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Preparation and Charactristic Study of PUR and K_2ODOPED CoO - ZnO Catalyst

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Abstract: The catalyst CoO-ZnO was prepared in the ratio of 50:50for the mixed oxides respectively, by using the co precipitation method of their mixed bicarbonates ,from their nitrates solution using 1M NaHCO3 solution at pH constant = 7, dried at 70°C and calcinations at temperature (450) °C for 3 hours . The doped mixed oxide were prepared by impregnating method with a solution containing different amounts of potassium nitrate (2%,4%,6% and8%) then dried at 100°C ,and added separately to a fixed quantity of cobalt and zinc nitrates that dissolved in smallest amount of distill water sufficient to make paste. The paste was dried at 110°C and then calcind at 450°C for 3 hrs. The amounts of potassium, expressed as K2O. Surface and catalytic properties of the pure and doped catalyst were investigated using XRD, atomic force microscopic AFM techniques. The (AFM) results show that the roughness decreases with increased mixing ratios and wet impregnation method. The degree of crystallite and crystallite size of the produced phase increased progressively as a function of calcinations temperature from 250 to 500°C, but decreased at 600^0 and 700^0 .

Keywords: Cobalt Oxide-Zinc Oxide, Doped K2O, Low Temperature.

INTRODUCTION

Recently, nanostructure transition metal oxides have attracted a lot of attention due to their technological application and outstanding properties. The properties (such as magnetic, optic, catalytic, and electronic) of nonmaterials depend strongly on their size, structure, and shape. Co_3O_4 nano-particles exhibit weak ferromagnetic behavior [1]. CoO nano-crystals display super paramagnetic or weak ferromagnetism whereas bulk CoO is anti-ferromagnetic [2-3]. Metal oxide supports such as Al_2O_3 [4] MnOx [5], Fe_2O_3 [6], MgO–Al_2O_3 [7] were found to promote the activity of Au on selective CO oxidation. [8]synthesized Au/CeO_2 by three different methods (Impregnation, co-precipitation and sol gel method) and reported 1%Au/CeO_2 prepared by co-precipitation method is the most active by exhibiting high activity and good selectivity at 383 K. In the present study, mixed oxides, cobalt and zinc oxide with varying mole ratios were synthesized by co-precipitation method [9]. The cobalt and zinc spinal compounds can act as efficient catalysts in a lot of heterogeneous chemical processes.[10,11,12,13] ,this catalysts prepares by co precipitation method, The co precipitation method offers some advantages Applying this simple and rapid technique, the control of particle size and composition is easy. The precipitation method provides several possibilities to modify the particle surface and shape. Precipitation of various cobalt and zinc salts from nitrate [14-16] chloride [17] acetate [18-19] or an aqueous alcoholic-aqueous solutions yields cobalt and zinc oxide nano particles. The particle size of the co precipitated materials is strongly dependent on the pH of medium and the concentration of the initial materials. The precipitation agent may be oxalic acid or oxalate [20] carbonate,[21] ammonia[22]and sodium hydroxide.[21] Organic surfactants [15] can be used during the precipitation in processes and the weight loss occurred by heat treatments were recorded by thermal analysis in a controlled atmosphere . Mixed oxides containing transition metal oxides are used to design the catalytic materials, Zinc oxides are reported to be among the most efficient transition-metal compounds in catalytic combustion [23]. Mixing zinc with transition-metal oxides in many catalytic reactions might modify the catalytic activity of separate components [24 ,25].Mixed oxide solids containing Zn are active catalyst for oxidation-reduction reactions and combustion processes ,for example the oxides(Co, Zn, and Mn) were active in the reduction

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of nitrous oxide[26]. K_2O as an alkaline earth metal oxide acts as a solid base catalyst and as a support in a variety of organic reactions such as alcohol coupling [27], Knoevenagel condensation [28] aldol condensation [29] Deposition metal captions on K_2O-based catalysts for producing new centers with different acid-base properties have been reported.

Such actions as $Co^{2+,}$ $Fe^{3+,}Zn^{2+}$ and Cr^{3+} promoted K_2O and increased the basic properties and the catalytic activity for 2-propane dehydrogenation [21]. The acid-base properties of K_2O induced by promotion with alkaline actions depend on both the amount and the kind of the action added [22].

EXPERIMENTAL SECTION

Preparation of Catalyst

CoO- ZnO mixed oxide were prepared by co precipitation method of their mixed bicarbonates from their nitrates solution using 1M NaHCO3 (99% supplied from B.D.H Company) solution at pH constant equal 7 and temperature 70°C.

The carefully washed precipitate was dried at 110°C till constant weight, then formulated as tablets by diameter 10 mm, and then subjected to heating 300, 400, 500, 600 and 700°C for 3 hrs. Four K_2O - doped samples were prepared by impregnating a given dry weight of the mixed bicarbonates with calculated amount of potassium nitrate (purity 99% supplied from Fluke Company) dissolved in the least amount of distilled water sufficient to make paste. The paste was dried at 110°C and then calcind at 450 °C for 3 hrs. X – Ray powder diffract grams of various investigated.

