

## **Physicochemical Properties of doping NiO-CuO Catalyst Supported on Al<sub>2</sub>O<sub>3</sub> and its catalytic activity**

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**Abstract:** Three catalysts (C1, C2 and C3) were synthesized with 20 wt.% mixed oxide (NiO-CuO) supported on alumina and doped with zinc/barium nitrate. The catalysts were characterized by using Thermogravimetric/Differential Thermal Analysis (TGA/DTA), Scanning Electron Microscopy (SEM), BET Surface area and X-ray diffraction (XRD). The endothermic peaks of TGA/DTA showed a total 23.5% weight loss till the temperature of 200 °C. XRD result confirmed that the coexistence of CuO and NiO on the alumina calcined at 350 °C hinder the dissolution of both CuO and NiO in the alumina lattice due to a possible solid-solid interaction between them and yielding NiCuO<sub>2</sub>. The BET surface area of alumina decreased due to forming aluminate of copper, nickel, zinc and barium in the catalysts according to the components present in each catalyst. SEM results indicate that the average particle size reduced to very near to nanoscale due to doping of CuO/NiO with Ba/Zn nitrates on alumina oxide. The catalyst C2 (a mixture of NiO-CuO/Al<sub>2</sub>O<sub>3</sub> doped with zinc nitrate) exhibited the highest catalytic activity for saponification reaction was due to the formation of the zinc aluminates phase.

**Keywords:** mixed oxides; zinc nitrate; nickel nitrate; copper nitrate; saponification.

### **1. Introduction**

Catalyst preparation is a challenge for modern catalyst manufacturing industries to sustain within marketing price competitiveness. There are several cheaper metals exhibiting good catalytic activity so there is tremendous scope to develop a cheaper catalyst for today's need. Selectivity, yield and conversion ratio are the main factors for choosing a catalyst for the process. Significant investigations are going on to develop theories and models to overcome platinum and precious metal. The major challenge is to achieve high activity and selectivity which must fulfil the industrial needs. A catalyst can be prepared by several methods, the choice of method for a particular catalyst depends on what the researcher desires in the final composition. In short, for a particular base material variety of possibilities in preparation can be considered. A small amount of doping of certain foreign oxide can modify the catalytic activity and the selectivity of metal oxide catalysts[1-3]. The mixing of transition metal oxides leads to the formation of a complex structure of spinel or perovskite-type [4,5] due to their mutual interaction. In many research works, it has been founded that mixed oxides catalysts have higher catalytic activity compared to their individual oxides[6,7]. Amongst the most convenient

supports, alumina is considered the first choice and it is used for a wide range of catalysts synthesis and used in a wide variety of reactions, especially in oxidation-reduction reactions [8,9]. As the runtime of alumina supported catalysts increased the catalytic activity decreased continuously. This is because as the runtime of catalyst increases more metal alumina formations occur causing the lower catalytic activity compared without alumina support metal oxides[10,11]. The formation of metal aluminate is the product of the reaction between alumina and metal oxides and the formation rate and quantity highly depends on the nature of the transition metal element. The authors[11] have established some order of formation of aluminate as  $\text{Cu} > \text{Co} > \text{Ni} > \text{Fe}$  in their findings. NiO and CuO with an optical band gap of 3.6-4e V ( $E_g = 3.6-4 \text{ e.v}$ ) and 1.2 e V ( $E_g = 1.2 \text{ e V}$ ), respectively, act as a P-type semiconductor which has a various applications such as catalyst, sensors, optical devices, electrochemical super capacitor transparent P-type semiconducting layer and as an anti-ferromagnetic film and so on due to its unique optical and magnetic properties [ 12-16]. The semiconductor ZnO has large exciton binding energy about 60meV, which can be very useful for lasing action. ZnO is a semiconductor excited the research communities in large[ 17-19]. Due to its high exciton binding energy of ZnO polariton/exciton interaction becomes possible above the room temperature [20]. Adding zinc oxide as a promoter to copper oxide decrease Cu sintering. There is less information available regarding their growth, characterization and properties in the literature. The authors [21,22] have studied the growth, characterization and properties of copper-doped barium tartrate crystals and used it in different applications. The doping changes the properties of materials which has been extensively studied by Dishovsky and Boncheva-M Ladenova [23] Arora S. K. & Tony Abraham[24] and Dennis and Henisch [25]. Although the study of the effect of dopant on crystal growth and characterization is complicated, in recent years considerable attention has been put over the study of growth and characterization of doped crystals [26]. Chemical affinity cations, the solubility of products, diffusivity, enthalpy of dehydration and ionic radii etc. are the various factors on which growth and characterization of crystal growth depends [27]. Structural properties of prepared catalysts are influenced by many factors, including by the choice of the three major catalyst constituents; support, active component (metal, oxides) and promoters [28].

