9.20 Heterostructured materials synthesized via AACVD applied for direct water splitting irradiated with an AAA solar Simulator

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ABSTRACT

Binary metal oxides have been recently applied for electrocatalytic and photocatalytic water splitting. Common metal oxides are synthesized using earth's crust abundant elements such as Ti, Cu, Fe and Zn in order to reduce costs.On the other hand, ternary oxides as those of the delafossite group, have also proved to be suitable for direct water splitting. In either case, metal oxide materials intend to replace the utilization of noble metals for the generation of H_2. According to literature, the efficiencies obtained using noble metal nanoparticles, carbon based materials or several metal oxides coupled in a tandem configuration are superior than those obtained using a single metal oxide layer. Nevertheless, the synthesis process often requires the utilization of various techniques in order to obtain the desired heterostructured configuration. Besides, since surface area plays a determining role in direct water splitting, it is believed that the utilization of various nanostructured morphologies will result in an increase of the H_2 production.

Hence, this work presents an heterostructured material comprised of different layers distributed onto borosilicate glass following this order: BGS/TiO_2/ZnO/$CuFeO_2$/SnO_2/Pt. Zinc oxide was grown following a nanorod morphology while Pt was synthesized in the form of nanoparticles. All nanostructured layers were synthesized by a sequential five-stage method using solely the aerosol assisted CVD technique. The synthesized sample was characterized by means of electron microscopy, UV-Vis-Nir spectroscopy and grazing incidence x-ray diffraction. A customized batch reactor was used to measure the H_2 produced when the sample was immersed into a solution of water and 2% of methanol and irradiated with an AAA solar simulator. The obtained efficiencies were compared to those using individual layers of TiO_2, TiO_2/$CuFeO_2$ and TiO_2/$CuFeO_2$/SnO_2.

Keywords: Direct Water Splitting, Delafossite, AACVD

9.21 Use of the $Ti_xCu_yO_z$ oxide catalyst in water electrolysis

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ABSTRACT

Transition from fossil fuels to renewable energy is of paramount importance to halt the growing pollution associated to conventional energy production. A long-term and sustainable alternative to fossil fuels is the use of fuel cell technology. Fuel cells are devices capable of transforming chemical energy into electricity in a very clean and efficient manner. However, their operation is conditioned by the continuous supply of oxygen O2, and hydrogen H2. Presently, these gasses are obtained from complex and contaminant gas reformation and purification processes. Through water electrolysis, it is possible to produce O2 and H2 without the harmful carbon emissions implicit to gas reformation. A challenge in mass electrolysis implementation is that electrolyzers require the use of catalytic materials; often transition metal groups like Pt, Pd, and Ir are used. However, their scarcity and restrictive costs limit the possibilities of water electrolysis. This work presents a synthesis of a $Ti_xCu_yO_z$ catalyst with excellent activity compared to pure platinum in the oxygen evolution reaction. High-energy ball milling of Ti and Cu powders was performed for 2, 4, 6, 8, and 10 h; afterwards, the milled powders were subjected to a thermal treatment at air atmosphere and characterized through X-Ray diffraction (XRD), scanning electron microscopy (SEM), elemental chemical characterization (SEM-EDS), and voltammetries (cyclic, linear, and cronoamperometry).

Keywords: $Ti_xCu_yO_z$ catalyst, oxygen, electrolysis

9.22 Synthesis and characterization of ni-mo$_2$c catalysts supported on hydroxyapatite for hydrogen production reactions

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ABSTRACT

The search for new catalytic material to hydrogen production is very important for generation of new more efficient process and low cost. On the other hand, biomass is a renewable source for hydrogen production by green methods. Also, the green methods for hydrogen production are not emitting greenhouse gases. So, these methods can be considered friendly with the environment. Several studies have demonstrated Ni-Mo_2C catalysts exhibits high activity and selectivity in hydrogen production processes. While the molybdenum carbide has shown a catalytic behavior similar as some noble metals, the loads of nickel act as a promoter increasing selectivity and stability of the materials.

In this research, Ni-Mo_2C nanoparticles were synthesized by carburization of nickel and molybdenum oxides as precursors using sucrose as a carbon source. The carburization condition was varied in function of temperature (873 K to 1073 K), under Ar/H_2 flow. Hydroxyapatite was used as a support due its main constituent is CaO, which improve selectivity by CO adsorption capacity in the cases of hydrogen production processes with CO presence as a byproduct. All samples were characterized by Infrared Spectroscopy with Fourier Transform (FTIR), Scanning Transmission Electron Microscopy (STEM) and X-Ray Diffraction (XRD) to confirm the structure of the nanoparticles and observe the effects of thermal treatment in the thermal stability of the materials. The catalyst Ni-Mo_2C supported on hydroxyapatite could be a very well option to be used in green processes for hydrogen production. The properties of active phase and the properties catalytic support make the catalytic material have excellent thermal and mechanical stability.

