IJIE

http://penerbit.uthm.edu.my/ojs/index.php/ijie
ISSN : 2229-838X e-ISSN : 2600-7916

The International Journal of Integrated Engineering

Effect of Milling Time and PCA on Electrode Properties of Cu_2O-ZnO/C Catalyst Alloy used on Electrochemical Reduction Method of CO_2

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DOI: https://doi.org/10.30880/ijie.2022.14.02.022
Received 5 March 2022; Accepted 20 March 2022; Available online 02 June 2022

Abstract: Carbon dioxide is one of the greenhouse gases that cause climate change, thus the effort for reducing the concentration of CO_2 necessary, for example through the conversion of CO_2. The conversion of CO_2 into methanol plays important role, because in addition to reducing greenhouse gas, it is also creating a future energy carrier needed in fuel cell technology. One of the CO_2 conversion methods is the electrolysis method using MEA. The electrochemical CO_2 conversion in this study used a Cu_2O-ZnO/C composite catalyst made by milling methods at various milling times, as well as the effect of PCA utilization. The catalysts were characterized using Particle Size Analyzer (PSA), Brunauer-Emmett-Teller (BET), Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and SEM-EDX analysis. The results of PSA and BET characterization showed that the longer the milling time, the smaller the particle size and the higher the relative surface area. The use of PCA increased the unoxidized Cu content as indicated by the SEM-EDX results. Based on the results of CV analysis, the catalyst that has the largest ECSA (Electrochemical surface area) value is the catalyst milled using PCA and the milling time is three hours.

Keyword: Cu_2O-ZnO/C, CO2, PCA, Electrochemical reduction

1. Introduction

Carbon dioxide is widely produced in the production and processing of oil and natural gas. The presence of CO_2 is a problem in itself because its presence in large quantities causes the greenhouse effect [1]. The utilization of CO_2 is very important because it can overcome two things at once, namely reducing the presence of greenhouse gases and making CO_2 as valuable feedstock or as fuel. Among the methods for converting CO_2 into valuable feedstock or as fuel is the electrolysis method which has the advantage of being environmentally friendly, can convert CO_2 into various types of materials, and works at ambient temperatures [2]. The product resulting from the electrochemical decomposition of CO_2 is highly dependent on several parameters, including; electrode and electrolyte type and operating conditions (temperature and current) [2]. One of the results of CO_2 conversion by the electrolysis method is methanol. Methanol is the largest

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volume of chemical compounds produced in the world [3]. Methanol is produced commercially through natural gas reform [4] or coal gasification [5].

In terms of methanol production, there are several mechanisms that can be done, including the production of methanol through electroreduction of CO_2 with the help of a Cu_2O-ZnO catalyst and $KHCO_3$ electrolyte [1], or a combination of direct CO_2 electroreduction and combined water electrolysis and CO_2 electroreduction through the formation of intermediate products of CO and H_2 [6]. Methanolhas a fairly high energy density and stable in storage, is one of the most promising CO_2 electrochemical reduction products. Aside from being fuel for fuel cells, methanol is also a raw material for dimethyl ether (DME) [7]. Methanol (CH_3OH) is widely used as a solvent in the chemical industry [5] because of its ability to dissolve a variety of organic and inorganic compounds. The process of converting CO_2 into methanol by electrochemical method is highly depending on the use of a catalyst both at the cathode and the anode. The ideal catalyst for CO_2 reduction must have high hydrogen overpotential that can allow the carbon dioxide reduction reaction to achieve high selectivity. One of the catalysts used to reduce CO_2 to methanol is a Cu-based catalyst. Cu-based catalysts show high activity and have been widely used in the conversion of CO_2 to methanol. CO_2 catalytic conversion influenced by particle size and selectivity to methanol with a surface area [8]. Costentin (2013) stated that the reduction of CO_2 catalyzed by Cu_2O gave better results in rate and overpotential than ordinary Cu electrodes [9]. Regarding the catalyst used in electrochemical reduction, Albo (2015) conducted research on the electrochemical reduction of CO_2 to methanol at the Cu_2O and Cu_2O-ZnO electrodes using a 0.5 M $KHCO_3$ electrolyte solution. Cu_2O-ZnO electrodes remained stable for 20 hours, while on the surface Cu_2O experienced strong deactivation with time [10]. In addition to Cu-based catalysts, the use of platinum in the methanol conversion process has been carried out [11]. Shironita (2013) tested CO_2 reduction on electrocatalyst Pt/C and Pt-Ru/C using MEA and obtained *yield of* methanol 0.03% at Pt/C and 7.5% at Pt-Ru/C, with Coulombic efficiency of 35% at Pt/C and 75% at Pt-Ru/C. Among the factors that affect the performance of the catalyst is the process of manufacture/synthesis of the catalyst. The catalyst in the form of a composite is usually made by the milling method. In the milling process, the effect of milling time and the use of PCA (Process Control Agent) affect the performance of the catalyst. Milling time affects the particle size of the milled catalyst where the longer the milling process, the smaller the particle size. Meanwhile, the use of PCA is intended to prevent the reactants from sticking to the milling jar.

