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Preparation and Characteristic Study of Pure and Na_2O Doped NiO-ZnO Catalyst

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Abstract

The NiO-ZnO catalyst was prepared by coprecipitation method in equivalent quantity (50:50),and study of their crystallanty and physical properties at different temperature by using XRD techniques and wet impregnating method.

The Na_2O doped catalyst was prepared by wet impregnating method with different ratios of Na_2O , The best crystallanty and physical properties of NiO - ZnO catalyst were obtained at 600°C for 4 hrs.

The results showed that the porosity and pore volume of NiO – ZnO catalyst increased and decreased of its density with the increasing of Na_2O ratios in catalyst.

الخلاصة

حضر العامل المساعد أوكسيد النيكل – أوكسيد الخارصين بنسب كمية متكافئة باستخدام طريقة الترسيب المشترك ودرس تبلورها وخواصها الفيزياوية في درجات حرارة مختلفة باستخدام تقنية حيود الأشعة السينية XRD والتشبيع الرطب. حضر العامل المساعد المشوب بأوكسيد الصوديوم بطريقة التشبيع الرطب بنسب مختلفة من أوكسيد الصوديوم .

افضل حالة تبلور وافضل خواص فيزياويه للعامل المساعد NiO-ZnO كانت في درجة الحرارة ٦٠٠ْم لمدة ٤ ساعات. بينت النتائج ان المسامية والحجم المسامي تزداد وتقل الكثافة للعامل المساعد NiO-ZnO بزيادة نسبة اوكسيد الصوديوم.

الكلمات الدالة: العامل المساعد المشوب بأوكسيد الصوديوم ,اوكسيد النيكل,اوكسيد الخارصين.

Introduction

catalyst component interactions (CCI) have an important role in catalyst active phase formation, contribute to catalyst stability, or contrary, can accelerate catalyst aging (1).

The CCI can result in:1. Incomplete reduction of the metal; 2. Support induced cluster size; 3. Epitaxial growth of metals on the support; 4. Support effect on the morphology of metallic particles; 5. Contamination of the metal by the support.

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 (2) Mixing zinc with transition-metal oxides in many catalytic reactions might modify the catalytic activity of separate components (3,4).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 of nitrous oxide (5) and the Ni oxides supported on TiO_2 , ZnO has been reported to act as catalysts used in cracking of water and production of H_2,O_2 (1,6). The choice of a catalyst support largely depends on the surface area and pore size of the support itself. High surface area could provide high population of the active sites, while large pore size allows the accessibility of their rei actants to the active sites. Recently, mesoporous material such as Cu/MCM-41 (7). A number of catalysts consisted of various transition metals (V, Cr, Mn, Fe, Co, Ni and Cu) oxides on different commercial supports such as silica and alumina have been studied. Among these catalysts, manganese oxides such as $MnOx/Al_2O_3$(8),MnOx / NaY(9) and MnOx/TiO2(10,11) have attracted much interest due to their high catalytic activities. These catalysts were prepared by the solution impregnation method on supports using manganese nitrate or acetate. Unsupported MnOx catalysts generally showed less NOx conversion than did supported MnOx catalysts because of its low surface area (12).

1-Preparation of Catalyst:

NiO- ZnO mixed oxide were prepared by coprecipitation method of their mixed bicarbonates from their nitrates(purity 99% supplied from Merck and B.D.H.Companies) using 1M $NaHCO_3$(99% supplied from B.D.H Company) at pH equal to = 7 and temperature 70°C for 2 hrs. The carefully washed precipitate was dried at 110°C till constant weight, then formulated as a tablet in a diameter 10 mm ,and then subjected to heat 400 ,500 ,600 and 700°C for 4 hrs. Four Na_2O - doped samples were prepared by impregnating a given dry weight of the mixed Nikel and Zinc bicarbonates with a calculated amount of sodium nitrate(purity 99% supplied from Fluka Company)for the desired percentage (2,4,6,8,10)% dissolved in the least amount of distilled water sufficient to make apaste. The paste was dried at 110°C and then calcined at 600 °C for 4 hrs.

2- Identification of doped and Mixed oxide by XRD technique:

The mixed oxide NiO –ZnO and Na_2O doped were characterized by using XRD technique. X – ray powder diffraction grams of various investigated samples were carried out using a Bruker diffractometer (Bruker D8 advance target). The patterns were run with CuKα1 with secondly monochromator($\lambda = 0.1545$ nm) at 40 kV and 40 mA.

3-Physical Properties of Catalyst:

The physical properties of pure and Na_2O doped catalyst :Apparent porosity (P_A%), total pore Volume(V_P),and particle density(D_P),at different temperatures (400,500,600 and700) ˚C were determined by wet impregnation method (13).

4-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 Scherrer equation (14):

$d = K\lambda / \beta_{1/2} \cos \theta$

Where d: is the mean crystallite diameter, λ the X – ray wavelength, K the Scherrer 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.