Identification of Doped and Mixed Oxide by XRD Technique

X-ray diffraction (XRD) analysis was used to recognize the crystal structure of thin films. When incident beam of (X-ray) diffracts from a mono wavelength on film surface this will exhibit peaks on limit angels for each material because of Bragg's reflection on parallel crystalline surface. The (X-ray) diffract meter type (Shimadzu 6000) made in Japan Target: Cu-Kα, Wave length: 0.15405 nm, Voltage: 40 Kv, Current: 30mA, Speed: 5 deg/min.

Physical Properties of Catalyst

The physical properties of pure and doped catalyst: Apparent porosity (PA %), total pore Volume (VP), and particle density (DP), at different temperatures (300, 400,500,600 and700) °C were determined by wet impregnation method [31].

Determination the Average Particle Size of the Catalyst

The particle size of the crystalline phases present in the different solids was calculated from the line broadening profile analysis of the main diffraction lines of these phases using Scherer equation [32]$d = K\lambda / \beta 1/2 \cos \theta$

Where d: is the mean crystallite diameter, λ the X – ray wavelength, K the Scherer constant (0.89), β1/2 is the full – width at half maximum (FWHM) of the diffraction peaks of crystalline phases and θ is the diffraction angle .

Analytical Study

The percentage of elements (Co and Zn) in the prepared catalyst was determined by using atomic absorption spectrophotometer (AA-6300 supplied by Shimadzu Company).

Identification Morphology by Atomic Forces Microscopy (AFM)

In order to observe the surface roughness and topography of deposited thin films, Atomic Force Microscope (AFM) by using (AA 2000) instrument by (Angstrom Advanced Inc) with high analysis capability about (0.1-1) nm and scan angle (0~360) degree and scan rate (0.1~100) Hz with ability to zoom estimated to (5×102-108) to detect of prepared thin film surface and suitability for study and their properties to provide us with high accurate information about root mean square (RMS), roughness and grain size.

RESULTS AND DISSECTION

Analytical Study

The results of the percentage of elements (Co, and Zn), and their oxides in the catalyst are shown in table (1).

Table 1: The results of the percentage of Co, and Zn, and their oxides in the catalyst

Catalyst weight (gm)	**Co concentration (ppm)**	**Co %**	**CoO %**	**Zn concentration (ppm)**	**Zn %**	**ZnO %**	**The summation. of percentage of oxides 100 %**
0.1085	3.3994	39.163	49.606	3.4870	40.172	50.053	99.659

From the table (1), we can concluded that the exactly amount of Cobalt and Zinc metal and their oxide are obtained.

XRD Investigation of Pure and K_2O Doped CoO-ZnO

The X-ray diffract grams of single oxide and pure CoO-ZnO that were prepared at 450 °C shown in figures (1, 2) and (3)and forK_2O doped CoO-ZnO in different ratios in figures(4,5 ,6 ,7,8).

