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## Article

# Methanol Reforming over Cu-Ce-Al Catalyst Prepared by Solution Combustion Synthesis Method

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**Abstract:** Demand for environmentally friendly types of energy is growing all over the world, which naturally increases the intensity of work on the production of hydrogen-containing fuel mixtures. Steam reforming of methanol is one of the most effective areas of research, as it is a process with low energy consumption. The results of steam reforming of methanol on the catalysts prepared by solution combustion synthesis (SCS) and impregnation by moisture capacity are presented. Investigation of the activity of Cu-Ce-Al catalysts of different composition was carried out for production of hydrogen and comparison of SCS with traditional impregnation method. Methanol conversion reaches 99%, while the selectivity of H<sub>2</sub> was 88%, at 500 °C. It was found that CuAl<sub>2</sub>O<sub>4</sub> spinel formation is due to substitution of Al<sup>3+</sup> with Cu<sup>2+</sup> Ce<sup>3+</sup> cations. A consequence CuAl<sub>2</sub>O<sub>4</sub> and CeAlO<sub>3</sub> lattice parameters increase because of difference in ionic radius of Al<sup>3+</sup> (0.53 Å) and Cu<sup>2+</sup> (0.73 Å), Ce<sup>3+</sup> (1.07 Å). Advantages of SCS catalysts in steam reforming of methanol were shown. The aim of this research is to develop a new catalyst for conversion of methanol into hydrogen containing fuel mixtures, which will further promote the organization of a new era of environmentally friendly energy-saving production methods.

**Keywords:** hydrogen; methanol; steam reforming; Cu-Ce based catalysts; SCS method

## 1. Introduction

As we all know, population increases and economic growth naturally provoked increases in energy consumption [1]. Today, 70–80% of all energy produced in the world comes from fossil fuels, such as natural gas, oil and coal [2] and at the same time the cost of hydrogen synthesis is too high. As fossil fuel reserves decline, dependence on renewable energy has become crucial, while the continued use of fossil fuels leads to considerable environmental and economic costs. The increasing costs of our current energy systems highlight the potential of hydrogen proton-exchange membrane fuel cells as a viable alternative to internal combustion engines, though they require a reliable H<sub>2</sub> supply [3]. Consequently, having a liquid hydrogen source that can provide H<sub>2</sub> on demand is beneficial, with hydrogen production from methanol via steam reforming over copper-based catalysts emerging as a notable method.

Currently, hydrogen is indispensable due to its efficient and clean properties as an energy carrier [4]. The most used process in production organizations is steam reforming, which, in turn, involves the decomposition of molecules of hydrocarbons, alcohols, in particular methanol and ethanol, using superheated steam. The result of which is hydrogen and carbon oxides. But these processes are energy-consuming, since they take place at high temperatures and, in addition to the target products, produce a large number of undesirable accompanying and by-products. Alternatively, hydrogen can

be synthesized using the process of electrolysis of water [5] (which breaks down into O<sub>2</sub> and H<sub>2</sub>) - a less cost-effective method due to the amount of electricity required for electrolysis. The approach we propose can completely or partially solve all these problems. This method requires only an inexpensive catalyst and a mixture of methanol and water.

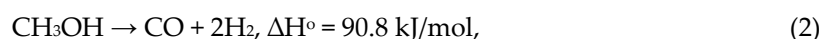
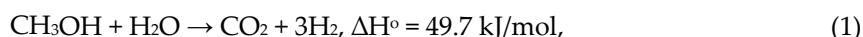
Under much milder conditions, catalytic processes of steam reforming of aliphatic alcohols take place, which, moreover, can be obtained from renewable raw materials - biomass (bioalcohols). Compared to gaseous hydrogen carriers, methanol, an affordable hydrocarbon liquid hydrogen carrier (a low-carbon alcohol) with high hydrogen content, can react with water to release H<sub>2</sub> under relatively mild conditions. This is due to methanol's lack of a strong C-C bond, unlike other multi-carbon hydrocarbon resources [6]. Steam reforming of methanol (SRM) seems attractive because the process is characterized by low energy costs and relatively cheap raw material itself [7], in addition to traditional methods, is combined with a wide range of alternative sources for methanol synthesis [8]:

- biomass (agricultural waste, timber);
- household waste with a high organic content;
- waste gases from enterprises.

Their gasification will make it possible to obtain a gas mixture for the subsequent synthesis of methanol along the "green" route, without using fossil organic fuel. Most likely, in the near future, alternative sources of methanol synthesis in the form of biogas will become one of the few solutions to energy supply problems in the world. It is no secret that reserves of natural hydrocarbons are being depleted every year and this direction may well become the only variable method of producing both motor fuel and petrochemical products.

A promising direction for using the resulting methanol is its use as a motor fuel for internal combustion engines and fuel cells. Compared to traditional fuels, methanol has a number of advantages such as renewability, smaller carbon footprint and high calorific value [9]. All of them are the main drivers of demand for methanol for use as a raw material and energy carrier in hydrogen production. It is expected that by 2030, methanol production in the world will exceed 130 million tons per year.

The SRM process involves following chemical reactions:



Reactions (1) and (2) are endothermic and reversible, accompanied by an increase in volume, while the exothermic reaction (3) without a change in volume is known as a water gas shift reaction [10]. As a result, a mixture of hydrogen and carbon oxides is formed, the ratio between which depends on the process conditions and the nature of the catalyst.

A development of a new effective catalyst for the process of steam reforming of methanol into hydrogen-containing gas is aim of this work, which will contribute to the further development of a new environmentally friendly, energy-saving method for hydro-gen production.