Keywords : Ni-Mo_2C Catalyst, Mo_2C nanoparticule, hydrogen production, hydroxyapatite.

1. Introduction

The necessity of use more energy every day, is a big problem because in the actually the most used energy sources are hydrocarbons. The use of hydrocarbons increases greenhouse gases by the combustion of hydrocarbons. Hydrogen could be an alternative energy source from renewable resources, also, the use hydrogen as clean fuels has benefits in the environment, because it doesn´t emit greenhouse gases.

The main processes for hydrogen production implicate the use hydrocarbons; being the natural gas the main source for hydrogen production through reforming steam methane [1-2].

Transition metal carbides have shown a special catalytic behavior similar to the noble metals [3-5]. Transition metals carbide have been using at extreme conditions of pressure and temperature [6]. The use at extreme conditions of these carbides is because of their great strength and durability. The physical and mechanical properties of carbides are similar to that of ceramic.

The physical and chemical properties of transition metal carbides including high thermal stability and mechanical hardness, superconductivity and show catalytic activity similar to those of metals noble in various catalytic reaction for hydrogen production as methane reforming, conversion biomass, water gas shift reaction, among other reaction [5,7].

The actual methods for the synthesis of molybdenum carbide involve direct carbonization of molybdenum at high temperature (> 1000 °C). Some authors [8,9] studied the effect of temperature on the synthesis of molybdenum carbide and concluded that the optimum temperature for the synthesis of molybdenum carbide is around 800 °C.

The modification of traditional catalysts Mo_2C with Ni shows an increase in thermal and mechanical stability, as well as in the catalytic activity of materials. The catalytic activity increase respect to the increases in the amount of Ni, but the Ni increase causes an oxidation of the material [10].

Some research [11 - 14] shows the use of calcium oxide to remove emissions of CO_2 in reaction for hydrogen production, also, CaO increase the hydrogen production. On the other hand, materials as hydroxyapatite have a high content of calcium oxide [15] and other compounds that give a high mechanical and thermal stability.

2. Materials and Methods

2.1 Preparation of Mo_2C

The preparation of Mo_2C precursors were prepared by an aqueous solution of ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}$ $4H_2O$] and an aqueous solution of sucrose with a molar ratio of C/Mo = 2 to form the hexagonal crystalline

structure of molybdenum carbide (β-Mo_2C) [16,17]. Then homogenize the two solutions the sucrose solution was added over ammonium heptamolybdate tetrahydrate solution stirring constantly for 15 min. the final solution was dried at room temperature at 120 °C for 24 h.

The Mo_2C precursors were thermally treated in situ in a quartz fix bed reactor under a reducing atmosphere of Ar/H_2 to get Mo_2C. The temperature was increased linearly at 10 °C/min, the conditions of reactor are show in the table 1.

Table 1. Carburization conditions used on the quartz fix bed reactor on Mo_2C precursors

Sample	Temperature (°C)	Pressure (atm)	Flow (Ar/H_2) (l/min)	Ramp (°C/min)	Time (min)
1	700	1	4	10	120
2	800	1	4	10	120
3	900	1	4	10	120

2.2 Preparation of Ni-Mo_2C catalysts

The synthesis of Ni-Mo_2C is similar to Mo_2C. The Ni-Mo_2C precursors were prepared by aqueous solution using nickel nitrate dihydrate as source of nickel. The load of nickel on the materials is 15 wt% and molar ratio C/Mo = 2. The nickel solution was added over ammonium heptamolybdate tetrahydrate solution stirring constantly for 4 h. the final solution was dried at temperature room at 120 °C for 24 h

The powder was dissolved using the minimum amount of water possible. The solution of sucrose was added over powder solution stirring constantly for 1 h the final solution was dried at temperature room at 120 °C for 24 h

The Mo_2C precursors were thermally treated in situ in a quartz fix bed reactor under a reducing atmosphere of Ar/H_2 to get Ni-Mo_2C. The temperature was increase linearly at of 10 °C/min, for 2 h and the temperature of reactor was 800 °C.

2.3 Extraction of hydroxyapatite

For extraction of hydroxyapatite were used bovine bones following the methodology of C.K. Rojas-Mayorga [18] by thermal decomposition.