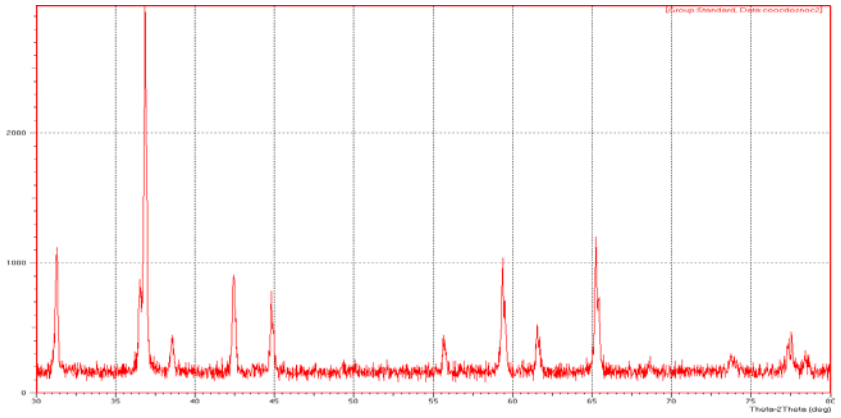

Figure 1: X-ray diffract grams pattern for single CoO

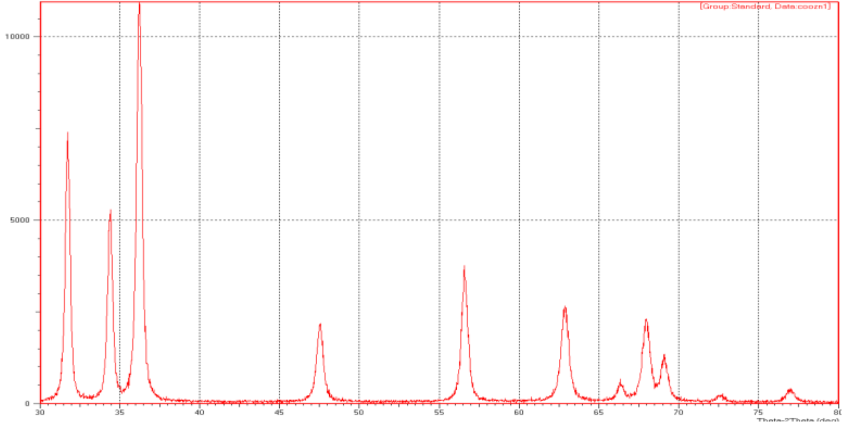

Figure 2: X-ray diffract grams pattern for single ZnO

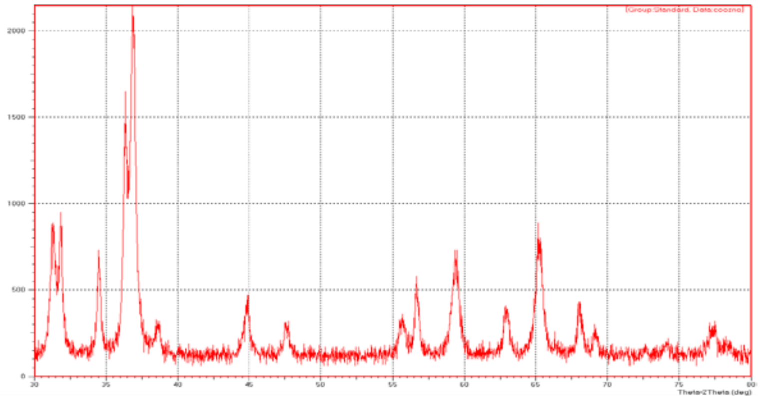

Figure 3: X-ray diffract grams pattern for CoO - ZnO catalyst

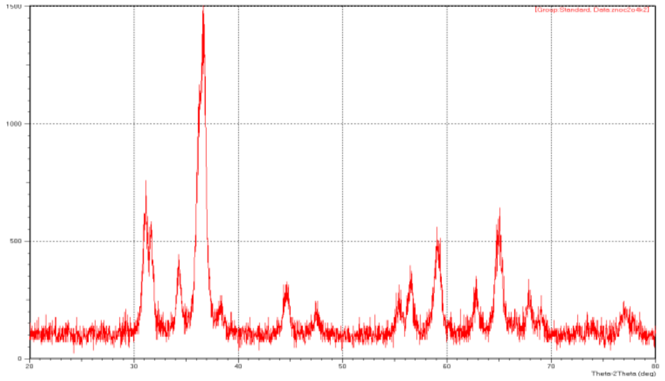

Figure 4: X-ray diffract grams pattern for (2%) K_2O doped CoO-ZnO catalyst

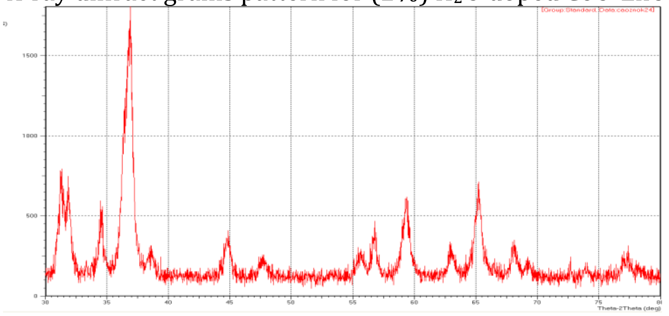

Figure 5: X-ray diffract grams pattern for(4%) K_2O doped CoO-ZnO catalyst

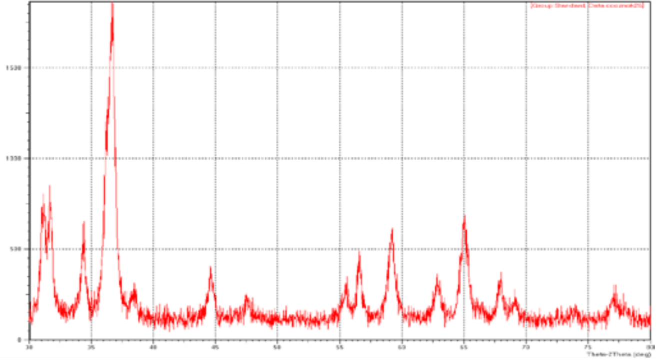

Figure 6: X-ray diffract grams pattern for (6%) K_2O doped CoO-ZnO catalyst

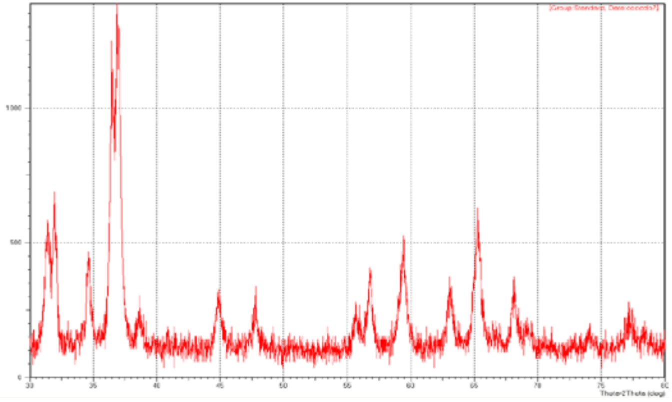

Figure 7: X-ray diffract grams pattern for (8%) K_2O doped CoO-ZnO catalyst

From the Comparison of X-ray diffract gram pattern of CoO-ZnO oxides in the catalyst and single CoO and ZnO show that there is a small deviation in the angles of diffraction and change in the relative intensity of the main absorption peaks this due to the interaction between the mixed oxides in the catalyst, The best crystalline phases produced in 450°C and obtained a complete crystal size of the catalyst pattern. The diffraction patterns of the sample prepared in 500 and 600°C become more broadening because of the sintering effect and overlapping of the oxides phases[33], this causes the decreases of the particle size of the catalyst as shown in figure(8) that are calculated by using Scherer equation [32]: $d = K\lambda / \beta 1/2 \cos \theta$.

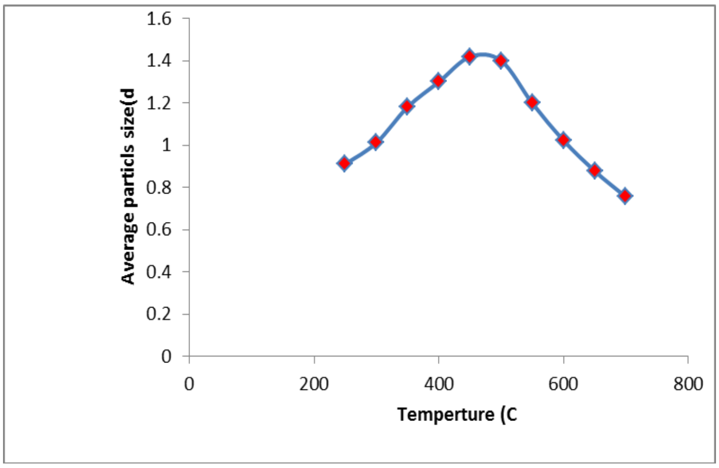