5-Analytical Study:

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

Results and discussion

1- Analytical Study:

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

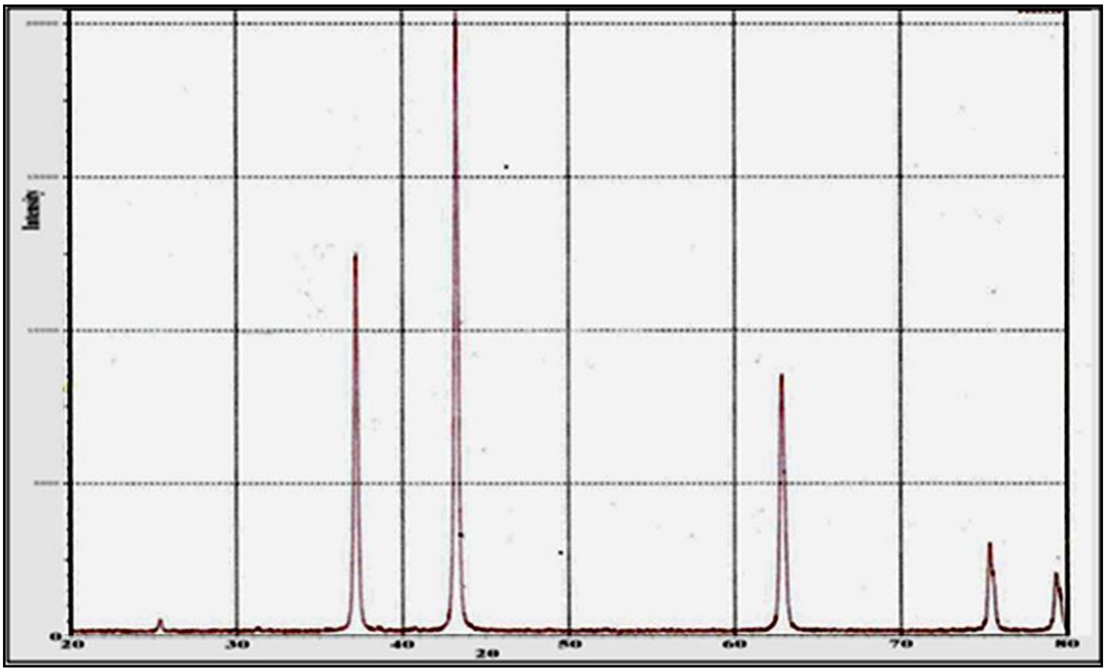
Table(1): The results of the percentage of Ni ,and Zn ,and their oxides in the catalyst

The SUM. of percentage of oxides 100 %	ZnO %	Zn %	Zn conc. (ppm)	NiO %	Ni %	Ni conc. (ppm)	Catalyst weight (gm)
99.515	49.947	40.1309	3.2169	49.568	38.95	3.1192	0.1001

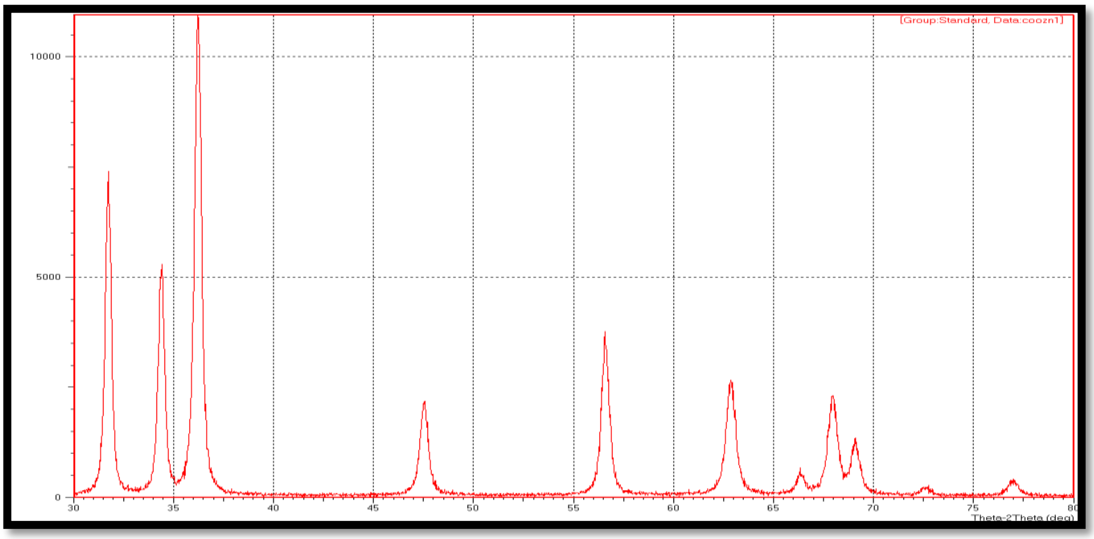
From the table(1),we can concluded that the exactly amount of Nickel and Zinc metal and their oxide are obtained.