Bulk metals [11,12] and oxides [13,14] as well as supported ones on various types of carriers [15] are used as catalysts for the conversion of hydrocarbons. However, in the recent years, new types of highly active catalysts made in the combustion process have appeared. Self-propagating high-temperature synthesis (SHS) [16] and in particular its modern modification – solution combustion synthesis (SCS) [17–19] is a new method for obtaining a modern class of catalysts of various uses based on metals, alloys, oxides, spinels, etc. The mode of a strong exothermic reaction (combustion reaction), in which the heat release is localized in the layer and transferred from layer to layer by heat transfer is carried out in the SHS process. Structures with a high concentration of defects, which are one of the reasons for the high activity of SCS catalysts, are formed under conditions of rapid rates of combustion and cooling reactions. Studies of the physicochemical and mechanical properties of a wide range of synthesized SHS and SCS catalysts were reported in the literature [20–26]. As a result

of these studies, SHS materials with high catalytic activity, promising for many industrial processes, such as partial oxidation, reduction, carbon dioxide conversion of methane, etc., were developed [27,28]. In this study a series of catalysts based on Cu, Ce and Al was synthesized by SCS and traditional impregnation methods and characterized by a range of physico-chemical methods. The catalysts were investigated in methanol steam reforming in a continuous fixed bed reactor.

2. Results

2.1. Characterization of catalysts

The study presents the results of catalysts based on the Cu-Ce-Al system, obtained through solution combustion synthesis method. Post-combustion, the catalysts were analyzed using X-ray diffraction (XRD) to identify and determine the phases. Scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) analysis were employed to ascertain the composition and specific surface area of the catalysts. The following reactions are possible in the process of solution combustion synthesis (Table 1).

**Table 1.** Solution combustion reactions of the Cu(NO<sub>3</sub>)<sub>2</sub> + Ce(NO<sub>3</sub>)<sub>3</sub> + Al(NO<sub>3</sub>)<sub>3</sub> + H<sub>2</sub>O + urea system.

Reactions	Remarks
$2\text{Al}(\text{NO}_3)_3 + 5\text{C}_2\text{H}_5\text{NO}_2 + \text{Cu}(\text{NO}_3)_2 + \text{Ce}(\text{NO}_3)_3 \rightarrow \text{Cu} + \text{CuO} + \text{Cu}_x\text{Al}_y + \text{CuCeO}_x + \text{Ce}_2\text{O}_3 + \text{Cu}_x\text{Al}_{2-x}\text{O}_3 + \text{CeAlO}_3 + 5\text{CO}_2 + 8\text{N}_2 + 10\text{H}_2\text{O}$	500 °C. The total reaction of the SCS process
$\text{Al}_2\text{O}_3 + \text{C} \rightarrow \text{Al} + \text{CO}_2, \text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO}_2$	Carbon is formed by burning urea and reduces oxides to metal
$\text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$	$\Delta H^\circ_{278} = -3352 \text{ kJ/mol}$ , exothermic reaction. The reduced metals can partially oxidize or react with another metal
$\text{Cu} + \text{O}_2 \rightarrow \text{CuO}$	$\Delta H^\circ_{278} = -475.8 \text{ kJ/mol}$ , exothermic reaction
$\text{Al}_2\text{O}_3 + \text{CuO} \rightarrow \text{CuAl}_2\text{O}_4, \text{Al}_2\text{O}_3 + \text{Ce}_2\text{O}_3 \rightarrow \text{CeAlO}_3$	Synthesis of spinel, endothermic reaction
$\text{Cu} + \text{Al} \rightarrow \text{Cu}_x\text{Al}_y$	Synthesis of intermetallic compound

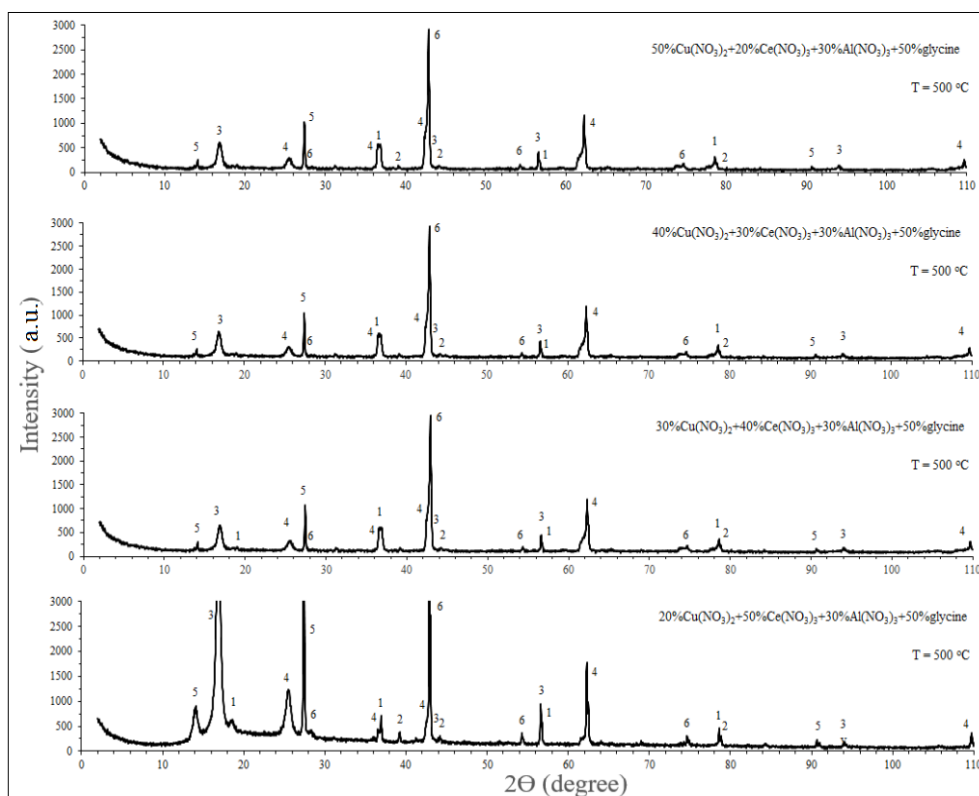
The composition of the initial mixture, combustion conditions and the final catalyst compositions are shown in Table 2.