Figure 8: Average particle size (d) for CoO-ZnO Catalyst at different temperature (250 to 700) °C

The figures (4-7) shows that the intensity of the diffraction lines and the particle size of ZnO increased with the increasing of the amount of K_2O added and increasing the degree of crystalline of CoO phase. The effect of K_2O is to lower the thermal conversion process of catalyst, and remained thermally stable even by heating at above 500 to 800 °C [34].

Physical Properties of Pure and Doped Catalyst

Figures(9),(10) and (11) showed that the physical properties of the pure catalyst Apparent porosity (PA%), total pore volume(VP), and particle density(DP), respectively at different temperatures (300,350,400,450, 500 , 550 ,and 600) ∘C, the best physical properties result at 450°C.

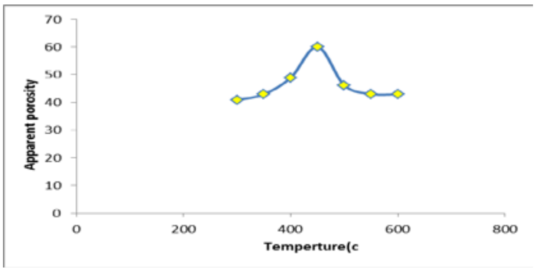

Figure 9: Apparent Porosity (PA) % of CoO - ZnO catalyst at temperatures (300,350,400,450, 500, 550 and 600) °C.

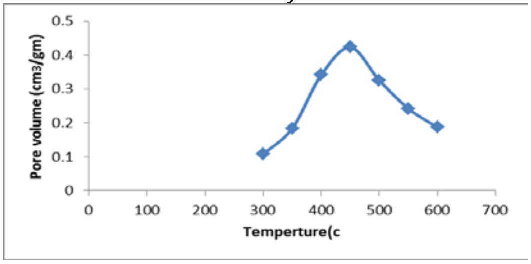

Figure 10: Pore Volume (cm3/g) of CoO - ZnO catalyst at ((300,350,400,450, 500, 550 and 600) °C

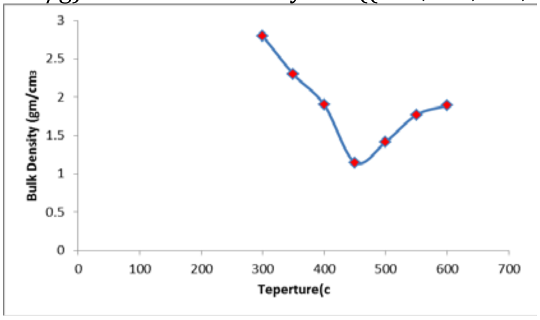

Figure (11): Bulk Density (g /cm3) of CaO - ZnO catalyst at (300,350,400,450, 500, 550 and 600) °C

When increasing the temperature from 300 to 450°C, increased the loss of carbon dioxide and water of crystallization and gets complete conversion of a metal carbonate to metal oxide at a temperature of 450°C, and the size of the total pore volume and porosity will become more, therefore the weight of catalyst grain tablets decreased according to their volume, this lead to decreasing of the bulk density.