2- **XRD Investigation of pure and Na_2O doped NiO-ZnO :**

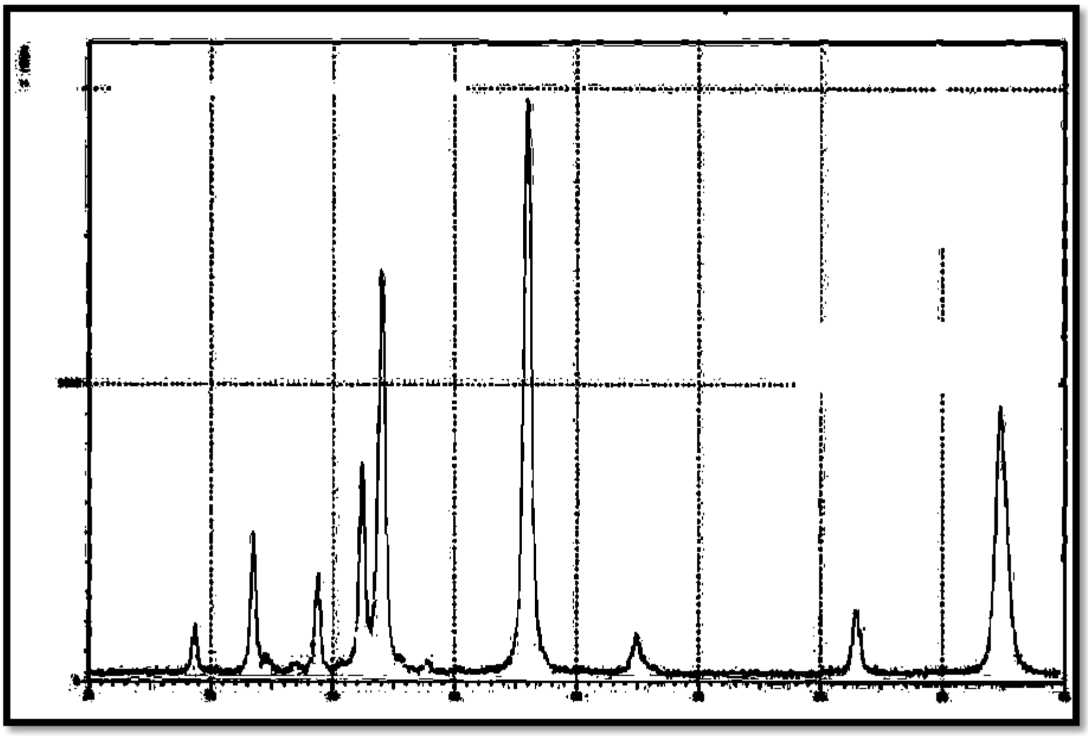
The X-ray diffractograms of single oxide and pure NiO-ZnO that were prepared at 600 °C shown in figures (1, 2) and (3)and for Na_2O doped NiO-ZnO in different ratios in figures(4,5 ,6 ,7,8).



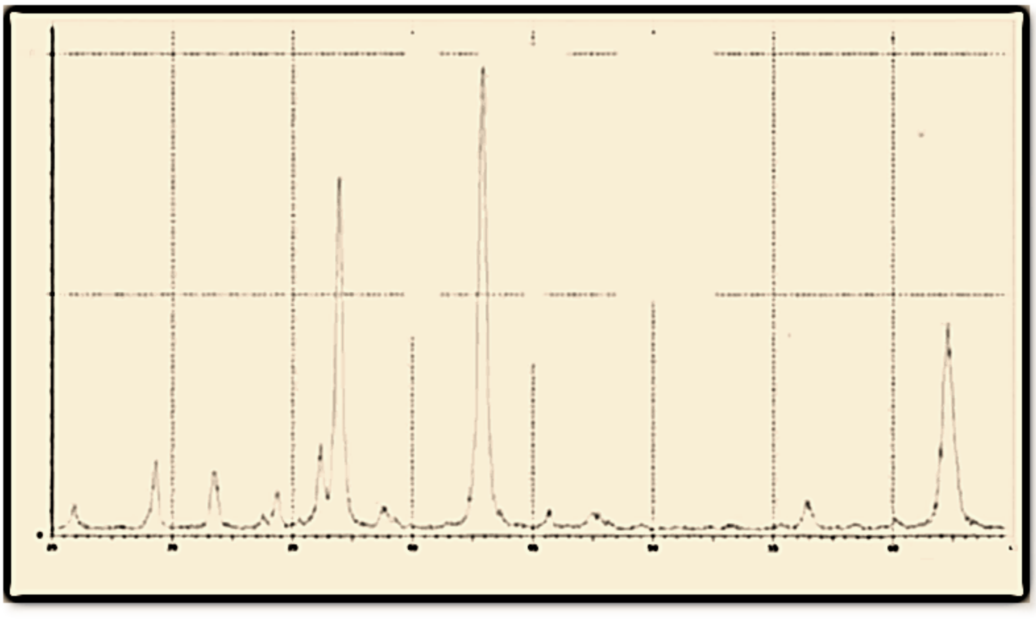
Figure(1): XRD pattern for single NiO.