In this study, electrodes were made with Cu2O-ZnO/C catalyst made by milling method at various milling times and with and without the addition of PCA. The characteristics of the Cu_2O-ZnO/C catalyst were analyzed using Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), Scanning Electron Microscope (SEM)-EDX, Particle Size Analyzer (PSA), and Brunauer Emmett Teller (BET) methods.

2. Methodology

Synthesis of catalyst alloys and electrode were carried out using materials Cu_2O (Sigma), ZnO (Sigma Aldrich), Carbon Vulcan XC-72R (Fuel Cell Store), Carbon Paper Avcarb P75T (Fuel Cell Store), Ammonium hydrogen carbonate (NH_4HCO_3) (Sigma Aldrich), Polytetrafluoroethylene (PTFE) Solution (Fuel Cell Store), and Nafion solution (Fuel Cell Store). The manufacture of catalyst alloys conducted by milling method using High Energy Milling (HEM) E3D. Characterization includes analysis of SEM-EDX (FEI 450 SEM Oxford EDX), gas sorption analyzer (Quantachrome Instruments Version 2.03), Particle Size Distribution Analyzer (PSA) (Horiba Laser Scattering PSA LA 960), Cyclic Voltammetry (CV) analysis) and Electrochemical Impedance Spectroscopy (EIS) using the PGSTST204N Potentiostat/galvanostat (Autolab, Methrom) device. The manufacture of Cu_2O-ZnO/C catalyst was carried out by mixing Cu_2O catalyst powder with ZnO catalyst powder with a mass ratio of 1:1 and adding carbon vulcan XC-72R so that the content of the catalyst mixture in carbon was 40 wt% with a catalyst loading of 1 mg/cm^2. The catalyst was milled with variations of 1, 2, and 3 hours using a HEM shaker with and without the addition of PCA. The milling process is carried out with a ball per ratio (BPR) (1:5). The catalyst obtained was stored in a dry and tightly closed container. The catalyst formed was analyzed for pore characteristics using BET equipment and particle size using PSA equipment. The resulting catalyst alloy was added with 2-propanol and Nafion solution and stirred using an ultrasonic homogenizer for 20 minutes, then PTFE was added and stirred again for 5 minutes until the ink was formed. The catalyst ink sprayed onto the gas diffusion layer (GDL) using a spray gun to form electrodes. Electrodes with Cu_2O-ZnO/C catalyst were analyzed using SEM-EDX equipment and tested for their catalytic surface characteristics using the CV method and their electrical conductivity characteristics using EIS analysis.

3. Results and Discussion

3.1 Particle Size Distribution Analysis (PSA)

Measurement of the particle size of the milled catalyst at various milling times was carried out to determine the optimum milling time to achieve good particle size of the catalyst. The particle size of the catalyst is related to the catalytic ability as well as the conductivity of the catalyst. Particle size measurement with PSA was carried out using the Laser Light Scattering (LLS) method in which the powder was dispersed in deionized water with a dispersant $(NaPO3)_6$ using an ultrasonic homogenizer for 15 minutes. The general trend when using the LLS method is the size distribution of the

agglomerated particles to enlarge the rough end of the distribution because LLS uses a longer axis than the agglomerated particles [12]. The PSA analysis of electrodes with the effect of milling time and using PCA is presented in figure 1.