When increasing the temperature above 450 to 600 C, the total pore volume and porosity, will be decreased and the bulk density become more, because of the sintering effect [33]. The physical properties of doped catalyst will be increase with the increasing of percentage of K_2O (2%, 4%, 6%, and 8%) in the catalyst, as shown in figures (12),(13) and (14).

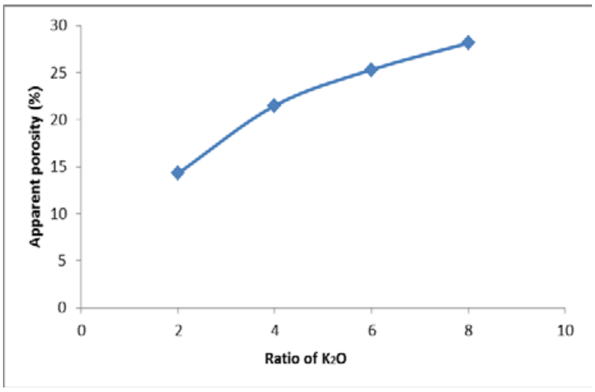

Figure 12: Apparent Porosity of the (K2O) % doped catalyst.

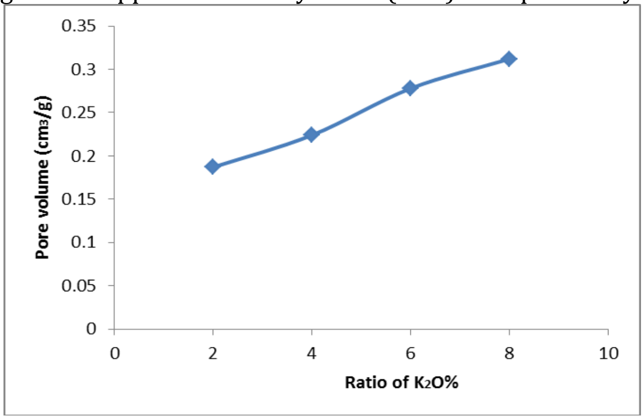

Figure 13: Pore Volume (cm3/g) of the (K_2O) % doped catalyst

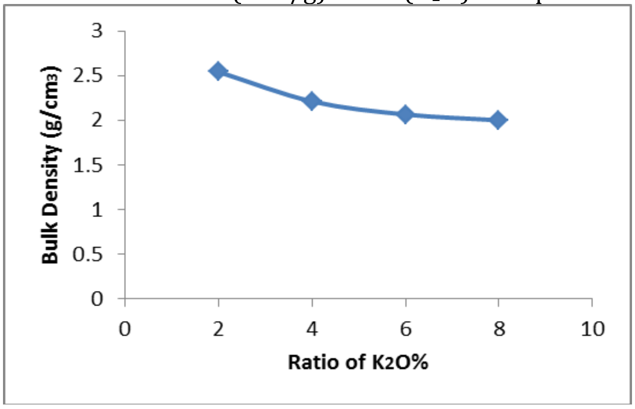

Figure 14: Bulk Density (g / cm^3) of the (K_2O) doped catalyst

Atomic Force Microscope (AFM)

The topography of the surface for prepared films and the effect of mixing ratio studied by using Atomic Force Microscope (AFM) with the ability to depiction and analysis of these surfaces and give the statistical values with high accuracy about surface roughness values depending on the Root Mean Square (RMS) of the average roughness. Through microscopic analysis (AFM) we can study the effect of (thickness, concentration, temperature, method of preparation ..... etc.) on the properties of the deposited film material to the fact that the study of the surfaces of film materials important to recognize how the distribution and arrangement of atoms on surfaces, and to identify the differences or homogeneity properties or attributes relating to each atom separately and illustrative image about the distribution rate of the crystalline size onto surfaces [35]. Table (2) shows that the average diameters (grain size) of pure (CoO, ZnO, CoO - ZnO) and for K_2O doped CoO-ZnO in different ratios. We can be observed a decrease the grain size with increasing of the mixing ratios this lead to surface homogeneity this result agree with XRD results.

Table 2: Atomic Force Microscope parameters of the percentage of Co, and Zn, and their oxides in the catalyst.