The present work aims to prepare suitable catalysts from abundant metals such as a mixture of nickel and copper materials supported on alumina using impregnation methods. The effect of doping of ZnO or BaO on the prepared mixed oxide supported on alumina were studied. Thermogravimetric and Differential Thermal Analysis (TGA/DTA), Scanning Electron Microscopy (SEM), BET Surface Area and X-ray diffraction (XRD) are the techniques which were employed for characterizations. The catalytic activities of the synthesized catalysts C1, C2 and C3 were also determined for the saponification reaction.

## **2. Experimental**

### **2.1 Materials**

High-quality chemicals of laboratory grade, included aluminum oxide, nickel nitrate, cupric nitrate, barium nitrate and zinc nitrate were purchased from by LOBA Chemie laboratory reagents and fine chemicals supplier. Ethyl acetate was supplied by Honeywell Riedel-de Haën® and Sodium Hydroxide pellets purchased from PanReac AppliChem. All the chemicals were used in catalysts preparation as received without any pre-purification.

### **2.2 Catalysts Preparation**

A given mass of a finely powdered alumina supplied by the supplier was impregnated with a solution mixture containing a known amount of nickel and copper nitrates dissolved in the

known amount of distilled water. The mixture was stirred for enough time for good mixing at the temperature of 50 °C. The further agent was added a calculated amount of zinc or barium nitrate as doping into the above mixture solution and left for enough time for good mixing, then dried at the temperature 110 °C in a dryer for overnight. After finishing the drying all samples were then crushed to a powder, then heated in a muffle furnace at the temperature 350 °C for 4 hrs. The components were expressed as wt10% NiO and wt. 10% CuO.

### **2.3 Catalytic Reaction Experiment**

The catalytic activity of different prepared catalysts was determined from the saponification reaction (a reaction between sodium hydroxide and ethyl acetate) in the liquid phase. The reaction was carried out batch-wise in a glass reactor of volume 100 ml at room temperature and pressure. The reaction progress was measured in term of conductivity of the reacting components. The reactions were stirred with magnetic stirrer continuously till the steady state achieved and the reaction stopped. The conductivity was recorded carefully at every 2 minutes by a well-calibrated conductivity meter.

### **2.4 Characterization**

The BET specific surface areas (SBET) of the synthesized catalysts were determined from N<sub>2</sub> adsorption isotherms measured at 77 K using NOVA 4200e apparatus. X-ray diffraction (XRD) measurements were carried out with Shimadzu LabX-XRD-6000 diffractometer with CuK $\alpha$  ( $\lambda=1.5406 \text{ \AA}$ ) radiation and secondary monochromator attached with Shimadzu software. Thermogravimetric and Differential Thermal Analysis (TGA-DTA) of prepared catalysts were performed on Shimadzu TGA 51 apparatus up to the temperature of 800 °C with a rate of 15 °C in the presence of inert N<sub>2</sub> flow with a flow rate of 20 cm<sup>3</sup>/min. Scanning Electron Microscope (SEM) micrographs were achieved by using JSM-7500 F, JOEL-Japan microscope operating at acceleration voltages of 16 kV.

## **3 Results And Discussions**

### **3.1 Synthesis and Characterization**

In this work, the catalysts from abundant metals were synthesized, which were cheaply available, and were studied their characteristics and reaction activities. Alumina (Al<sub>2</sub>O<sub>3</sub>), Nickel Nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>), Cupric Nitrate(Cu(NO<sub>3</sub>)<sub>2</sub>), Zinc Nitrate(Zn(NO<sub>3</sub>)<sub>2</sub>), Barium Nitrate (Ba(NO<sub>3</sub>)<sub>2</sub>) were used. The first catalyst coded C1 has NiO-CuO supported Alumina, the second catalyst coded C2 is NiO-CuO supported Alumina doped with zinc nitrate and the second catalyst coded C3 is NiO-CuO supported Alumina doped with barium nitrate. Catalysts were prepared as discussed above in section 2.2, all the steps from weight to the calcination had performed in a professional way. Prepared catalysts were stored comprising with the scientific method and then characterized. BET Surface Area, X-ray Diffraction (XRD), Thermogravimetric and Differential Thermal analysis (TGA/DTA), Scanning Electron Microscopy (SEM) techniques were used for characterization of the prepared catalysts C1, C2 and C3 and Alumina which as coded as S1 in its pure form, also characterized to compare with the synthesized catalysts.