**Table 2.** The initial compositions of salts and final catalyst composition at 500 °C preheating temperature of solution.

Starting compounds	Catalysts composition
50% Cu(NO <sub>3</sub> ) <sub>2</sub> + 30% Al(NO <sub>3</sub> ) <sub>3</sub> + 20% Ce(NO <sub>3</sub> ) <sub>3</sub> + 50% glycine + 10 mL H <sub>2</sub> O	CuAl <sub>2</sub> O <sub>4</sub> , CeAlO <sub>3</sub> , CeO <sub>2</sub> , CuO, Al, AlCu
40% Cu(NO <sub>3</sub> ) <sub>2</sub> + 30% Al(NO <sub>3</sub> ) <sub>3</sub> + 30% Ce(NO <sub>3</sub> ) <sub>3</sub> + 50% glycine + 10 mL H <sub>2</sub> O	CuAl <sub>2</sub> O <sub>4</sub> , CeAlO <sub>3</sub> , CeO <sub>2</sub> , CuO, Al, AlCu
30% Cu(NO <sub>3</sub> ) <sub>2</sub> + 30% Al(NO <sub>3</sub> ) <sub>3</sub> + 40% Ce(NO <sub>3</sub> ) <sub>3</sub> + 50% glycine + 10 mL H <sub>2</sub> O	CuAl <sub>2</sub> O <sub>4</sub> , CeAlO <sub>3</sub> , CeO <sub>2</sub> , CuO, Al, AlCu
20% Cu(NO <sub>3</sub> ) <sub>2</sub> + 30% Al(NO <sub>3</sub> ) <sub>3</sub> + 50% Ce(NO <sub>3</sub> ) <sub>3</sub> + 50% glycine + 10 mL H <sub>2</sub> O	CuAl <sub>2</sub> O <sub>4</sub> , CeAlO <sub>3</sub> , CeO <sub>2</sub> , CuO, Al, AlCu

2.1.1. XRD and BET analysis

The resulting catalysts had a similar qualitative composition, but different in the phase ratio. The approximate ratio between the phases was determined from the relative intensities of the X-ray diffraction peaks for each phase (Figure 1).



**Figure 1.** X-ray spectra for the  $\text{Cu}(\text{NO}_3)_2 + \text{Ce}(\text{NO}_3)_3 + \text{Al}(\text{NO}_3)_3 + \text{glycine} + \text{H}_2\text{O}$  system at a preheating temperature of the initial mixture of 500 °C.

In Figure 1 which demonstrates the XRD diffraction patterns of the synthesized catalysts were shown that after preparation of catalyst by the solution combustion method  $\text{Cu}(\text{NO}_3)_2$  species were identified as  $\text{CuO}$ ,  $\text{Al-Cu}$  (intermetallic) and  $\text{CuAl}_2\text{O}_4$  (spinel). As for aluminum nitrate, it mainly passed through an intermediate product in the form of aluminum oxide into cerium and copper spinels, as well as into intermetallites. Evident overlap between these diffraction peaks and other diffraction peaks points to a low concentration of  $\text{Al}_2\text{O}_3$ .

Research on methanol adsorption and decomposition on copper-based surfaces revealed that methanol undergoes dissociative adsorption, resulting in the formation of methoxy species ( $\text{CH}_3\text{O}$ ) [29]. It is assumed that absorbed O is the initiator of the formation of methoxy forms. Studies by some authors [30] have shown that the O could be available from an incomplete reduction of the catalyst, such as the lattice oxygen of ceria, or from moisture that was present in the methanol feed.

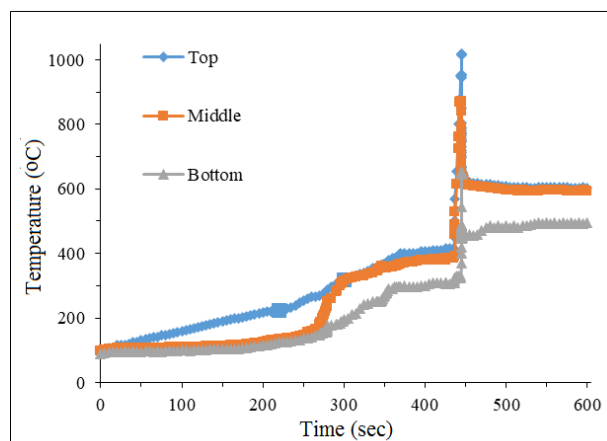
The cerium species in prepared catalysts system of  $\text{Cu}(\text{NO}_3)_2 + \text{Ce}(\text{NO}_3)_3 + \text{Al}(\text{NO}_3)_3 + \text{glycine}$  in each options were recognized as cerium oxide ( $\text{CeO}_2$ ) and spinel ( $\text{CeAlO}_3$ ). As it is shown in the XRD patterns of catalysts the wide diffraction peaks of  $\text{CuO}$  indicates that cerium reduced crystalline size of Cu and increased the degree of dispersion, which is also mentioned in previous studies [31].

The temperature curves recorded during SCS exhibit a second peak following the SCS, as shown in Figure 2. This can only be accounted for by the reaction between carbon and metal oxides. In this case the reaction  $\text{Al}_2\text{O}_3 + \text{C} \rightarrow \text{Al} + \text{CO}_2$  may give an explanation for presence of Al in the product of reaction, because hydrogen, which appears during reaction can't reduce  $\text{Al}_2\text{O}_3$  under conditions of synthesis. This has already been found in early studies [32].