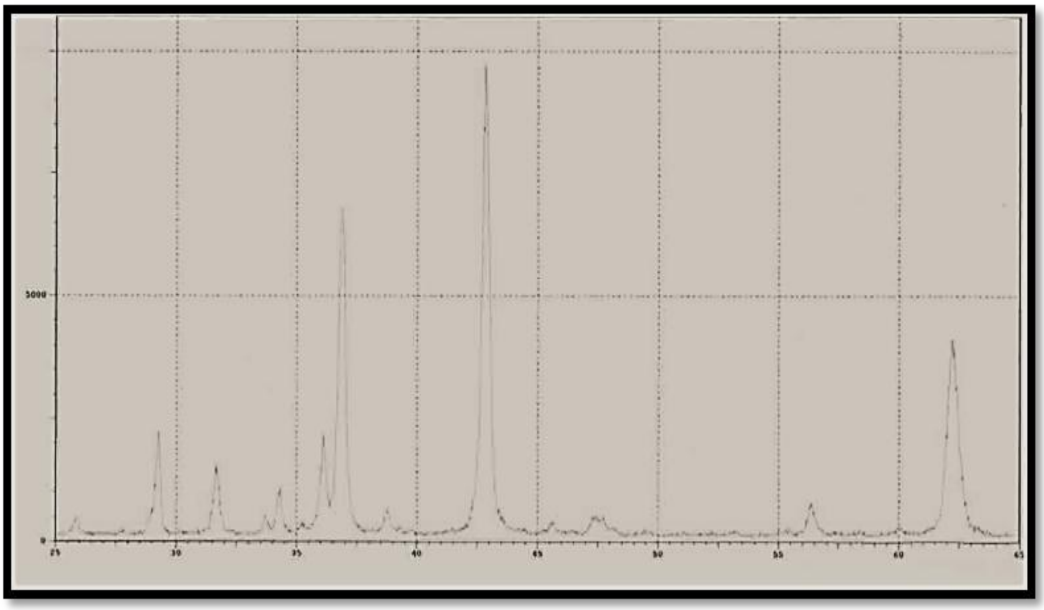
Figure(2): XRD pattern for single ZnO.



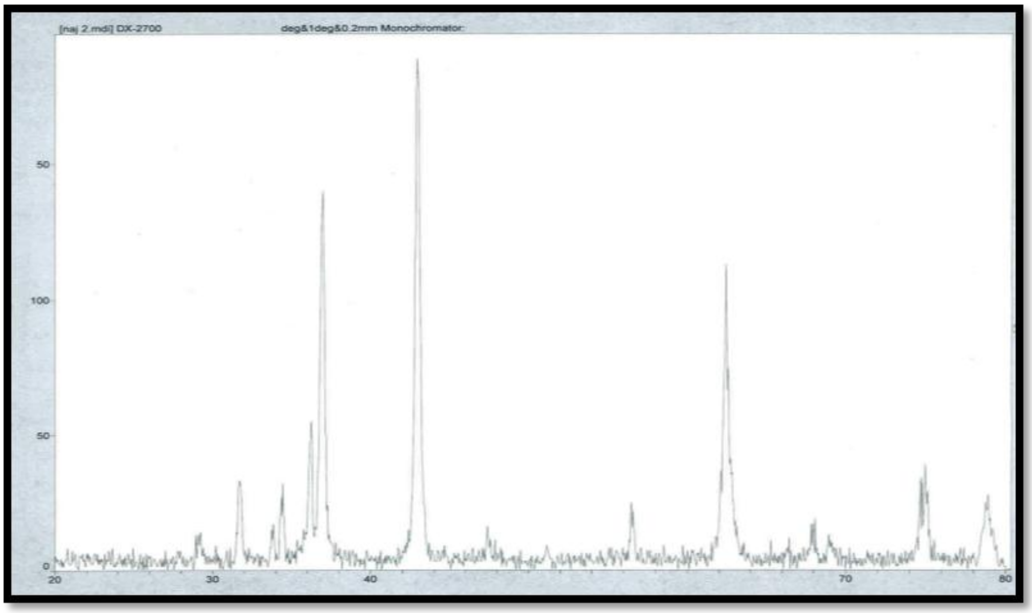
Figure(3): XRD pattern for NiO - ZnO catalyst