### **3.2 BET Surface Area**

The specific surface areas (SBET) of the three synthesized catalysts C1, C2, C3 and pure were determined from N<sub>2</sub> adsorption isotherms measured at 77 K using NOVA 4200e apparatus. All samples were degassed at the 300 °C for 3.0 hours under vacuum before undertaking BET measurements. The BET analysis is listed below in table 1 for all catalysts which were

synthesized. A comparative graph of adsorbed per gram of weight of each catalyst with reduced pressure can be observed in figure 1. BET characterization results, which include the average pore diameter in nanometer(nm), the pore volume in cubic centimetre per gram(cc/g) and the BET surface area in meter square per gram(m<sup>2</sup>/g) of the catalysts S1, C1, C2 and C3 shown in table 1.

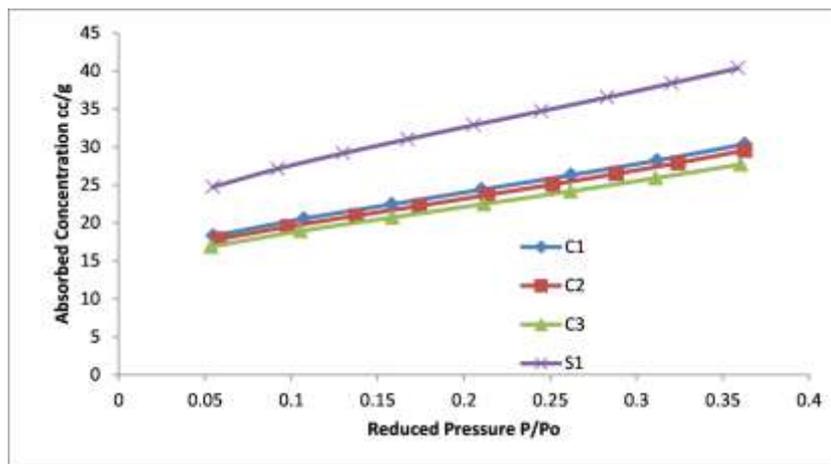
**Table 1.** BET Surface Characteristics of the Catalysts.

Sample Code	Composition	Calcination temperature (°C)	BET area m <sup>2</sup> /g	Pore volume cc/g	Average pore diameter (nm)
S1	Al <sub>2</sub> O <sub>3</sub>	350	115.00	0.05367	0.9335
C1	10%NiO- 10%CuO/ Al <sub>2</sub> O <sub>3</sub>	350	86.49	0.03980	0.9105
C2	10%NiO- 10%CuO-0.2% ZnO/ Al <sub>2</sub> O <sub>3</sub>	350	83.56	0.03662	0.8764
C3	10%NiO- 10%CuO- 0.2% BaO/Al <sub>2</sub> O <sub>3</sub>	350	77.68	0.03623	0.9327

The results indicate that the surface area of the untreated alumina (S1) is 115 m<sup>2</sup>/g, while treated alumina with mixture of nickel and copper oxide revealed that the coexistence of CuO and NiO oxide on alumina support lead to a decrease in its specific surface area from 115 m<sup>2</sup>/g to 86.49 m<sup>2</sup>/g. The SBET of the catalysts C2 and C3 doped with zinc nitrate and barium nitrate decreased progressively from 115 m<sup>2</sup>/g to 83.56 m<sup>2</sup>/g and 77.68 m<sup>2</sup>/g respectively compared with surface area of catalyst C1 ( 86.49 m<sup>2</sup>/g). These findings may be due to forming the new phases such as copper/nickel aluminate, zinc aluminate and barium aluminate in C1, C2 and C3 according to the components present in each catalyst. It was assumed that, the CuO and the NiO phases were well dispersed on the support and give small change in porosities. Results indicated that decreased in the surface area of treated alumina compared with untreated alumina with a mixture of mixed oxides, which might be ascribed to change in the crystal structure.

### 3.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) measurements were carried out with Shimadzu LabX-XRD-6000 diffractometer with CuK $\alpha$  ( $\lambda=1.5406 \text{ \AA}$ ), radiation and secondary monochromator attached with Shimadzu software with the pdf-2 library for the analysis of XRD data. X-ray diffractograms terial of Alumina (S1) and synthesizes catalysts C1, C2 and C3 which were calcined at 350 °C for 4 hours, was carried out at room temperature. The obtained diffraction patterns were studied carefully, figure 2 represents the diffraction pattern of all four catalysts C1, C2, C3 and S1. The diffraction pattern of pure alumina sample indicated the presence of Gamma-alumina ( $\gamma\text{-Al}_2\text{O}_3$ ), that having a degree of crystallinity. The strongest three peaks were,  $d= 1.39 \text{ \AA}$  ( 100% Al<sub>2</sub>O<sub>3</sub> ),  $d=1.40 \text{ \AA}$  ( 45% Al<sub>2</sub>O<sub>3</sub>) and  $1.98 \text{ \AA}$  (37% Al<sub>2</sub>O<sub>3</sub>).

