailand.

[17] Zhuravlev, VD, Bamburov, VG, Beketov, AR, Perelyaeva, LA, Baklanova, IV, Sivtsova, OV, Vasilev, VG, Vladimirova, EV, Shevchenko, VG & Grigorov, IG 2013, "Solution combustion synthesis of α-Al_2O_3 using urea", Ceramics International, 39, pp. 1379–138.

[18] Sharma, A, Rani, A, Singh, A, Modi, O & Gupta, G 2014, "Synthesis of alumina powder by the urea–glycine–nitrate combustion process: a mixed fuel approach to nanoscale metal oxides", Appl. Nanosci., 4, pp. 315–323.

[19] Kingsley, JJ & Patil, KC 1988, "A novel combustion process for the synthesis of fine particle α-alumina and related oxide materials", Materials Letters, 6 (11–12), pp. 427-432.

[20] Erri , P, Pranda, P & Varma, A 2004, "Oxidizer−Fuel Interactions in Aqueous Combustion Synthesis. 1. Iron(III) Nitrate−Model Fuels", *Ind. Eng. Chem. Res.*, *43* (12), pp. 3092–3096.

[21] Gorboletova, GG, Gridchin, SN & Lutsenko, AA 2010, "Thermochemical study of processes of complex formation of Cu^{2+} ions with L-glutamine in aqueous solutions", *Russian Journal of Physical Chemistry A*, Vol. 84, № 11, pp. 1856–1861.

[22] Ivanov, KI, Kolentsova, EN & Dimitrov, DY 2015, "Alumina Supported Copper-Manganese Catalysts for Combustion of Exhaust Gases: Effect of Preparation Method", *World Academy of Science, Engineering and Technology International Journal of Chemical, Nuclear, Materials and Metallurgical Engineering*, Vol:9, No:4, pp. 548-557.

[23] Ivanov, KI, Kolentsova, EN, Dimitrov, DY, Avdeev, GV & Tabakova, TT 2015, "Alumina Supported Copper-Manganese Catalysts for Combustion of Exhaust Gases: Catalysts Characterization", World Academy of Science, Engineering and Technology, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering Vol:9, No:6, pp. 692-697.

[24] Yablokov, VY, Smel'tsova, IL, Zelyaev, IA & Mitrofanova, SV 2009, "Studies of the Rates of Thermal Decomposition of Glycine, Alanine, and Serine", *Russian Journal of General Chemistry*, Vol. 79, No. 8, pp. 1704–1706.

[25] Dunn, MS & Brophy, TW 1932, "Decomposition points of amino acids", The Chemical Laboratory, University of California at Los Angelis, pp. 224-225.

[26] O'Neil, MJ (ed.) 2006, The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals. Whitehouse Station, NJ: Merck and Co., Inc., p. 943.

[27] Mukasyan, A, Costello, C, Sherlock, K, Lafarga, D & Varma, A 2001, "Perovskite membranes by aqueous combustion synthesis:synthesis and properties", *Separation and Purification Technology*, 25, pp. 117–126.