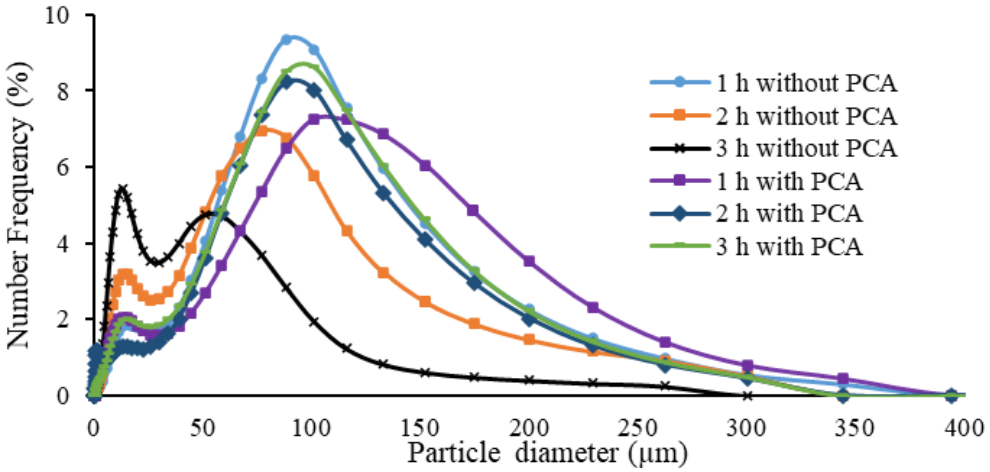

Fig 1 - Results of PSA analysis with variations in milling time with and without PCA

Figure 1 shows the results of the analysis test using a Particle Size Analyzer (PSA) on variations in milling time with and without PCA. The use of methanol as PCA is usually used in mechanical alloying processes to avoid agglomeration and bonding between powder particles and balls as well as powder agglomeration during grinding [13]. In addition, PCA is useful for preventing the sticking of the milled material or PCA from being adsorbed on the surface particle [14]. PCA can modify/deform particles to minimize agglomeration, reduce particle size and change the morphology to a granular structure [15]. PSA test results on catalysts milled without PCA show that the longer the milling time, the smaller the particle size distributed. The result obtained were in line with expectation because the smaller the size, the catalytic activity, and selectivity for H_2 and CO likely will increase for Cu-based catalysts [16]. Meanwhile, the catalyst milled using PCA had a larger particle size than the catalyst milled without PCA. This is possible because the amount of PCA is too much to reduce the possibility of collisions between the ball and the powder causes an inhomogeneous particle size distribution [17]. The results of PSA testing on catalysts milled for 3 hours using PCA suspected agglomeration. This is supported by Figure 9, where Cu metal builds up in the measured spot. The presence of agglomeration can reduce the surface area and produce a larger pore size.

3.2 *Brunauer-Eemmett-Teller* (BET) Analysis

High surface area needed for a good catalyst support function, BET surface area measurements were carried out to assess specific surface area of the catalyst [18]. The results of the BET analysis of the Cu_2O-ZnO/C catalyst samples at various milling times and the use of PCA and without PCA are presented in Figure 2. Based on the BET analysis, the Cu_2O-ZnO/C catalyst with the addition of PCA has a smaller pore diameter with increasing of milling time. The smaller the pore diameter, the larger the surface area of the catalyst [19]. The larger the surface area of the catalyst will increase the catalytic function and selectivity of the catalyst. The surface area of the catalyst which was milled with a milling time of 3 hours without PCA is decreased. This finding reflects changes in the sample structure during milling [18].