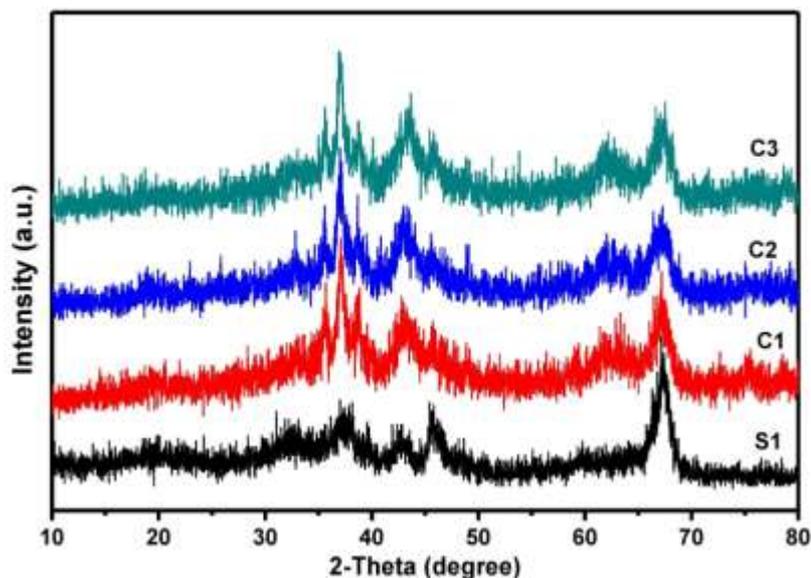


**Figure. 1.** BET Adsorption isotherms of S1, C1, C2 and C3 catalysts.

It was observed that the treatment of alumina with a mixture of copper and nickel nitrates and this mixture later doped with zinc or barium nitrates. It was inferred that the degree of crystallinity decreased for alumina phase which is nearly proportional to the quantity of oxides added. The diffraction pattern of catalyst C1 showed the presence of diffraction peaks of CuO, the strongest peak at  $[d= 2.52 \text{ \AA}^0]$  ( 100% CuO ). These findings may suggest that CuO existed as a separate phase, a portion of CuO with NiO reacted as solid-solid interacted together at 350 °C forming copper nickel oxide, the strongest peak  $d= 1.21 \text{ \AA}^0$  ( 100% NiCuO<sub>2</sub> ) and  $1.5 \text{ \AA}^0$  ( 80% NiCuO<sub>2</sub> ). Other portion of nickel interacted with alumina yielding nickel aluminates, the strongest peak  $d=2.40 \text{ \AA}^0$  (100% 9Al<sub>2</sub>O<sub>3</sub>.2NiO) and  $d=2.77 \text{ \AA}^0$  (80% 9Al<sub>2</sub>O<sub>3</sub>.2NiO). The diffraction pattern of catalyst C2 showed the presence of copper oxide phase, zinc and alumina interacted together with subsequent formation yielding zinc aluminates, the strongest peak  $d=2.42 \text{ \AA}^0$  (100% ZnAl<sub>2</sub>O ). The diffraction pattern of catalyst C3 showed that the solid-solid interaction yielding the copper aluminates,  $d=2.4 \text{ \AA}^0$  (100% CuAl<sub>2</sub>) and nickel barium aluminate phases  $d=2.4 \text{ \AA}^0$  (100% Al<sub>9</sub>BaNi<sub>2</sub> ).