Sample	**Root Mean Squa(RMS) (nm)**	**Roughness (nm)**	**Average Grain size (nm)**
CoO_{pure}	0.513	0.429	75.35
ZnO_{pure}	7.79	6.72	66.46
$CoO - ZnO_{pure}$	9.31	7.83	91.11
$CoO - ZnO - K_2O_{2\%}$	4.38	3.64	35.31
$CoO - ZnO - K_2O_{4\%}$	2.25	1.95	59.11
$CoO - ZnO - K_2O_{6\%}$	0.415	0.342	81.93
$CoO - ZnO - K_2O_{8\%}$	1.78	1.54	66.73

Figures (15) and (16) show the Atomic Force Microscope (AFM) images within the scanning area (1800×1800) nm and analytical ability (pixels= 612,612) of all samples deposited at glass with temperatures of Ts = 648K.

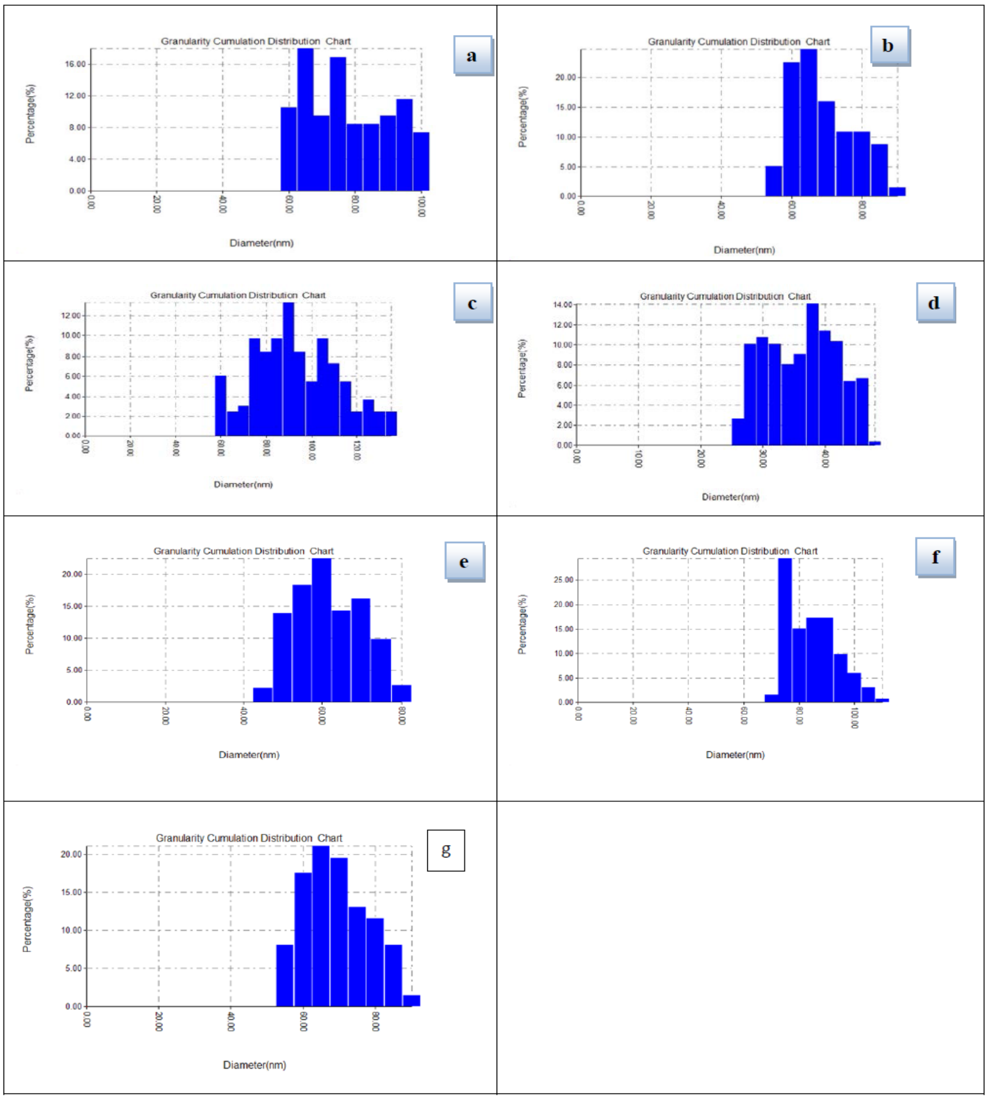

Figure (15): Diagrams of granularity distribution for: (a) CoO pure, (b) ZnOpure, (c) CoO- ZnO pure (d)CoO –ZnO –$K_2O_{2\%}$, (e) CoO –ZnO –$K_2O_{4\%}$, (f) CoO –ZnO –$K_2O_{6\%}$, and (g) CoO –ZnO –$K_2O_{8\%}$.