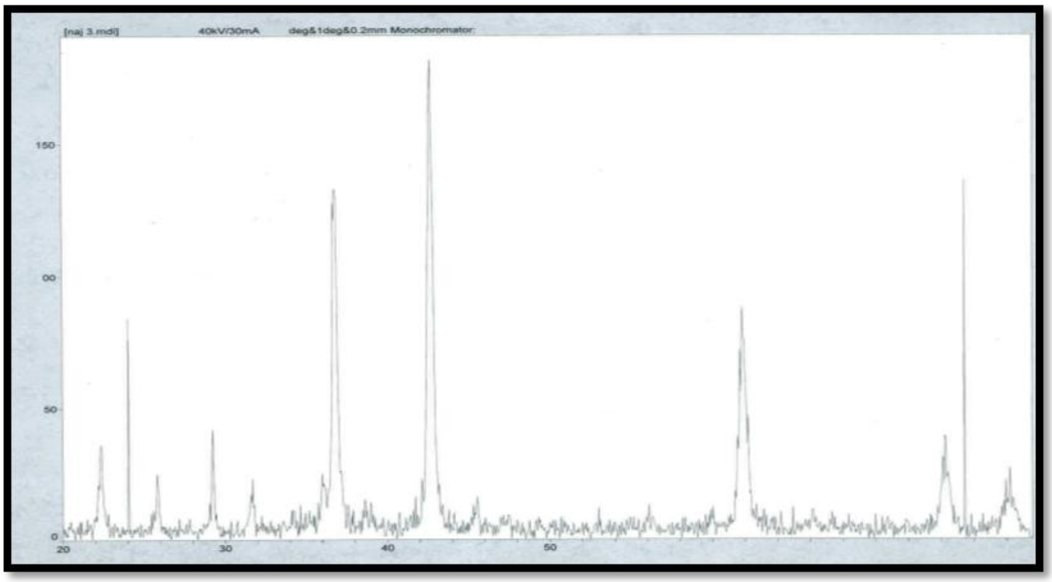
Figure(4): XRD pattern for(2%) Na_2O doped NiO-ZnO catalyst.



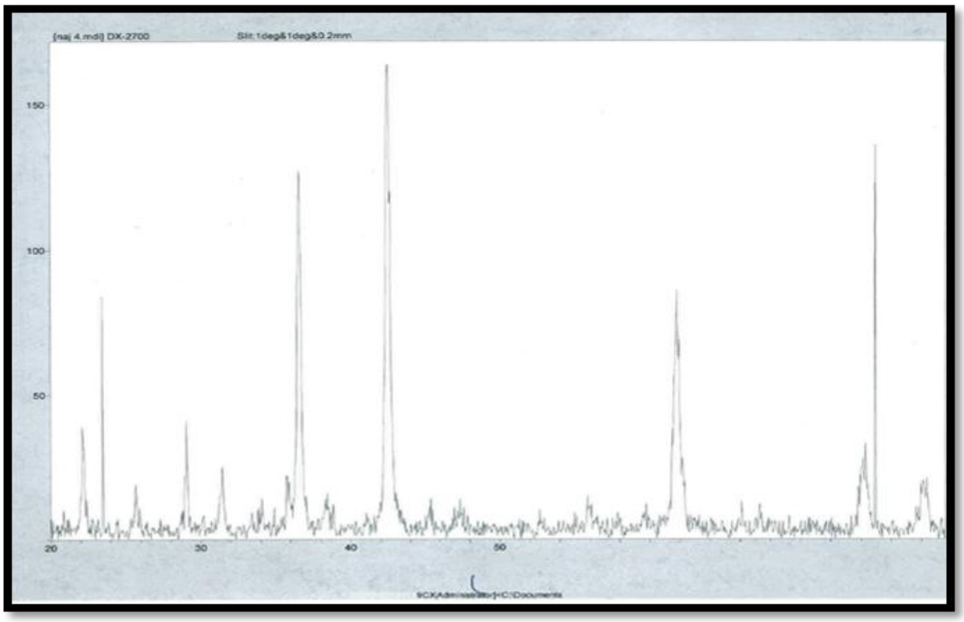
Figure(5): XRD pattern for(4%) Na_2O doped NiO-ZnO catalyst



Figure(6): XRD pattern for(6%) Na_2O doped NiO-ZnO catalyst

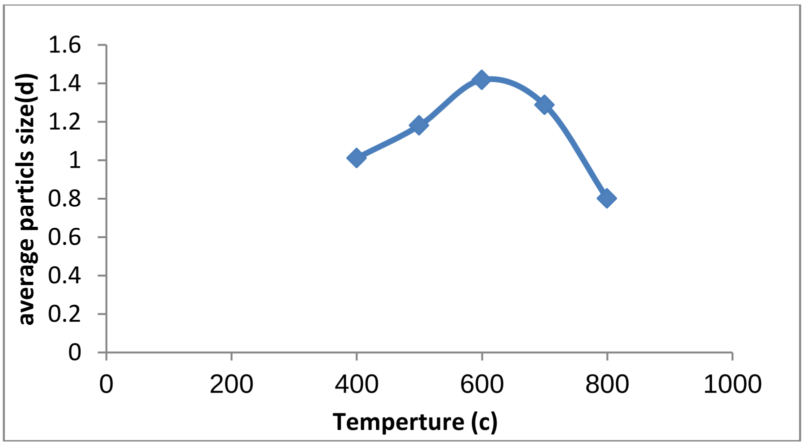


Figure(7): XRD pattern for(8%) Na_2O doped NiO-ZnO catalyst



Figure(8): XRD pattern for(10%) Na_2O doped NiO-ZnO catalyst

From the Comparison of X-ray diffractogram pattern of NiO-ZnO oxides in the catalyst and single NiO 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 600°C and obtained a complete crystal size of the catalyst pattern . The diffraction patterns of the sample prepared in 700 and 800°C become more broadening because of the sintering effect and overlapping of the oxides phases(15), this causes the decreases of the particle size of the catalyst as shown in figure(9) that are calculated by using Scherrer equation (14): $d = K\lambda / \beta 1/2 \cos \theta$.