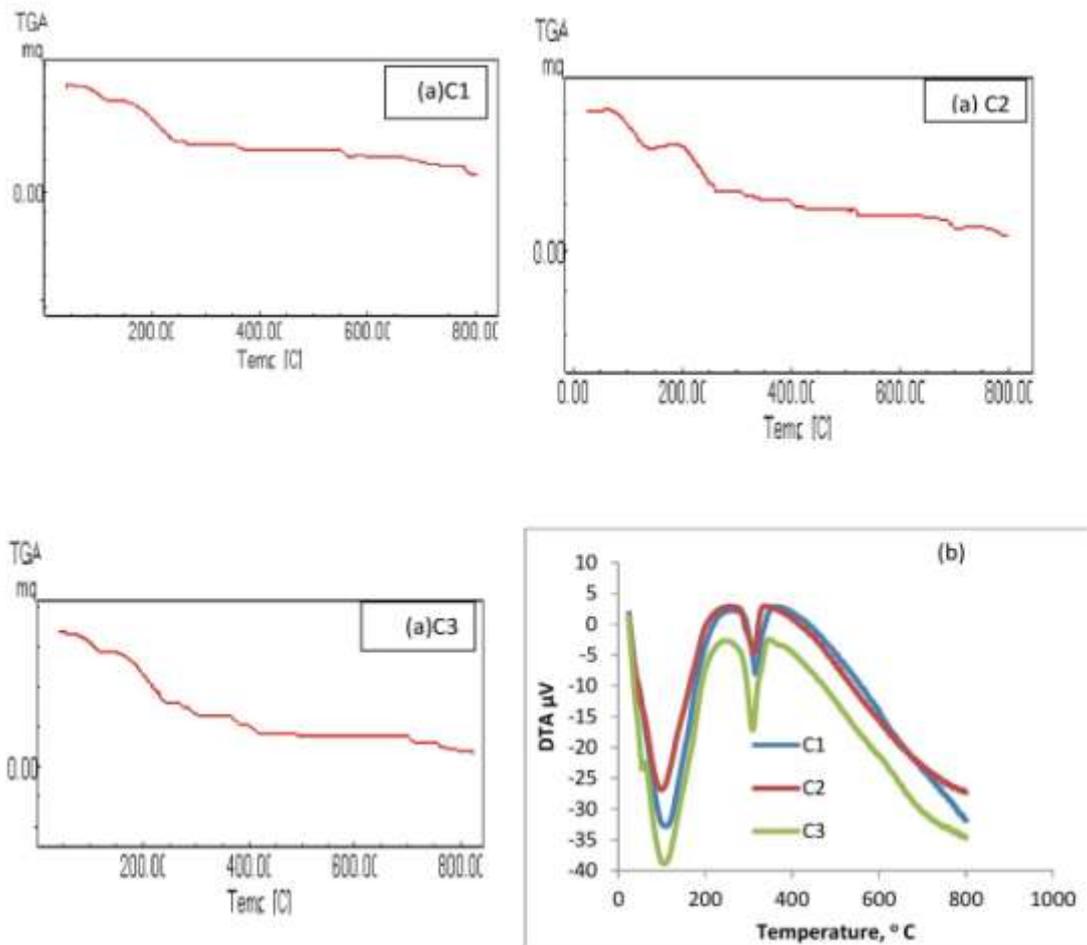
### 3.4 Thermogravimetric and Differential Thermal analysis (TGA/DTA)

During the preparation of supported active catalysts and during the catalytic reaction; these inorganic materials were exposed to different temperature profiles in the presence or absent of different gases or liquids. To establish the change of properties of inorganic materials when exposed to high temperatures, Thermal Analysis techniques such as Thermogravimetric and Differential Thermal Analysis (TGA /DTA) were utilized.



**Figure. 2.** X-ray diffractograms of Alumina and mixed oxides supported alumina solid samples calcined at 350 °C upto 4 hours.

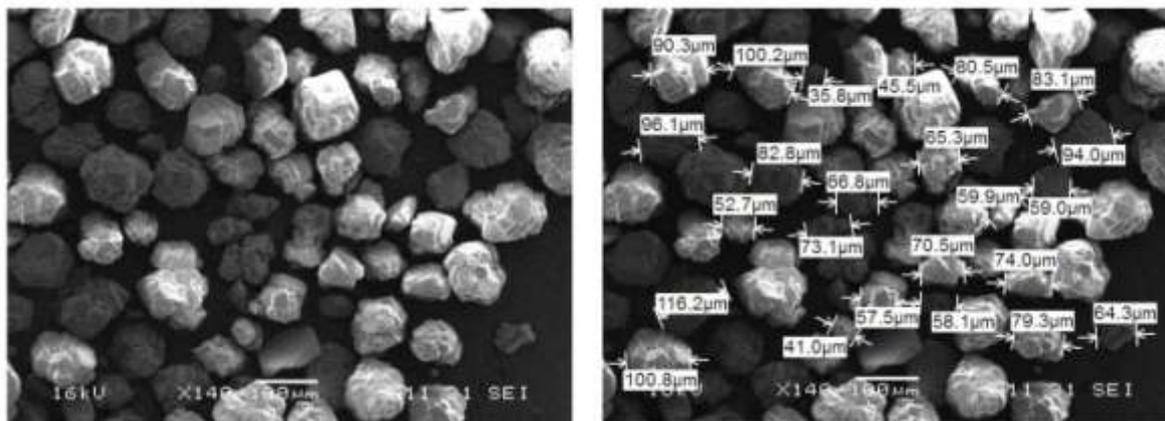
Thermogravimetric and Differential Thermal Analysis (TGA/DTA) were used to study the mass change occurring in the prepared catalysts. 15mg of the sample was used for TGA/DTA analysis at temperature up to 800 °C with a rate of 15 °C in an inert atmosphere with a flow rate of 20 cm<sup>3</sup>/min at Shimadzu TGA 51 apparatus. The thermal analysis of dried catalysts samples has been carried out to determine the weight loss. The thermograms of dried samples C1 ( treated alumina with mixture of nickel and copper nitrate), C2 ( treated alumina with mixture of nickel, copper and zinc nitrate) and C3 ( treated alumina with mixture of nickel, copper and barium nitrates) was studied carefully and presented in figures 3(a) and (b) as below. The thermograms of all three catalysts had three endothermic peaks, indicating gradual decomposition steps with a constant weight loss till the temperature 200 °C with the total loss of weight about 23.5 %. The first two peaks of weight lost till temperature 200 °C showed the decomposition of surface and crystal water, the result also justified from the work reported by several authors [29]. The third peak indicated the decomposition of metal nitrates which starting from 250 °C and ending around 400 °C, the similar result also discussed by other authors [30, 31].