2.3.1 Bovine bone preparation

The bovine bones were cleansed by water and acetone to remove the impurities and fasts. After clean the bovine bones were reduced to size of 1 mm. The powder was dried at 120 for 24 h The bovine bones were thermally treated (pyrolysis) in quartz reactor by synthesis of bone char. The synthesis of bone char needs specific condition of heating rate, temperature and time of thermal treatment. For the pyrolysis process, nitrogen gas (400 ml/min) was used to

provide an inert atmosphere during the thermal treatment. The conditions of synthesis are show in table 2.

Table 2. Synthesis of hydroxyapatite

Sample	Temperature (°c)	Pressure (atm)	Flow (Ar/H_2) (ml/min)	Ramp (°c/min)	Time (min)
1	700	1	400	10	120
2	800	1	400	10	120
3	900	1	400	10	120

3. Results and Discussion

3.1 X-ray diffraction

Fig. 1 shows the experimental x-ray diffraction patterns of Mo_2C synthesized at different temperature of carbonization and also shows the experimental x-ray diffraction patterns of Mo_2C precursor.

According with the fig. 1 the experimental x-ray diffraction patterns correspond with hexagonal structure of Mo_2C [17]. Mo_2C presented XRD patterns with different diffraction peaks at 34.40°, 38.10°, 52.26°, 61.78°, 69.77°, 74.94° and 75.98 of 2θ, corresponding to the (021), (200), (221), (023), (321), (223) and (104) diffraction planes. The crystallite size was calculated with Scherrer Equation; the table 3 shows the crystallite size of Mo_2C sample at different carbonization temperature.

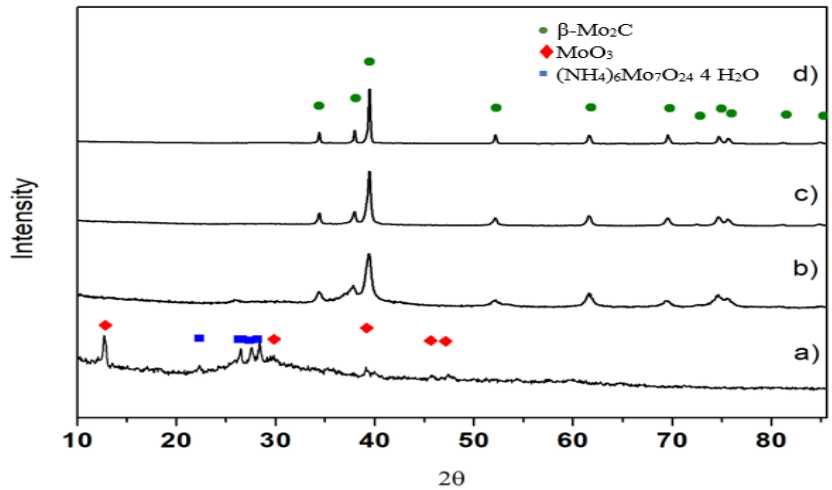


Fig. 1. Experimental X-ray diffraction patterns of Mo_2C a) Mo_2C precursor b) Mo_2C synthesized at 700 °C, c) Mo_2C

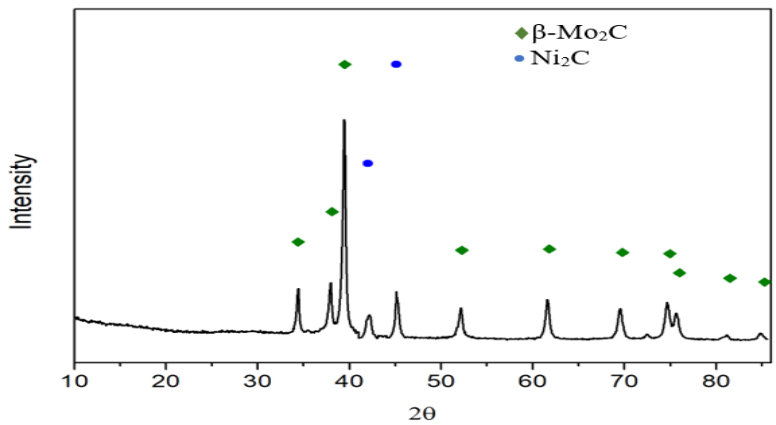


Table 3. Crystallite Size of Mo_2C

Sample	Temperature (°c)	Crystallite size (nm)
1	700	1.9335
2	800	3.6169
3	900	5.7199

Also, the experimental x-ray diffraction patterns of Mo_2C show a high thermal stability by showing the same diffraction patterns at different temperature synthesis

of Mo_2C. According to Malinee Kaewpanha et al. [19] the optimal temperature to synthesis of Mo_2C is at 800 °C.