3.3 *Cyclic Voltammetry* (CV) Analysis

Analysis using CV serves to obtain the value of electrochemical surface area (ECSA) which shows the size of the number of active electrochemical sites per gram of catalyst. In addition, ECSA can determine the reactivity of the electrode by observing the reduction and oxidation (redox) reactions of the sample. The voltammogram consists of 2 peaks, namely an oxidation peak in the positive current region and a reduction peak in the negative current region [20]. The measurement results are shown in Figure 3. Figure 3 shows the oxidation and reduction peaks of some of the electrodes characterized. The results of the calculation of ECSA values from several samples are shown in Figure 4. The highest ECSA values are found at the Cu2O-ZnO/C electrode with the addition of PCA, which is 114.96 cm^2/g. A high ECSA value indicates the number of active sites on the electrode surface so that the electrochemical reactions that occur at the electrodes take place optimally. The ECSA value is also influenced by the size of the particle, where the smaller the particle size, the ECSA value is generally larger [21]. Particle size is affected by milling time. The longer the milling time, the smaller the particle size [22]. From these two theories, it can be concluded that the milling time can affect the ECSA value. The addition of PCA also affects the ECSA value because the use of PCA can reduce the particle size more quickly so that the longer milling time using PCA will make the ECSA value larger [15]. The ECSA value of electrode with Cu_2O-ZnO/C catalyst at varied milling time is presented in figure 4.

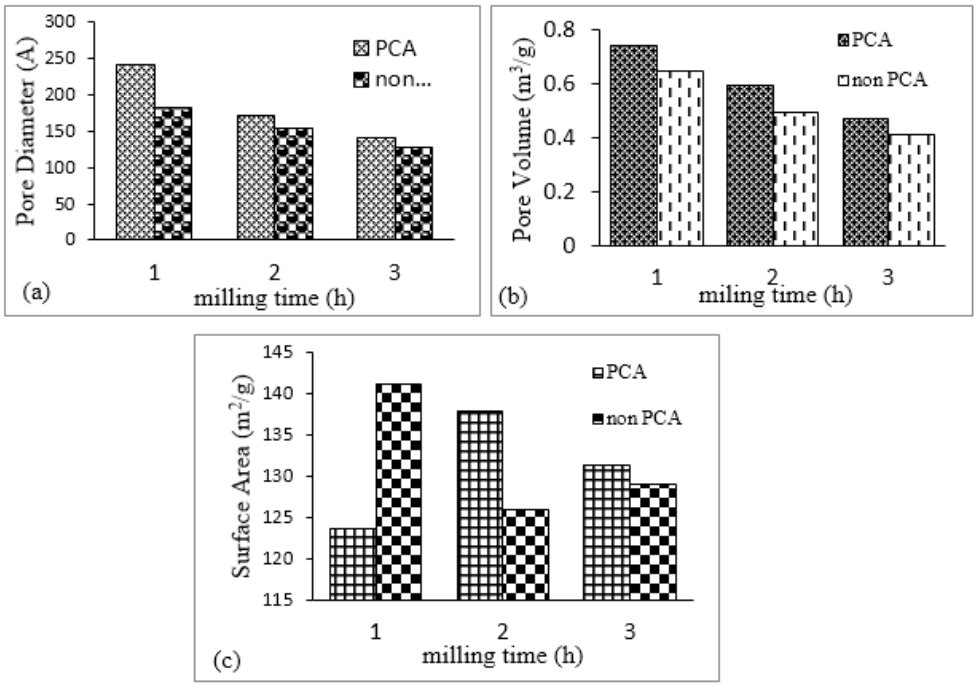

Figure 2. The relationship between milling time to pore, volume pore, and surface area.