**Figure. 3.** (a) TGA plots of Catalysts C1, C2 and C3. (b) DTA plot of Catalysts C1, C2 and C3.

### 3.5 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) micrographs were achieved using JSM-7500 F; JOEL-Japan microscope operating at acceleration voltages 16 kV, to determine the surface morphology of the prepared supported catalysts. The surface of synthesized supported catalysts depends on various parameters such as preparation methods of catalyst, their interaction with the support, history of catalyst treatment and their size. The SEM micrographs and particle size distribution of S1 represented in figure 4 below. The size of alumina oxide was found to be in the range from 35.8 $\mu\text{m}$  to 116.2 $\mu\text{m}$ , the average particle size was observed to 74.4 $\mu\text{m}$ . The SEM results at magnification 20,000 of mixed oxides catalysts supported on alumina (C1, C2 and C3) can be seen in figure 5(a). The figure 5(b) showed the particle size distribution of catalysts C1, C2 and C3 measured in SEM. The particles size of C1 catalyst was observed in the range from 100 to 407nm with average particle size 213nm size of catalyst C2 were in the range from 95nm to 313nm with average particle size 173nm and for catalyst C3 in the range from 131nm to 381nm with average particle size 230nm. All the synthesized catalysts C1, C2 and C3 had highly reduced particle size compared with alumina oxide (S1).



**Figure. 4.** SEM images and Particle size distribution of S1 @ 140 magnification.

Hence from SEM imaging and particle size calculation, it is very clear that the average particle size reduced from microscale to very near to nanoscale due to doping of CuO/NiO with Ba/Zn nitrates on alumina oxide. The shapes and size (in nanoscale) of supported mixed oxides have a significant effect on the determination of the performance of the catalysts. Particular faces of catalyst particles were observed to be active during structure-sensitive catalytic reactions while other faces of catalyst were not active for the reaction. The result of SEM indicated that the copper and nickel oxides of fresh catalysts C1, C2 and C3 were highly dispersed.