Fig. 2 shows the experimental x-ray diffraction pattern of Ni-Mo_2C synthesized at 800 °C. According with experimental x-ray diffraction patterns the crystalline structure of Mo_2C corresponds with hexagonal. Also, the experimental x-ray diffraction patterns show that the crystalline structure of Ni_3C correspond with hexagonal.

Fig. 3 shows the experimental x-ray diffraction pattern of hydroxyapatite extracted from bovine bone and heat treatment at different temperature.

The XRD patterns show a gradual increase in the degree of sharpness of peak with heat treatment [15]. P. Shipman [20] reported that results of XRD patterns in terms of alteration in crystal size. They found that there was gradual increase in hydroxyapatite crystal size associated with increased heat-treating temperature. This alteration in hydroxyapatite crystal size could be for a recrystallization [15].

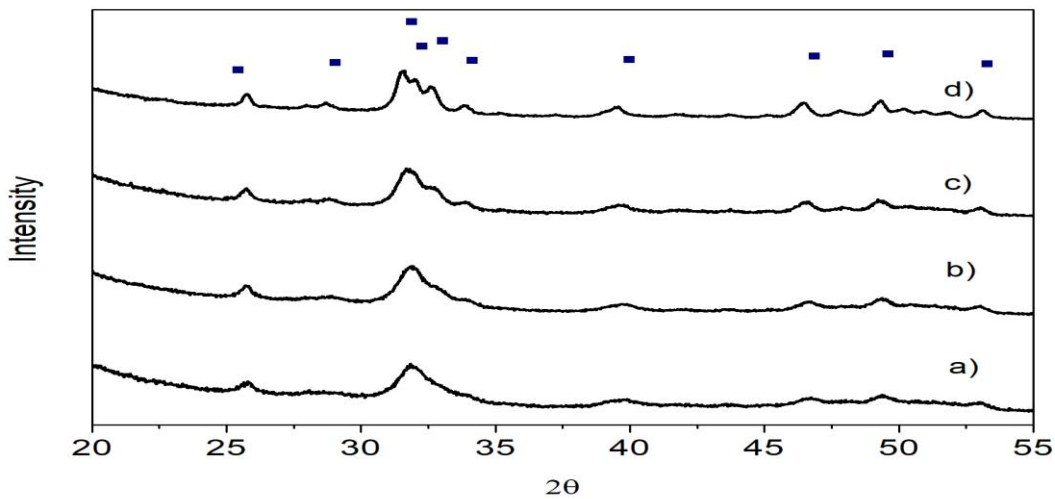


Fig. 3. Experimental X-ray patterns diffraction of precursor and bone chars obtained at different pyrolysis

3.2 FT-IR analysis

The FT-IR spectra show a decomposition of organic material and a dihydroxylation on bovine bone by effect of heat treatment staring at 700 °C. But the structure remains almost point Fig. 4 shows spectra of bovine bones and bone char after the pyrolysis process, and In table 4 shows the compounds / bond of FT-IR spectrum.

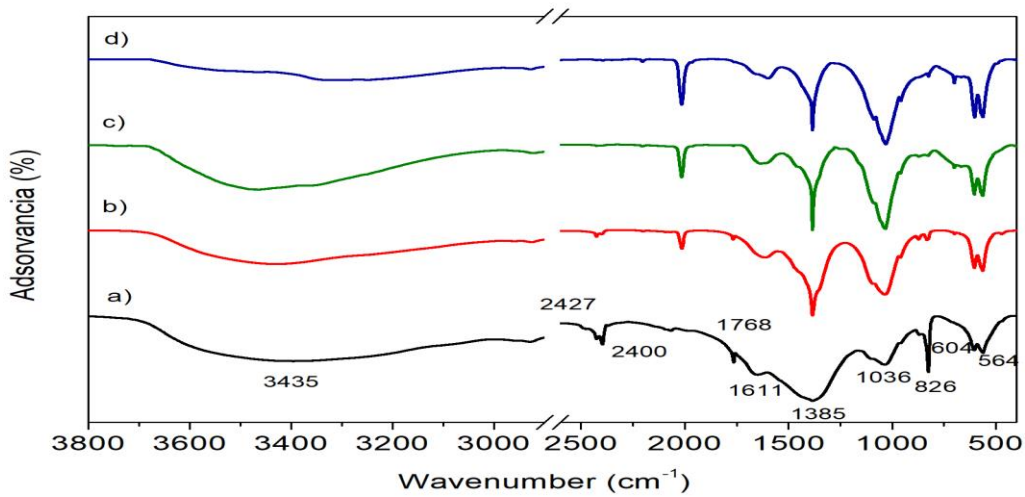


Fig. 4. FT-IR spectra of precursor and bone chars obtained at different pyrolysis temperature. a).