The catalysts of this series were prepared in a muffle furnace heated to 500 °C. Temperatures were measured by 3 different thermocouples, which were placed in a glass



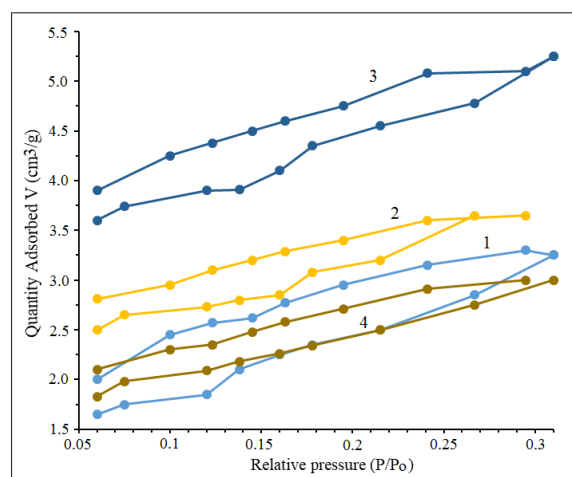
with a solution of nitrates and glycine. During the synthesis process, two combustion modes were carried out: volumetric explosion and self-propagating mode. In the volume of the explosive mode, the solution is heated and the water evaporates. After the water evaporates, a gel forms. The temperature in the furnace gradually increases to a critical point, and then the exothermic reaction occurs throughout the entire volume of the catalyst.



**Figure 2.** Temperature curves during SCS of sample with initial batch 30%  $\text{Cu}(\text{NO}_3)_2$  + 40%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine.

As shown in Figure 2, during the synthesis of the catalyst, the solution evaporates when it reaches  $T = 100^\circ\text{C}$ , and when it reaches  $172^\circ\text{C}$ , a gel is formed. The maximum temperature peak reaches at 445 seconds and the main synthesis reactions take place in this zone.

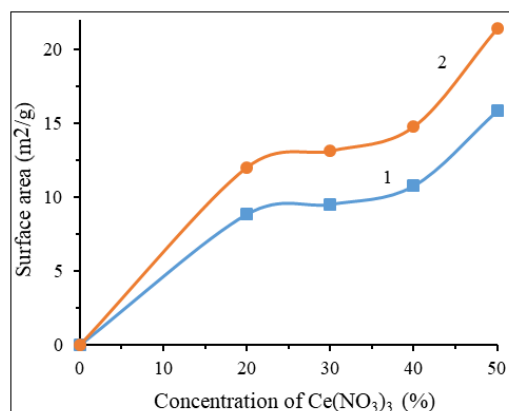
Unspent catalysts were examined by the BET method and adsorption and desorption isotherms by nitrogen were plotted for those catalysts (Figure 3). According to the IUPAC classification, all samples were identified and classified as type IV isotherms, suggesting the presence of mesoporous structures.



**Figure 3.**  $\text{N}_2$  adsorption isotherm of synthesized catalysts: 1 - 50%  $\text{Cu}(\text{NO}_3)_2$  + 20%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 2 - 40%  $\text{Cu}(\text{NO}_3)_2$  + 30%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 3 - 20%  $\text{Cu}(\text{NO}_3)_2$  + 50%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 4 - 30%  $\text{Cu}(\text{NO}_3)_2$  + 40%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine.

The synthetic catalysts all exhibited  $\text{H}_2$  hysteresis rings, indicating that their pore sizes were broad and varied. These included different pore types such as "ink bottle" pores, tubular pores with uneven sizes, and tightly packed spherical particle gap pores [33].

The surface area of all obtained catalysts was measured by the BET method. The areas are shown in the Figure 4.

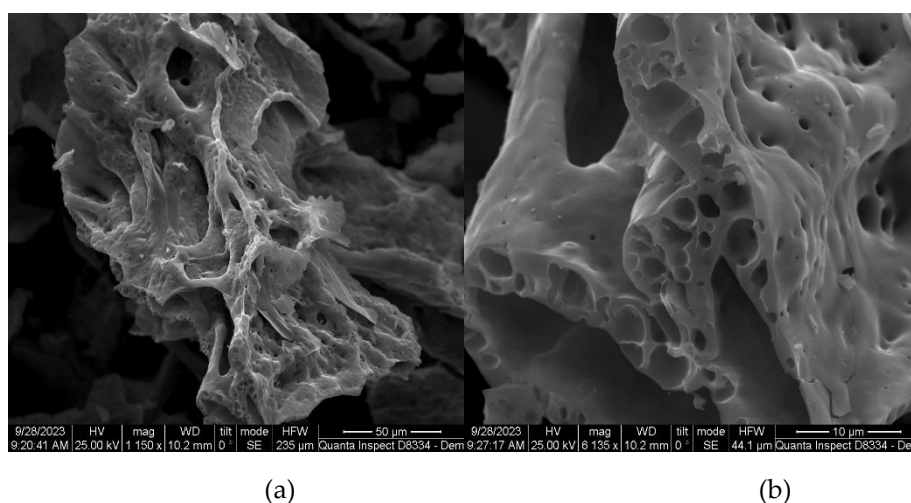


**Figure 4.** The influence of the  $\text{Ce}(\text{NO}_3)_3$  content in  $\text{Cu}(\text{NO}_3)_2 + \text{Ce}(\text{NO}_3)_3 + \text{Al}(\text{NO}_3)_3 + \text{glycine} + \text{H}_2\text{O}$  system on the surface area: 1 – multi-BET area, 2 – Langmuir area.