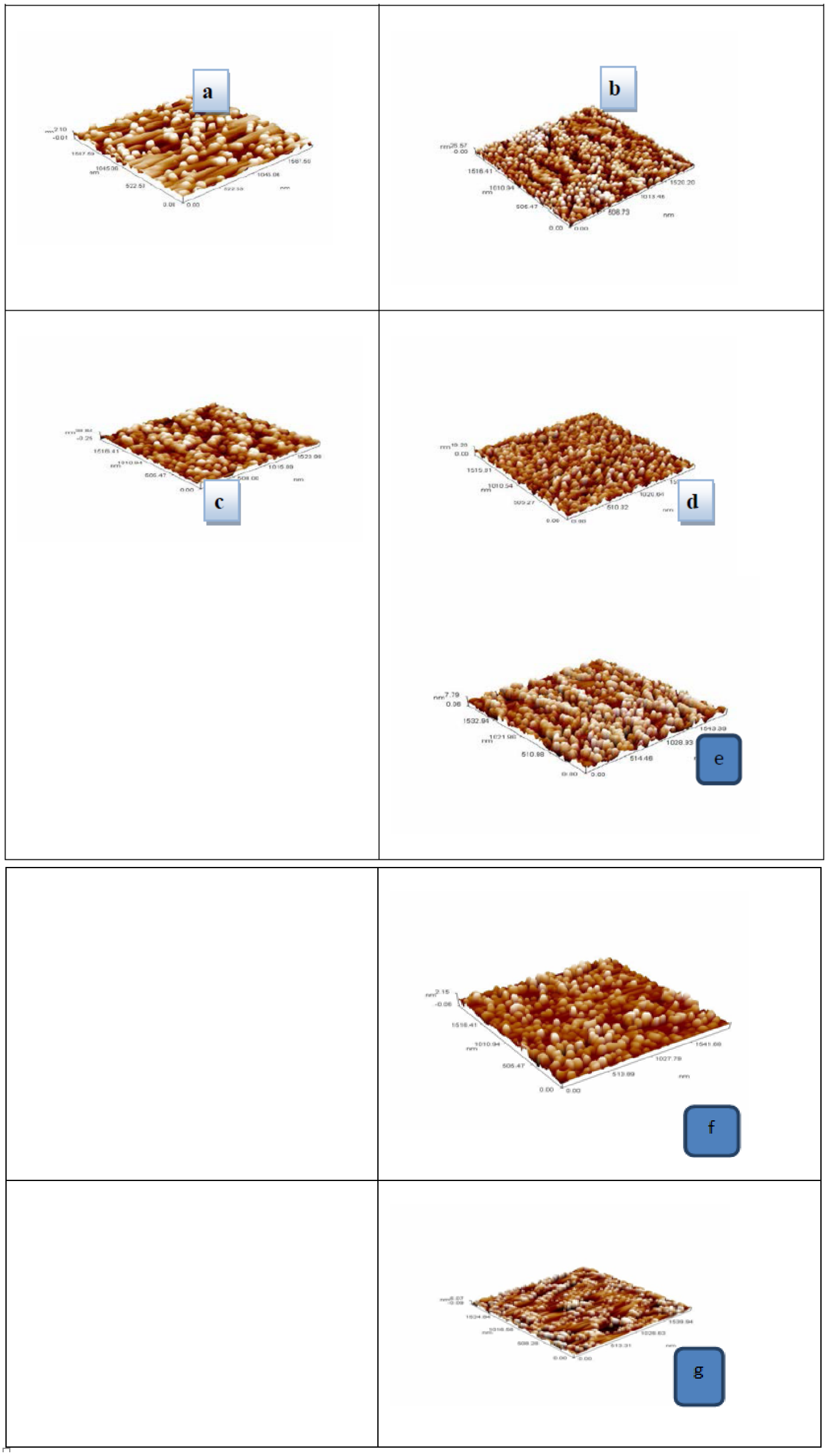

Figure 16: AFM images for: (a) ZnOpure , (b) CoO pure, (c) ZnO-CoO pure (d) ZnO –CoO – K_2O $_{2\%}$, (e)ZnO –CoO – K_2O $_{4\%}$,, (f)ZnO –CoO – K_2O $_{6\%}$,and, (g)ZnO –CoO – K_2O $_{8\%}$.

from this images we can found that the surface thickness of the thin films value decreases in thickness which mean getting homogeneous crystalline growth along horizontal direction lead to uniform granular surface morphology thin film, while Figure (16) the crystalline defects have led to get un uniform granular surface morphology thin film.

CONCLUSION

From the results that obtained from this research we can conclude the following-:

1. The best temperature and calculated time to prepare catalyst is 450 °C for 3hrs., it's give high pore volume and porosity.
2. The increasing of calculated temperature (450C°) lead to increase the pore volume and porosity but high temperatures 600 and 700°C ,the porosity and pore volume will be decrease causes to decreasing surface area and pore volume.
3. AFM images shows that the RMS, roughness and average grain size decrease with increases the mixing ratio.