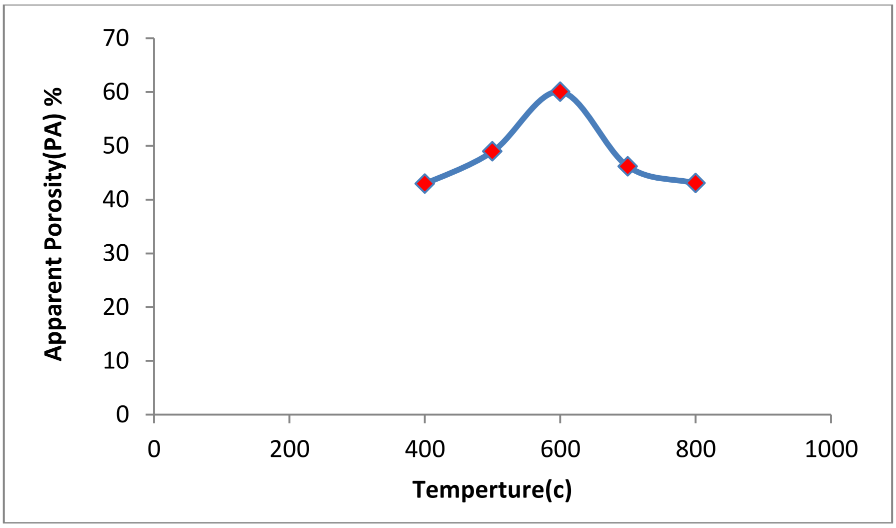


Figure(9):Average particle size(d) for NiO-ZnO Catalyst at different temperature(400 to 800) °C

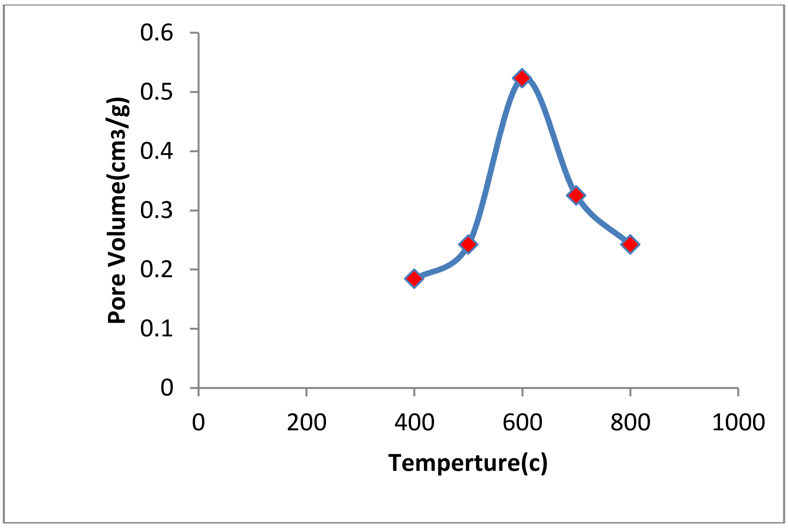
The figures(4,5,6.7,8) shows that the intensity of the diffraction lines and the particle size of ZnO increased with the increasing of the amount of Na_2O added and increasing the degree of crystallinity of NiO phase. The effect of Na_2O is to lowered the thermal conversion process of catalyst, and remained thermally stable even by heating at above 600 to 1000 °C (16,17).

3-Physical Properties of pure and doped Catalyst

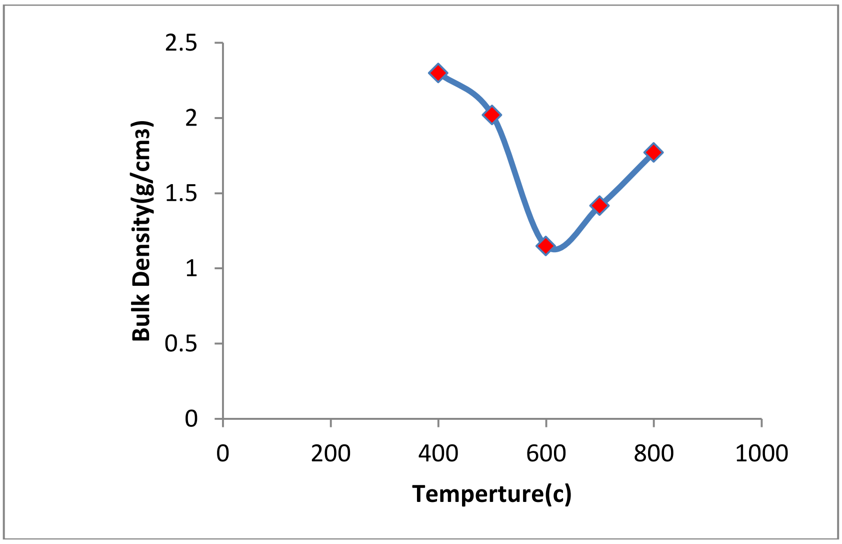
Figures(10),(11) and (12) showed that the physical properties of the pure catalyst :Apparent porosity (P_A%), total pore volume(V_P),and particle density(D_P),respectively at different temperatures(400,500,600,700,and 800) ˚C ,the best physical properties result at 600°C.