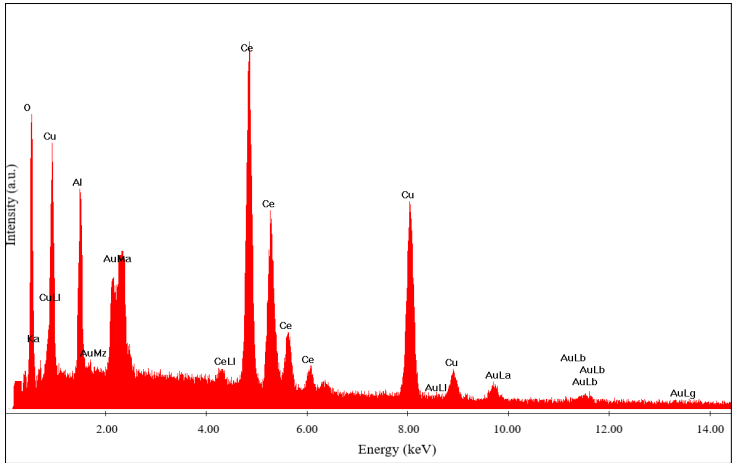
The concentration of cerium nitrate directly affects the surface area of these catalysts. As can be seen from the Figure 4, an increase in  $\text{Ce}(\text{NO}_3)_3$  content leads to an increase in surface area, which further affects the activity of the catalyst. As it is clear, 20%  $\text{Cu}(\text{NO}_3)_2 + 50\% \text{Ce}(\text{NO}_3)_3 + 30\% \text{Al}(\text{NO}_3)_3 + 50\%$  glycine catalyst had the largest specific surface area between them. It should be noted that the specific surface area of the catalysts in this system is relatively low. This is explained by the high combustion temperatures during the preparation of the catalyst. Despite this, the synthesized catalysts have high activity, which allows them to be on par with expensive catalysts.

### 2.1.2. SEM analysis

The surface structure and morphology of the synthesized catalysts were analyzed using scanning electron microscopy. The results of SEM analyzes for catalysts containing 50% cerium nitrate and 20% copper nitrate are presented in the Figures 5, 6, 7 and 8. Chemical analysis confirmed that the phase composition ( $\text{CuAl}_2\text{O}_4$ , Al, Al-Cu, CuO,  $\text{CeO}_2$ ,  $\text{CeAlO}_3$ ) aligns with the XRD data.

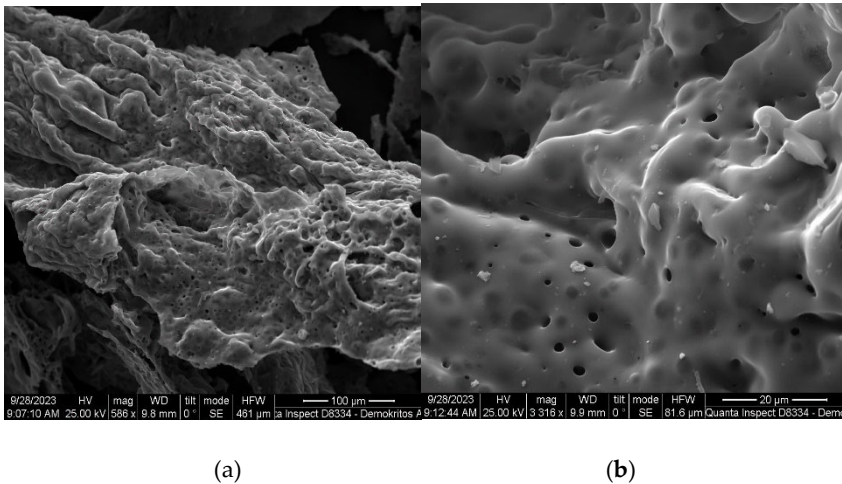


**Figure 5.** SEM images of the catalyst with the initial composition of 20%  $\text{Cu}(\text{NO}_3)_2 + 50\% \text{Ce}(\text{NO}_3)_3 + 30\% \text{Al}(\text{NO}_3)_3$  at  $T = 500^\circ\text{C}$  with different magnification: (a) 1150, (b) 6135.



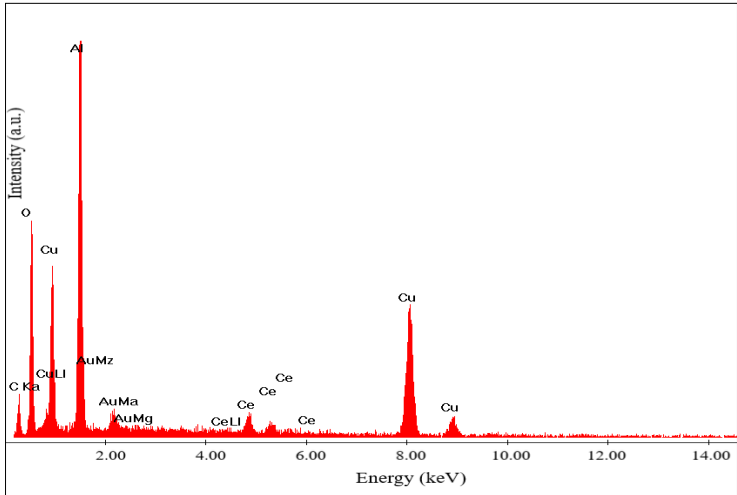
**Figure 6.** Chemical analysis of the 20% Cu(NO<sub>3</sub>)<sub>2</sub> + 50% Ce(NO<sub>3</sub>)<sub>3</sub> + 30% Al(NO<sub>3</sub>)<sub>3</sub> catalyst.

The contents of cerium, copper, aluminum and oxygen located and identified in different areas (Figure 6). Very high content of these components match to the mentioned above spinel phases.



**Figure 7.** SEM images of the catalyst with the initial composition of 50% Cu(NO<sub>3</sub>)<sub>2</sub> + 20% Ce(NO<sub>3</sub>)<sub>3</sub> + 30% Al(NO<sub>3</sub>)<sub>3</sub> at T = 500°C with different magnification: (a) 586, (b) 3316.

Chemical analysis (Figure 8) was carried out for the catalyst shown in Figure 7.