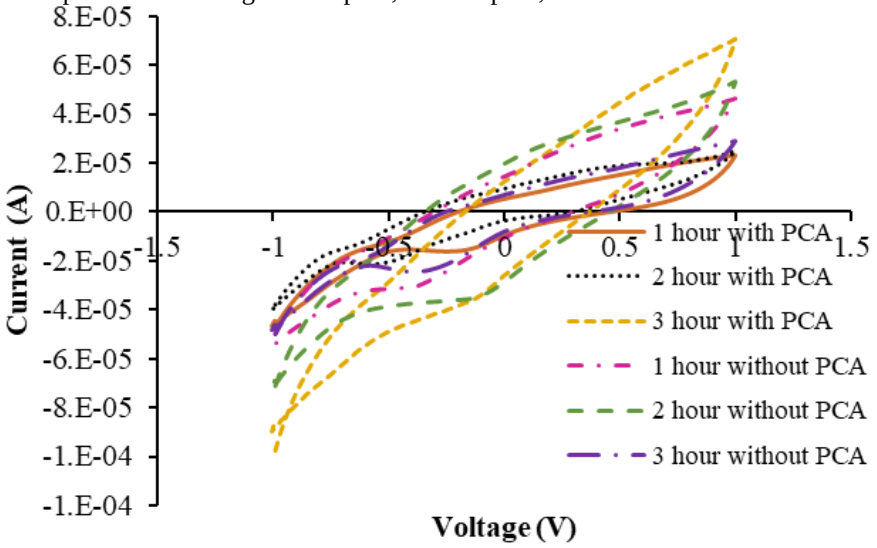

Fig. 3 - Voltamogram of each electrode

3.4 *Electrochemical Impedance Spectroscopy* (EIS) Analysis

Measurements using the EIS method produce a Cu2O-ZnO/C electrode conductivity value which shows the ability of an electrode to conduct electricity. Based on the results of the EIS electrode measurements, a Nyquist curve is obtained in the form of a semicircle diagram with data in the form of real impedance values (Z') and imaginary impedance (Z") [23]. The Nyquist curve of the electrode with the Cu2O-ZnO/C catalyst is shown in Figure 5 and the electrical conductivity value of the EIS data processing is shown in Figure 6. Based on the EIS characterization, the best electrical conductivity value was found at the Cu_2O-ZnO/C electrode with a milling time of 2 hours without the addition of PCA. A large conductivity value indicates the ability of the electrode to conduct electricity better. The conductivity value is influenced by the impedance value where the greater the impedance value, the higher the conductivity value. The impedance value is influenced by the particle size where a smaller particle size will also produce a small impedance value[22]. The data of electrical conductivity of electrode seem not to correlate with the ECSA data which the ECSA data indicate that the best performance is the electrode with PCA and 3-hour milling time. Basically, electrical conductivity is not always correlated with the ECSA result. The conductivity determines the performance of electrical conduction, and the ECSA indicated the area of catalytic activity.

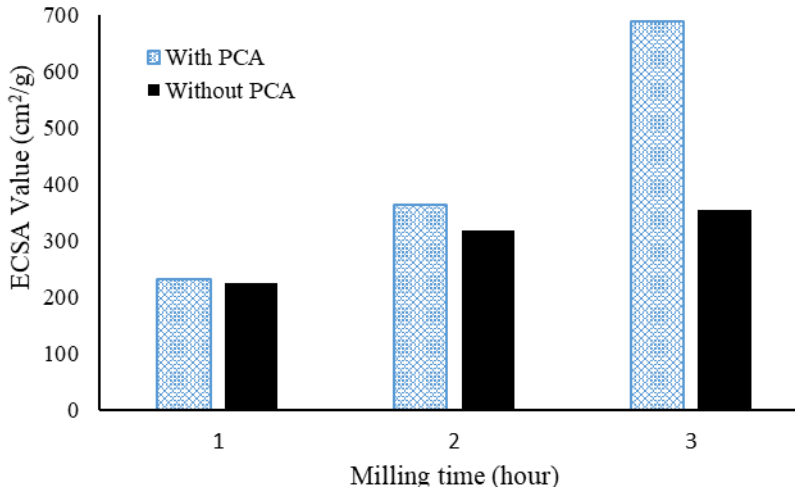

Fig 4 - ECSA Value for electrode with Cu_2O-ZnO/C Catalyst at varied milling time