### 3.6 Determination of Catalytic Activity

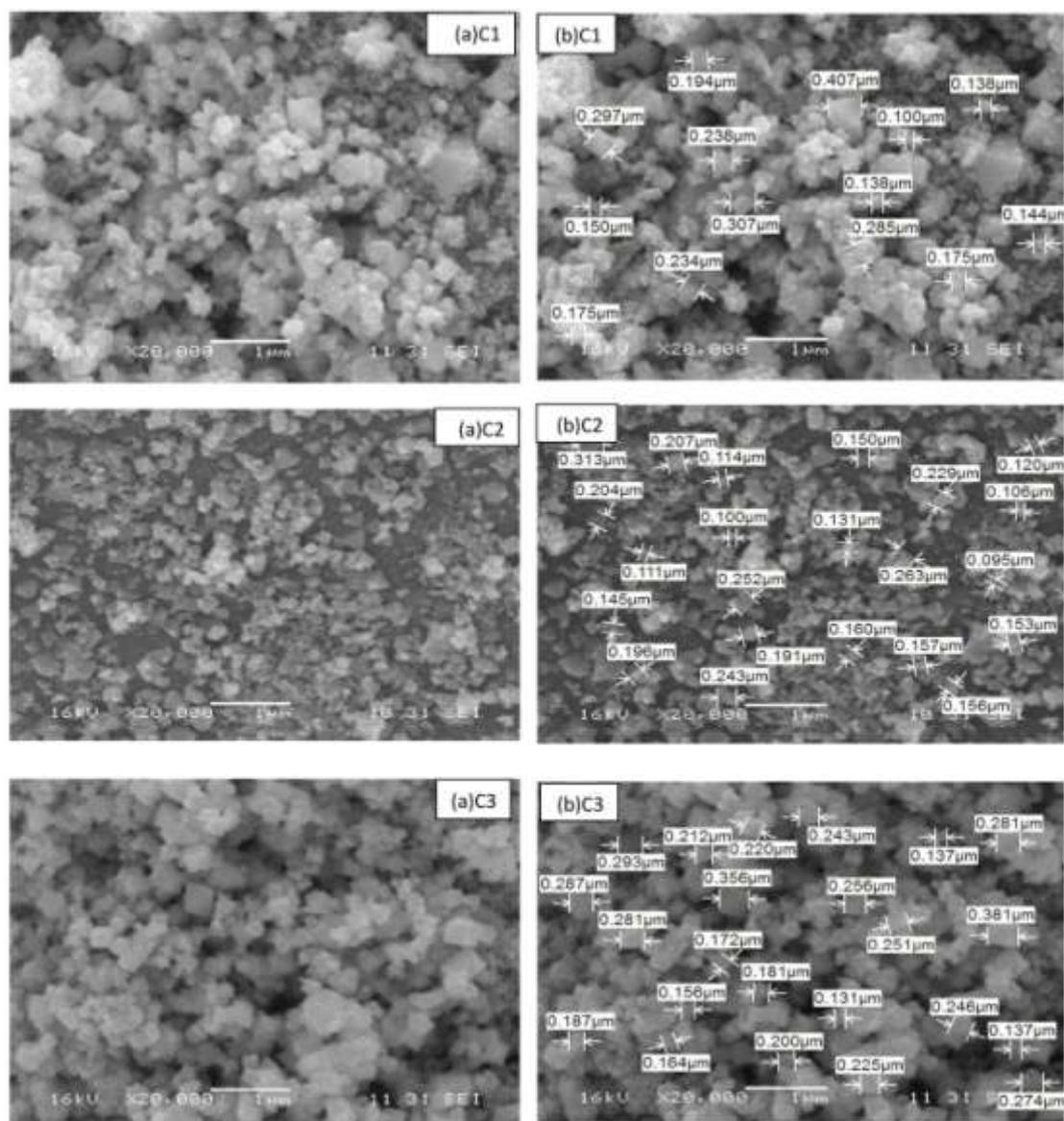
The catalytic activity of all synthesized samples was determined using the saponification reaction, a reaction between Sodium hydroxide and Ethyl acetate, the stoichiometric equation is as below.



The batch reactor was used for the saponification reaction at room temperature and pressure. The reaction was carried out in order to investigate the conversion and the rate of reaction of all three catalysts C1, C2 and C3 to analyze the catalytic activity of catalysts.

#### 3.6.1 Catalyst Dose Optimization

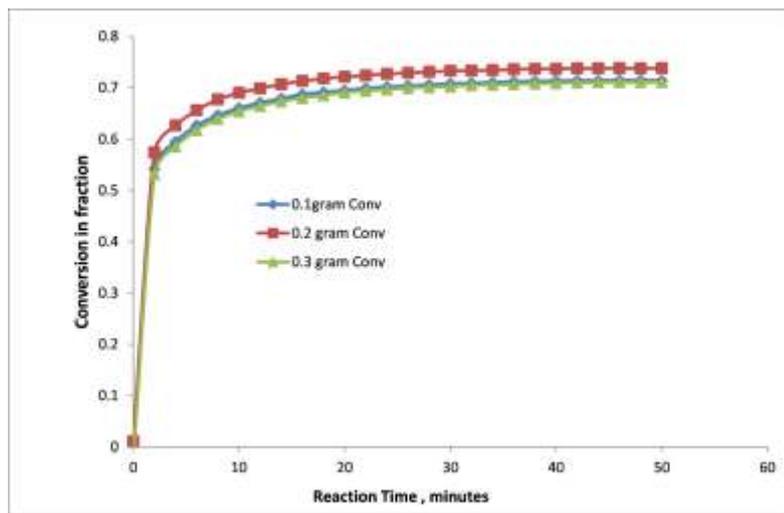
The catalytic activity of prepared catalysts (C1, C2, C3) was investigated for the above model reaction. The reactions were performed in a glass batch reactor of total volume 100 ml. 0.1M of NaOH solution were reacted with 0.1M of  $\text{CH}_3\text{COOC}_2\text{H}_5$  liquid solution with a known weight of catalyst. Three different weights 0.1g, 0.2g and 0.3g catalysts were taken for 100ml volume of reactor to optimize the weight, figure 6 represents the effect of catalyst weight on the conversion of ethyl acetate, from the figure 6 it can be concluded that the 0.2g catalyst was the optimum amounts for the above said reaction at room temperature and pressure and at constant stirrer speed.