REFERENCES

[1] Q. Yuanchun, Z. Yanbao, and W. Zhishen, Mater. Chem. Phys, (2008), 110, 457,.

[2] R. H. Kodama, J. Magn. Magn., Mater,(1999), 200, 359.

[3] M. Ghosh, E. V. Sampathkumaran, and C. N. R. Rao, Chem. Mater, (2005) ,17, 2348 .

[4] G. K. Bethke and H. H. Kung, Appl. Catal., , vol. 194, no. 43.(2000)

[5] R. M. T. Sanchez, A. Ueda, K. Tanaka and M. Haruta, J. Catal., vol. 168, no. 125.(1997)

[6] L. Guczi, D. Horváth, Z. Pászti and G. Petõ, Catal. Today,vol. 72, no. 101.,(2002)

[7] R. J. H Grisel, C. J. Weststrate, A. Goossens, M. W. J. Crajé, A. M van der Kraan and B. E Nieuwenhuys, Catal. Today, vol. 72, no. 123.(2002)

[8] A. Luengnaruemitchai, S. Osuwan and E. Gulari, Int. J. Hyd. Energy,vol. 29, no. 429.(2004)

[9] Hyun Tae Jang, Eui Min Jung, Sang Hyun Park and Pushparaj Hemalatha ,International Journal of Control and Automation ,Vol.8, No.6 (2013) pp.31-40 .

[10] G. Fornasari, S. Gusi, F. Trifiro', and A. Vaccari, Ind. Eng. Chem.Res, 26, 1500.(1987)

[11] M. M. Natile and A. Glisenti, Chem. Mater, 14, 3090. (2002)

[12] G. Fierro, G. Ferraris, R. Dragone, M. Lo Jacono, and M. Faticanti,Catal. Today ,116,38. (2006)

[13] M. Wojciechowska, W. Przystajko, and M. Zielinski, Catal. Today , 338, 119.(2007)

[14] Y. Zhang, Y. Chen, T. Wang, J. Zhou, and Y. Zhao, Microporous and Mesoporous Materials , 114, 257 . (2008)

[15] R. V. Narayan, V. Kanniah, and A. Dhathathreyan, J. Chem. Sci. , 179,118.(2006)

[16] I. Luisetto, F. Pepe, and E. Bemporad, J. Nanopart. Res., 10, 59.(2008)

[17] Y. Ichiyanagi and S.Yamada, Polyhedron ,24, 2813.,(2005)

[18] K. An, N. Lee, J. Park, S. C. Kim, Y. Hwang, M. J. Han, J.Yu, and T. Hyeon, J. Am. Chem. Soc. , 128, 9753. (2006)

[19] J. Ahmed, T. Ahmad, K. V. Ramanujachary, S. E. Lofland, and A. K.Ganguli, J. Colloid and Interface Sci. ,321, 434.(2008)

[20] C. Xu, Y. Liu, G. Hu, and G. Wang, Chem. Phys. Lett., 366, 567 .(2002)

[21] Herrero, P. Benito, F. M. Labajos, and V. Rives, Catal. Today ,129 ,128.(2007)

[22] L. Zhuo, J. Ge, L. Cao, and B. Tang, Cryst. Growth Des., 9, 1.(2009)

[23] Álvarez- Galván, M.C.; de la Pena Óshea, V.A.; Fierro, J.L. G. and Arias, P.L., Catal. Commun., 4, 223.(2003)

[24] Li, W.; Lin, Y.; Zhang, Y., Catal. Today, 83, 239.(2003)

[25] Morales, M.R.; Barbero, B. P. and Cadús, L.E., Appl. Catal. B Environ., 67, 229.(2006)

[26] Deraz,N. M., Materials Lett., 51, 470.(2001)

[27] V.K. Diez, C.R. Apesteguia, J.I. Dicosimo, Catal. Today , 63, 53.(2000)

[28] A. Corma, S. Iborra, J. Primo, F. Rey, Appl. Catal. ,114 , 215.(1994)

[29] J.I. Dicosimo, V.K. Diez,, C.R. Apesteguia, Appl.Catal.,149 .(1996)

[30] S.A. El-Molla, Appl. Catal.,A. 280,189 .(2005)

[31] Satterfield C.N., Heterogeneous Catalysis in Practice ,Mc Graw-Hill ,Book Company ,New York,(1980), p.1

[32] Cullity, B.D., Elements of X-ray Diffraction, 3rd ed., Addison- Wesley , Reading , MA.(1967)

[33] Satterfield,C.N., Chemical Engineering Series ,New York,75.(1976)

[34] Ghozza,A. M. ,J. of Thermal Analysis and Calorimetry , 75,135–151.(2004)

[35] G. A. Kadhim AL-Lamy, Fabrication and Study the Optoelectronics Properties of Detector NiO/c-Si by Spray Pyrolysis Technique, (2013).