Figure(10):Apparent Porosity of NiO - ZnO catalyst at temperatures (400,500,600,700 and 800) °C.

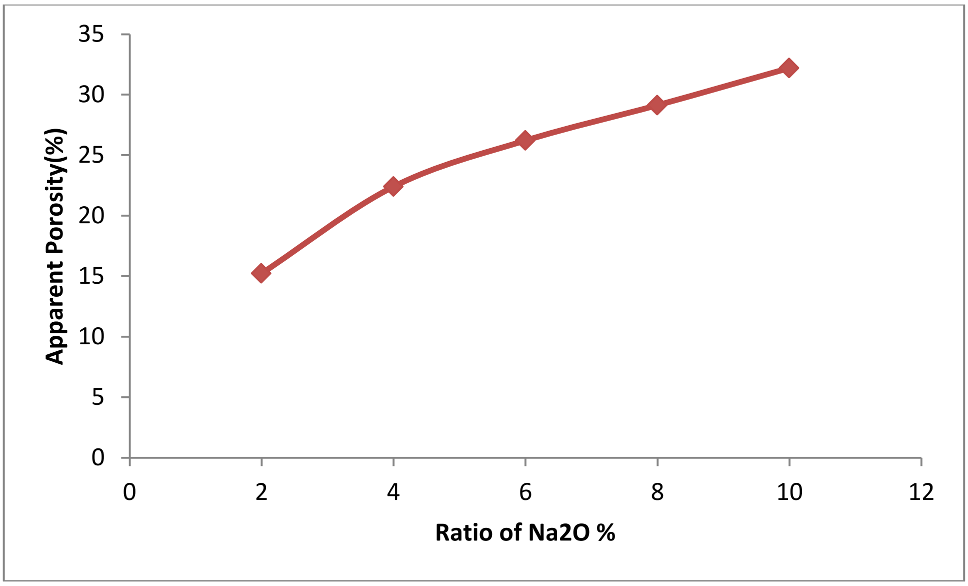


Figure(11):Pore Volume(cm^3/g) of NiO - ZnO catalyst at (400,500,600,700,and800) °C

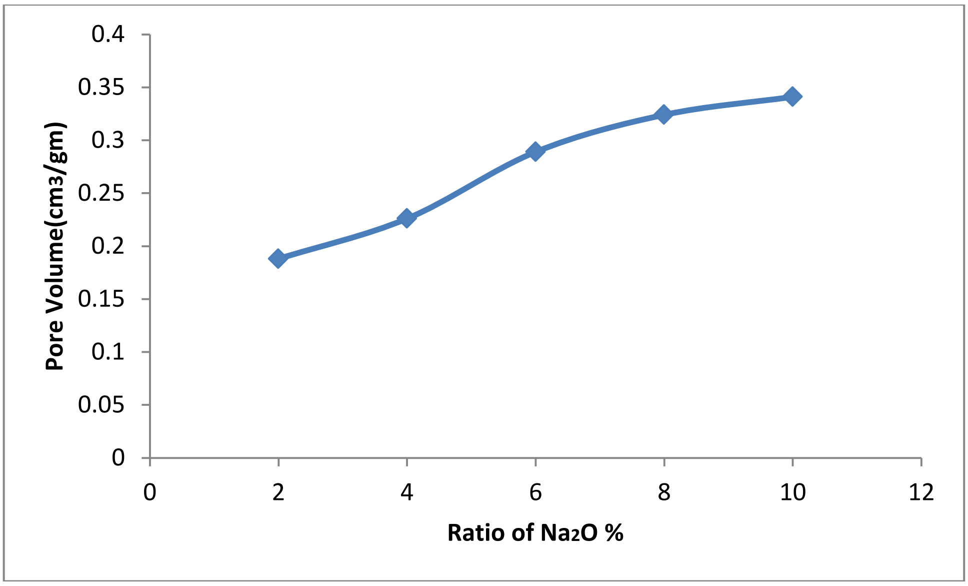


Figure(12):Bulk Density(g /cm^3) of NiO - ZnO catalyst at(400,500, 600,700,and 800) °C