**Figure. 5.** (a) SEM Images of catalysts C1, C2 and C3 @ 20,000 magnification , (b) Particle size

### 3.6.2 Conversion and reaction rate

The optimization of catalyst weight was performed after selecting the best catalyst among the prepared catalyst C1, C2 and C3. For a certain total time of reaction, all three catalysts were used for the above stated reaction. The operating condition like temperature, pressure and stirrer speed were kept the same for each reaction.



**Figure. 6.** Optimization of catalyst mass for saponification reaction

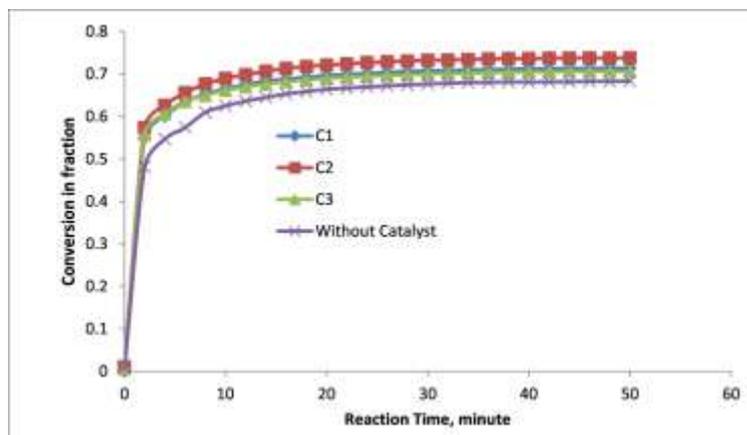
Figure 7 shows the effect of time on stream versus conversion for C1, C2, C3 and without the catalyst. The catalytic activity of three catalysts C1, C2 and C3 were observed as 70%, 75% and 70% respectively and without a catalyst, it was 64%. The same reaction was also tested by the author [32] and they found the maximum possible conversion without catalyst as 63.3% at reaction temperature 35 oC, which was closer to the experiment without catalyst performed in this paper. The results indicated that the best catalytic activity was shown by the catalyst C2 compared with other prepared catalysts. C2 was a mixture of NiO-CuO/Al<sub>2</sub>O<sub>3</sub> doped with zinc nitrate, the doping of the zinc nitrate and forming of zinc aluminates phase in the catalyst, enhanced the catalytic activity compared with C1 and C3 catalysts activities. The similar conversion for C1 and C3 indicated that the addition of barium as promoter did not increase the conversion. The ethyl acetate saponification reaction was established as a second order reaction in many findings in literature [33-35]. The reaction rate constant of catalysts C1, C2 and C3 were found 0.1557, 0.1673 and 0.1590 L mol<sup>-1</sup> min<sup>-1</sup> respectively.

## Conclusions

The design of a catalyst covers all aspects from the choice of catalytically active material to the method of forming particles. The role of alumina support to stabilize metal oxide species in valence and coordination state different from those typical of the unsupported oxide and to give optimal surface and pore size distribution to the active species. The loading of copper nitrate and nickel nitrate on the alumina solid sample up to 10 wt % NiO and 10 wt% CuO followed by calcination at 350 °C for 4hrs., resulted in partial dissolution of nickel and copper species in the alumina lattice forming solid solutions and the other portion remained as separate CuO. The coexistence of CuO and NiO on the alumina calcined at 350 °C hinder the dissolution of both CuO and NiO in the alumina lattice due to a possible solid-solid interaction between them yielding NiCuO<sub>2</sub>.

The catalysts C2 which was doped with zinc nitrate creates small particles with average size 172nm is smaller compared to without doped catalyst C1 and catalyst C3 doped with barium nitrate. The doping changes the properties of materials that match with ref [23-25]. The catalytic activity of catalyst C2 as tested on saponification reaction showed better conversion compared to catalyst C1 and C3. It can be concluded that the addition of zinc nitrate compared to barium nitrate in term of catalyst doper to the original composition C2 (nickel-copper oxide

supported on alumina) exhibited the higher catalytic activity due to formation of the zinc aluminates phase, therefore the addition of zinc to mixed oxides system proved better than barium in term of effect of doper on mixed oxides catalyst system.



**Figure. 7.** Catalytic conversion results of all three catalyst and without catalyst.

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