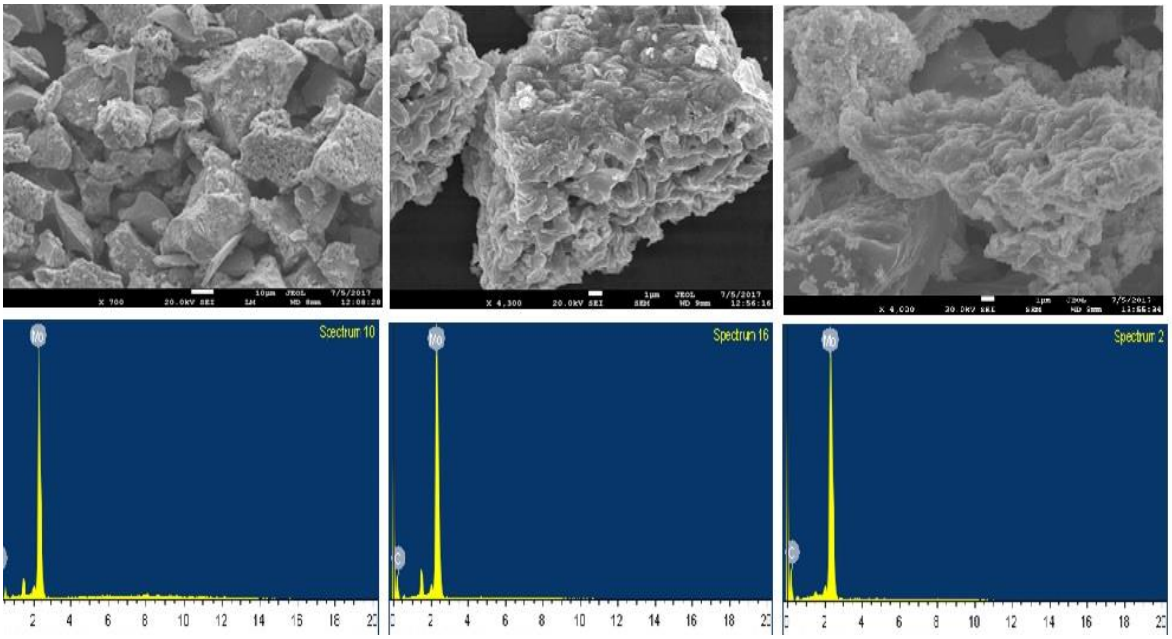
Table 4. bands of FT-IR spectra

Band (cm^{-1})	Bond	Band (cm^{-1})	Bond
3435	Group O-H	826	CO_3^{-2}
2427	P	604	PO_4^{-3}
2400	P	564	CO_3^{-2}
1768	-C=O	----	--
1611	-NH	----	--
1385	CO_3^{-2}	----	--
1036	PO_4^{-3}	----	---

3.3 Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy analysis

Fig. 5 shows the SEM images and EDS analysis of samples Mo_2C synthesized at different temperature. As it can be seen in the figure 5 the carbide is composed of large particle which seem the particles to be covered with some small particles.

The EDS analysis shows the composition of three samples corresponds to molybdenum carbide. The Results of EDS are shows in table 5.



a) b) c)

Fig. 5. SEM images and EDS analysis of Mo_2C samples synthesized at different temperature. a) Mo_2CT-700

Table 5. EDS analysis of Mo_2C samples.

Sample	*Element*	*Weight%*	*Atomic%*
a)	Mo	80.70	34.29
	C	19.30	65.31
b)	Mo	80.00	40.13
	C	20.00	59.86
c)	Mo	80.19	38.91
	C	19.61	61.12

4. Conclusion

The method of Mo_2C synthesis using sucrose as carbon source is effective to synthesize Mo_2C with hexagonal structure, also, it is show that Mo_2C has a high thermal stability, and it is confirmed that the optimal temperature of Mo_2C synthesis is at 800 °C.

The variation of this method is effective for doping Ni in Mo_2C.

The results of hydroxyapatite extraction showed the heat treatment remove organic materials, and the hydroxyapatite has a thermal and mechanical stability to be used as a catalytic support.

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