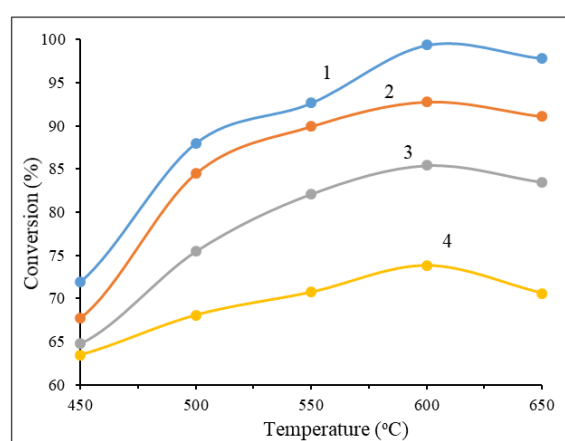


**Figure 8.** Chemical analysis of the 50%  $\text{Cu}(\text{NO}_3)_2$  + 20%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  catalyst.

Thus,  $\text{Cu}(\text{NO}_3)_2$ - $\text{Ce}(\text{NO}_3)_3$ - $\text{Al}(\text{NO}_3)_3$  catalysts with different element ratios were synthesized, and their combustion characteristics, composition, structure, and specific surface area and pores were analyzed.

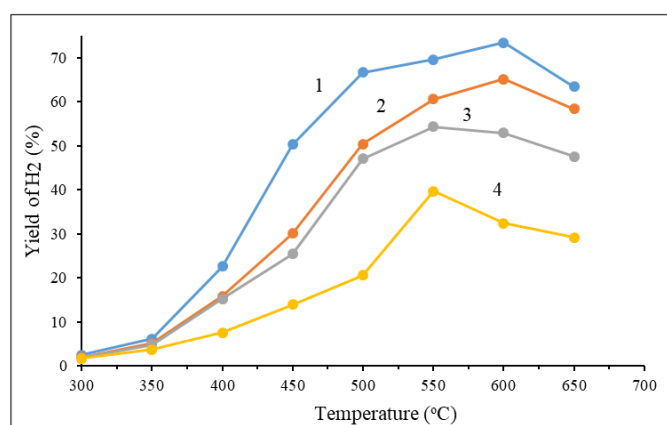
## 2.2. Catalytic results

For determining of activity of synthesized series of catalysts were studied in the process of steam reforming of methanol at temperature range between 250-650 °C. According to the data [34] the catalytic activity of the catalyst is directly affected by the methanol's steam reforming temperature. Figure 9 shows the results of these catalyst series activity on the conversion of methanol depending on the process temperature.



**Figure 9.** Temperature dependence of methanol conversion for a series of catalysts: 1 - 20%  $\text{Cu}(\text{NO}_3)_2$  + 50%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 2 - 30%  $\text{Cu}(\text{NO}_3)_2$  + 40%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 3 - 40%  $\text{Cu}(\text{NO}_3)_2$  + 30%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 4 - 50%  $\text{Cu}(\text{NO}_3)_2$  + 20%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine.

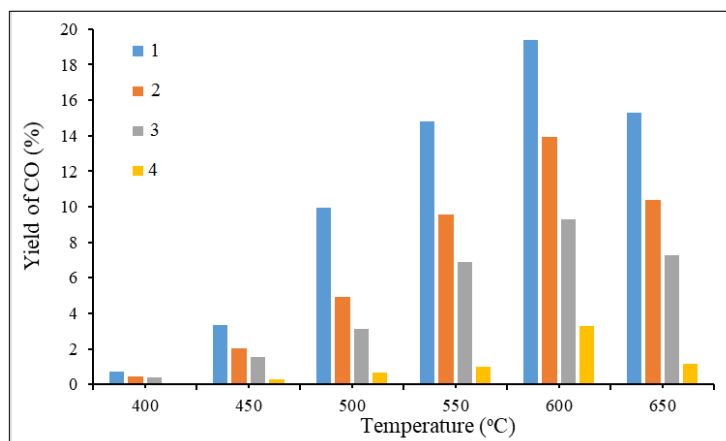
As its demonstrated in Figure 9 the highest  $\text{CH}_3\text{OH}$  conversion (99.3%) is observed on a catalyst containing 20%  $\text{Cu}(\text{NO}_3)_2$  + 20%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  at the 600 °C temperature and then it starts to falling down. Actually, the good results shown between 500-650 °C for all samples, but the amount of the cerium nitrate plays a big role in this system of catalysts. Decreasing the content of  $\text{Ce}(\text{NO}_3)_3$  naturally leads to a decrease in catalyst activity, which confirms the previously discussed results of BET analyzes. The results of studies of the influence of temperature and component content of catalysts on the yield of the target product are shown in Figure 10.



**Figure 10.** Influence of temperature and component content of catalysts on  $\text{H}_2$  generation: 1 - 20%  $\text{Cu}(\text{NO}_3)_2$  + 50%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 2 - 30%  $\text{Cu}(\text{NO}_3)_2$  + 40%  $\text{Ce}(\text{NO}_3)_3$  + 30%

$\text{Al}(\text{NO}_3)_3$  + 50% glycine; 3 - 40%  $\text{Cu}(\text{NO}_3)_2$  + 30%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 4 - 50%  $\text{Cu}(\text{NO}_3)_2$  + 20%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine.

As displayed in Figure 10, the hydrogen yield of the four catalysts showed a trend of first increasing and then reducing (600 °C) with the increase in temperature. 50%  $\text{Cu}(\text{NO}_3)_2$  + 20%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine has a larger difference with the change of temperature. This may be due to the sintering of the active components of Cu at high temperature, which caused the reducing of hydrogen yield. In this case, also the content of Ce shows the same effect as in the conversion of methanol. The sample, which has 50% of cerium nitrate, had a higher catalytic activity than the 20% sample it might be explained by the dispersion of Cu was improved by increasing the content of cerium. The yield of carbon oxide is shown in Figure 11.