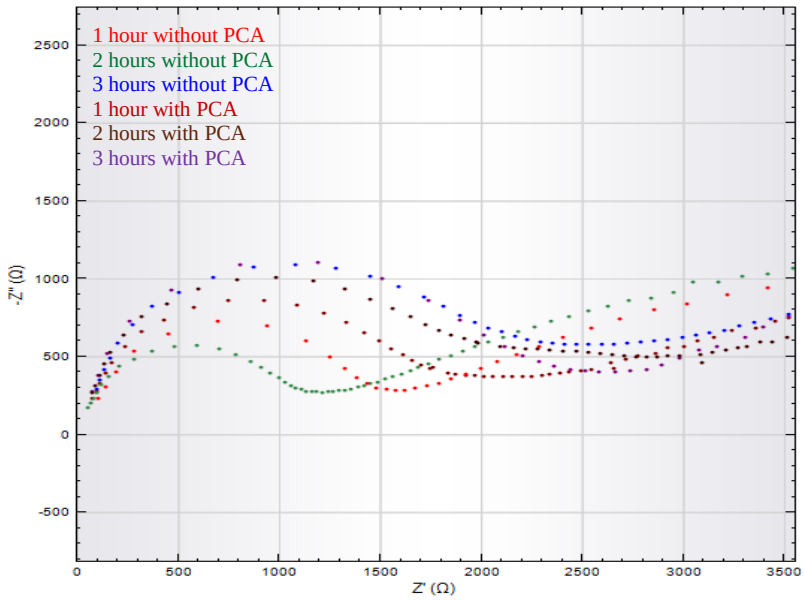

Fig 5 - The Nyquist curve for each electrode

3.5 SEM-EDX *Analysis*

Observation of the microstructure of Cu2O-ZnO/C catalyst powder using SEM – EDX is carried out to analyze the morphology of the surface and the average percentage of elements on the spots of the Cu2O-ZnO/C catalyst powder [24]. The results of the SEM-EDX test with variations in milling time and the addition of PCA are shown in Figure 7. Based on the figure 7, it can be seen that the electrode with 3 hours milling time with the addition of PCA has the highest content of Cu, which is 46,51 wt%. This indicates that the addition of PCA will retain Cu metal so that it is not easy to oxidize.

4. Conclusions

The characterization of electrodes with Cu2O-ZnO catalysts at the variations of milling time and using PCA showed that 3 hours milling time produce the catalyst with a smaller particle size dan higher surface area compared with shorter milling time. Furthermore, the application PCA to the catalyst in the milling process inhibited the oxidation of Cu and prevent the reactants from sticking to the milling jar. The analysis of ECSA indicated that using 3 hours milling time and PCA have the highest ECSA value and highest Cu percentage in catalyst from SEM-EDX results.

Acknowledgment

This research has been carried out with collaborations of the University of Sriwijaya and The PT. Pertamina (Persero) with Matching Fund Program Batch III from the Ministry of Education, Culture, Research, and Technology the Republic of Indonesia 2021 with Announcement of Determination of Aid Beneficiaries no. 0463/E/TU.00.01/2021.