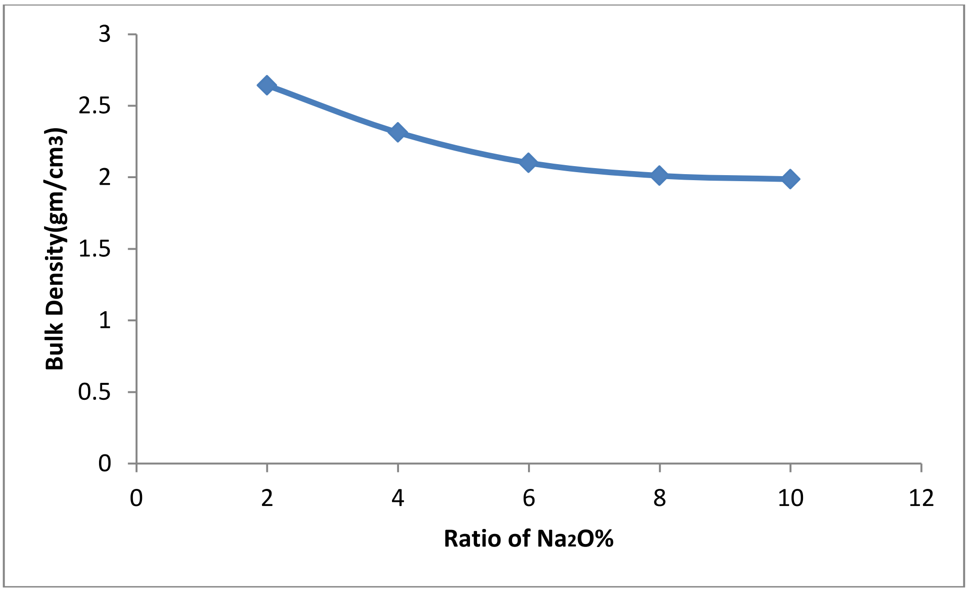
When increasing the temperature from 400 to 600°C, increased the loss of carbon dioxide and water of crystallization and gets complete conversion of a metal carbonate to metal oxide at a temperature of 600°C ,and the size of the total pore volume and porosity will become more, therefore the weight of catalyst grain tablets decreased according to their volume ,this lead to decreasing of the bulk density. When increasing the temperature above 600 to 800 C , the total pore volume and porosity ,will be decreased and the bulk density become more, because of the sintering effect(15,18,19). The physical properties of doped catalyst will be increase with the increasing of percentage of Na_2O(2% , 4% , 6% , 8% and 10%) in the catalyst (20), as shown in figures (13),(14) and (15).



Figure(13):Apparent Porosity of the Na_2O doped catalyst



Figure(14): Pore Volume(cm^3/g) of the Na_2O doped catalyst



Figure(15): Bulk Density(g / cm^3) of the Na_2O doped catalyst

Conclusion:
From the results that obtained from this research we can conclude the following:
1- The best temperature and calcinated time to prepare catalyst is 600 °C for 4hrs.,it's give high pore volume and porosity.
2- The increasing of calcinated temperature (600C°) lead to increase the pore volume and porosity but high temperatures 700 and 800°C , the porosity and pore volume will be decrease causes to decreasing surface area and pore volume.

CONFLICT OF INTERESTS

There are no conflicts of interest.

References

[1] G. Sheen, ***Recent Patents on Nanotechnology*** **,** 2,160. **2008.**

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

[3] Li, W.; Lin, Y.; Zhang, Y., ***Catal. Today***, *83*, 239. **2003**.

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

[5] Deraz,N. M., ***Materials Lett***., *51*, 470. **2001** .

[6]Fierro, G.; Lo Jacono, M.; Inversi, M.; Dragone, R.and Ferraris, G., **Appl. Catal. B Environ.,** 30, 173. **2001**.

[7] M. Hepel, J. Luo, ***Electrochim. Acta,*** 47 729. **2001.**

[8] L. Singoredjo, R. Korver, F. Kapteijn, J. Moulijn, ***Appl. Catal.*** B: Environ.1, 297. **1992.**

[9] U. Bentrup, A. Bruckner, M. Richter, R. Fricke, ***Appl. Catal***. B: Environ.32, 229. **2001.**

[10] P.G. Smirniotis, D.A. Pna, B.S. Uphade, Angew. ***Chem. Int***. Ed. 40, 2479. **2001.**

[11] G. Qi, R.T. Yang, ***Appl. Catal.,*** B: Environ. 44 ,217. **2003.**

[12] H. Bahruji, M. Bowker, L. Saeed Al-Mazroai, A.Dickinso, J. Greaves, D. James,**Journal of Photochemistry and Photobiology** A: Chemistry 216 , 115–118. **2010.**

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

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

[15] Satterfield,C.N., ***Chemical Engineering Series*** ,New York,75. ***1976.***

[16] Leyrer,J.; Zaki,M.I. and Knözinger,H.,***J.Phys.Chem***. *90*,4775. 1**996.**

[17] Ghozza,A. M. ,***J. of Thermal Analysis and Calorimetry***, *75*,135–151. **2004**.

[18] Church,J.M. and Joshi,H.K.,***Ind.Eng.Chem***. *43(8)*,1804. **1951.**

[19] Thomas,C.L., ***Catalytic process and Proven Catalyst*** ,Academic Press. NewYork,68. **1970.**

[20**]** Kansal, S. K. and Navjeet, K., ***Nanoscale Res Lett, 4*****,**709–716**. 2009.**