**Figure 11.** Influence of temperature and component content of catalysts on CO yield: 1 - 20%  $\text{Cu}(\text{NO}_3)_2$  + 50%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 2 - 30%  $\text{Cu}(\text{NO}_3)_2$  + 40%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 3 - 40%  $\text{Cu}(\text{NO}_3)_2$  + 30%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine; 4 - 50%  $\text{Cu}(\text{NO}_3)_2$  + 20%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine.

From the Figure 11, it can be seen that an increase in temperature promotes carbon oxide generation. Also, it can be recognized that an increase in the concentration of cerium nitrate in the composition of the initial catalyst unexpectedly leads to a decrease in the ratio of hydrogen to carbon monoxide ( $\text{H}_2/\text{CO}$ ) in this series of catalysts for almost three times. It is because of cerium may suppress the methanol decomposition and reverse water gas shift reactions eventually end-up with the low CO and hydrogen rich product stream.

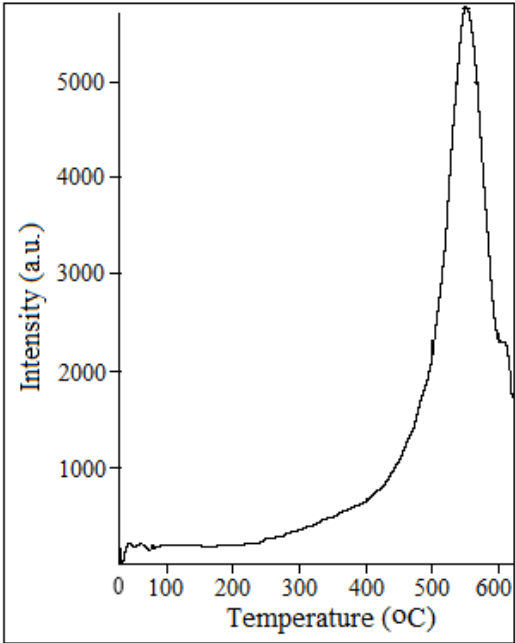
Based on the results of the above-described analyses, the most active catalyst (20%  $\text{Cu}(\text{NO}_3)_2$  + 50%  $\text{Ce}(\text{NO}_3)_3$  + 30%  $\text{Al}(\text{NO}_3)_3$  + 50% glycine sample) among those synthesized by the SCS method was identified, and additional analysis was carried out for it in the form of temperature programmed desorption of oxygen. Results of it is shown in the Figure 12.

The high intensity (over 5000) of oxygen desorption were noticed at 550-570 °C, but in spent catalyst sample the intensity decreased. The total amount of released oxygen monotonously changes in this heat treatment temperature range.

The catalysts maintained a constant weight following the catalytic studies, indicating no coke formation. The stability of the catalysts was tested over a span of 70 hours. During this period, the conversion rates of  $\text{CH}_3\text{OH}$  exhibited minor fluctuations. Further, more comprehensive investigations into coke formation are currently being conducted.

The best SCS catalyst was evaluated against samples of identical composition that were prepared using the impregnation and self-propagating high temperature methods. The steam reforming of methanol was carried out in the reaction mixture of it with  $\text{H}_2\text{O}$  in ratio 2.5 : 1 respectively under Ar flow with 50 ml/min rate. Table 3 presents the results of the study.

Methanol conversion values are the best on the SCS catalysts, then and for samples prepared by SHS and the impregnation methods, respectively. The H<sub>2</sub> selectivity is higher also for SCS catalysts and is at 88%, compared to 63–74% for the other catalysts. The largest surface (Langmuir) area had a catalyst synthesized by impregnation method and its over 100 m<sup>2</sup>/g and the next is SCS catalyst with almost 26 m<sup>2</sup>/g then SHS sample with 18 m<sup>2</sup>/g. Therefore, new composite materials produced through the SCS method possess a notable advantage. The generated hydrogen and CO mixture is pure and does not need further purification.



**Figure 12.** Intensity of oxygen desorption from the surface of catalyst depending on temperature.

**Table 3.** Comparison of Cu-Ce-Al catalysts prepared using the SCS, SHS and impregnation methods.

Catalyst preparation method	Conversion of CH <sub>3</sub> OH (%)	Selectivity of H <sub>2</sub> (%)	Specific surface area (m <sup>2</sup> /g)
SCS	99.3	88.8	25.8
Impregnation	75.6	74.7	102.9
SHS	83.8	63.2	18.5

3. Materials and Methods

Catalysts based on Cu, Ce and Al were prepared by solution combustion synthesis method. For the preparation of catalysts, pre-calculated amounts of nitrate salts were used: Cu(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O (98-99% Sigma, Aldrich), Ce(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O (98-99% Sigma, Aldrich), Al(NO<sub>3</sub>)<sub>3</sub> × 9H<sub>2</sub>O (98-99% Sigma, Aldrich), and glycine (98%, Oxford lab fine Chem LLP). These salts are pre-ground in an agate mortar and then mixed in a porcelain cup. Thereafter 10 mL of distilled water was gradually added to this mixture of salts, the resulting mixture was stirred in air for several minutes until complete dissolution. The muffle furnace was preheated to the required temperature (up to 500 °C). The prepared mixture was transferred from a porcelain cup to a heat-resistant glass beaker with a volume of 200 mL and placed in a heated muffle furnace. After 2-3 minutes, when the muffle furnace door was not fully opened, it was visually possible to observe combustion in the solution, in which this mixture rised over the walls of the glass when boiling. Urea was added to the composition of SCS catalysts to improve the combustion process. The presence of urea in the catalyst promoted a change of the solution into brown color during combustion. The beaker is then cooled in air and the prepared catalyst was placed in a glass jug.