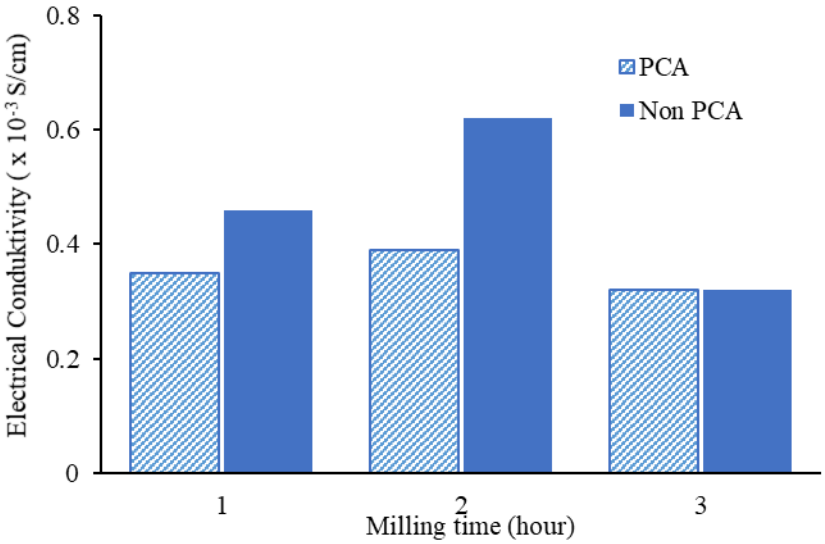

Fig. 6 - Value of Electrical Conductivity of Electrode with Varied milling time

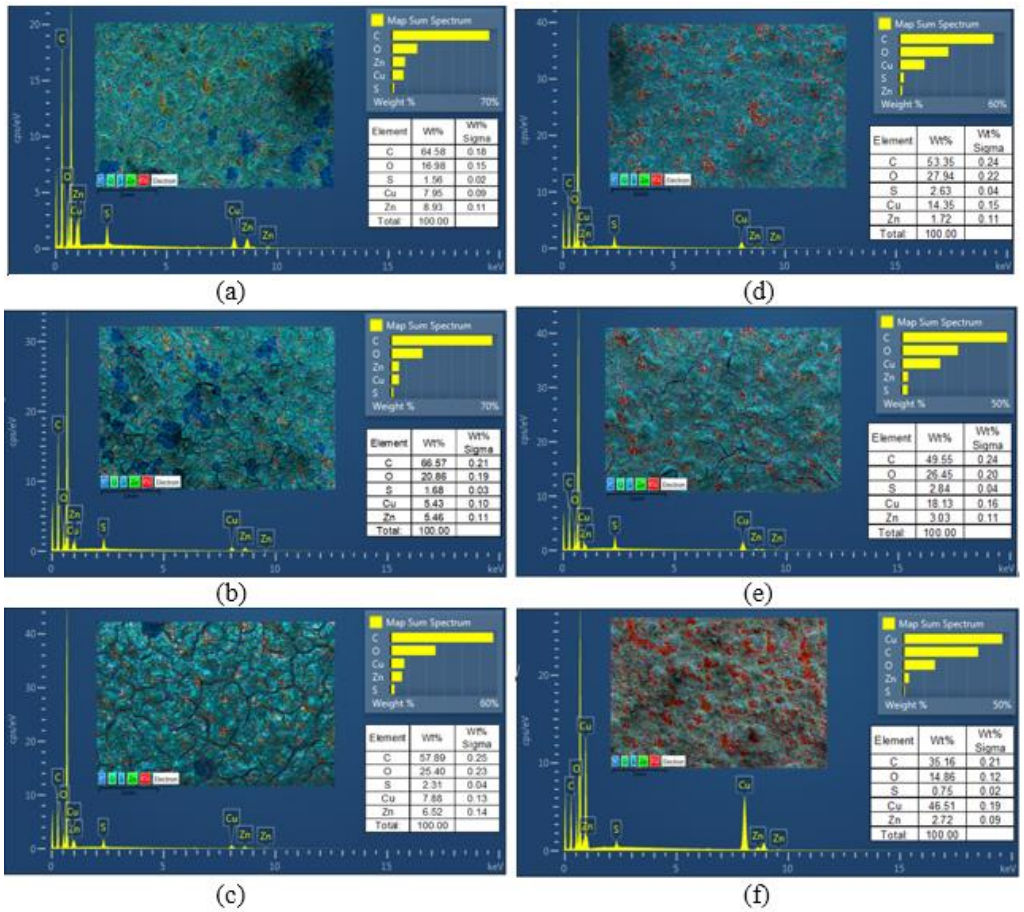

Fig. 7 - The analysis of SEM-EDX of electrode with Cu_2O-ZnO/C catalysts (a) 1 hour without PCA; (b) 2 hours without PCA; (c) 3 hours without PCA; (d) 1 hour with PCA; (e) 2 hours with PCA; (f) 3 hours with PCA

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