The second series of catalysts was prepared by the incipient wetness impregnation. Analytically pure copper nitrate hexahydrate  $\text{Cu}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$  (98-99% Sigma, Aldrich), cerium nitrate hexahydrate  $\text{Ce}(\text{NO}_3)_3 \times 6\text{H}_2\text{O}$  (98-99% Sigma, Aldrich) were used for preparing the catalyst. The catalyst was prepared by using the equal amount impregnation method.  $\text{Cu}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \times 6\text{H}_2\text{O}$  were weighed on an electronic balance, and a needed concentration of the metal element active component precursor solution was prepared, controlling the molar ratio of Ce : Cu. The pretreated activated alumina was placed in a conical flask, and the precursor solution was poured in until it was submerged in the activated alumina. The conical flask was shaken in a water bath shaker for 2 h, and the water bath temperature was set at 25 °C. The supporter was dried at 110 °C for 8 h. The catalyst was roasted in a muffle furnace at a controlled roasting temperature of 500 °C for 6 h.

SHS catalysts from the same material composition. Uniaxial pressing under a pressure of about 10 MPa was used to prepare cylindrical specimens that were 10 mm in diameter and 20 mm long. The initial reaction mixture was preliminarily heated in a muffle furnace at a temperature of 500-700 °C for 3–5 minutes before initiating the SHS reaction.

Temperature profiles were recorded during SCS in a muffle furnace preheated to 500 °C. Three thermocouples were positioned at the top of the muffle furnace, all placed within the glass. These thermocouples monitored the bottom, middle, and top layers of the solution. During the catalyst synthesis by solution combustion, two combustion modes were observed: a volumetric explosion and a self-propagating mode. In the volumetric explosion mode, the solution was heated and water evaporated. After the water evaporated, a gel formed. The temperature in the muffle furnace gradually rose to a critical point. Once this critical temperature was reached, an exothermic reaction occurred throughout the entire volume of the catalyst.

Atomic structure of the catalysts was determined by X-ray diffraction measurements on a Siemens Spellman DF3 spectrometer with Cu-K $\alpha$  radiation. 10% KCl was added to samples as an internal standard to allow for a semi-quantitative XRD analysis. Brunauer–Emmett–Teller (BET) specific surface area was carried out on a GAPP V-Sorb 2800 Analyser using nitrogen as a carrier gas. In the process of solution combustion synthesis, the nanopowders were obtained, and therefore the porosity for them was not measured. The microstructure of the materials was examined after sputter coating with gold (coating thickness 5–10 nm) by a scanning electron microscope (Quanta Inspect from FEI) together with point EDX elemental analysis.

Experiments on the steam reforming of methanol to hydrogen and carbon oxides were carried out on flow type installation at atmospheric pressure in a tubular quartz reactor with a fixed catalyst bed without any pre-reduction. Catalyst was placed in the central part of reactor and quartz wool placed above and below the catalyst bed. The catalytic reaction was carried out at temperature range between 250-650 °C using a mixture of  $\text{CH}_3\text{OH}$  :  $\text{H}_2\text{O}$  in the ratio of 2.5 : 1 as the feed. Such by-products were observed for majority of catalysts in very small amounts, indicating very high selectivity for  $\text{H}_2$ .

The analysis of the initial mixture and reaction products was carried out using a chromatograph "Chromos GC-1000" with the "Chromos" software and on a chromatograph "Agilent Technologies 6890N" (USA) with the corresponding computer software. Chromatograph "Chromos GC-1000" is equipped with packed and capillary columns. The packed column was used for the analysis of  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3$ - $\text{C}_4$  hydrocarbons,  $\text{CO}$  and  $\text{CO}_2$ , while the capillary column was used to analyze hydrocarbons. Temperature of the TC detector was 200 °C, the evaporator temperature 280 °C, column temperature 40 °C. Carrier gas Ar velocity was 10 mL/min. A HP-PLOT Q capillary column 30 m long and 0.53 mm in diameter filled with polystyrene-divinylbenzene was used for analysis on an "Agilent Technologies 6890N" chromatograph.

The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances (accurately measured quantities of pure component or mixture of substances with known concentrations was injected into the chromatograph using a microsyringe). Based on the measured areas of the peaks corresponding to the amount of the introduced substance, a calibration curve  $V = f(S)$  was constructed, where  $V$  -

amount of substance in ml, S - peak area in cm<sup>2</sup>. Concentrations of the obtained products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was  $\pm 3.0\%$ .

#### 4. Conclusions

The catalysts prepared by SCS method based on Cu(NO<sub>3</sub>)<sub>2</sub>-Ce(NO<sub>3</sub>)<sub>3</sub>-Al(NO<sub>3</sub>)<sub>3</sub> systems in different ratio of components were investigated in steam reforming of methanol. The analysis of the catalysts using XRD, SEM, TPD and BET methods provided useful information in understanding the catalytic activity. Influence of the composition of initial components on formation of spinels, which were active in steam reforming of methanol was established. The best results showed the catalyst with 50% content of Ce(NO<sub>3</sub>)<sub>3</sub> at T - 450-550 °C and P – 0.27 bar. Those conditions are very suitable for industry. There are advantages of SCS catalysts in comparison with the catalysts prepared by traditional impregnation and SHS methods in steam reforming of methanol. SCS is a rapid synthesis method, completing the catalyst production within minutes. It is cost-effective, utilizing exothermic reactions to create spinels at lower temperatures. The process allows for the synthesis of spinels by forming oxides from nitrates with a high defect structure, enabling reactions at significantly lower temperatures compared to oxides with well-formed crystal lattices. Due to the exothermic nature of SCS, temperatures exceed 1000 °C, resulting in a fast reaction rate and the formation of a defective crystal lattice, which is highly active in catalysis. These conditions are also ideal for adjusting the crystal lattice of spinels and enhancing the catalysts' activity.

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