Synthesis and Characterization of Nano CuO-NiO Mixed Oxides

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Abstract A series of single and mixed oxides of nano CuO-NiO were prepared by thermal decomposition of the $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and/or CuC_2O_4 precursors which obtained via the reaction between alcoholic metal nitrates and oxalic acid solutions. Thermal behavior of the single and mixed salts has been studied using thermal analysis (TG and DTA). Thermal products were characterized using Fourier transform infrared (FTIR), X-ray diffraction (XRD), Electron microscopy (SEM&TEM), Nitrogen adsorption at -196°C and surface excess oxygen measurements. The results revealed that, pure $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and CuC_2O_4 decomposed at 355 and 325°C , respectively. Also, it was found that the addition of NiO to CuO brought a significant increase in the degree of crystallinity of the mixed oxides which is accompanying with an increase in their particle size and a decrease in the surface area. Moreover, addition of NiO to CuO, also reduces the amount of surface excess oxygen of CuO due to a synergistic effect.

Keywords Mixed Oxides, CuO-NiO, Cu-Ni oxalates, FTIR, XRD, Nanoparticles, SEM&TEM

1. Introduction

A great deal of fundamental researches has been done on mixed catalysts in the field of heterogeneous catalysis [1-3]. These mixed systems may be more active than their separate components [4, 5]. The so-called mixed catalysts are often produced by thermal decomposition of the mixed components of their metal salts [6]. It is well known that, nanostructured materials have been extensively explored for the fundamental scientific and technological interests in accessing new classes of functional materials with unprecedented properties and applications [7-9]. Thus a reduction in particle size to nanometer scale results in various interesting properties compared with their bulk properties. Therefore, many methods have been studied to synthesize nanostructured copper oxide [10-16]. CuO is an important oxide in many chemical processes such as degradation of nitrous oxides, selective catalytic reduction of

nitric oxide with ammonia and oxidation of CO, hydrocarbons and fine chemicals [17-19]. Up to date, many studies have been reported about the preparation of CuO nanomaterials such as nanorods[20], nanowires[21], Shuttke-like structure [22], nanoribbons and nanoparticles[11,16,23-26].

NiO is a very prosperous material extensively used in catalysis and other applications [27-29]. It is well known that the powder characteristics (particle size, particle size distribution, and shape) are strongly influenced by the preparation process. Thus a variety of strategies have been employed for synthesis nano-sized NiO [30-36]. In addition pure and doped copper-nickel mixed oxides have been investigated [37-40]. CuO-NiO supported $\gamma\text{-Al}_2\text{O}_3$ was efficiently used in N-Alkylation of ethylenediamine [41] and morphine [42] with alcohols.

It is well known that, the precipitation of oxalates is often used for the elaboration of precursors of high purity and high quality. Whereas preparation of nano crystalline CuO-NiO via their oxalate route, to our knowledge, is not reported. So, The present investigation reports the results of an extensive studies on synthesis, structural and surface characterization of nano-crystalline Cu-Ni mixed oxide systems by a variety of techniques including thermal analysis (TG & DTA), Fourier transform infrared (FTIR), x-ray diffraction (XRD), nitrogen adsorption measurements at -196°C , surface excess oxygen and electron microscopy (SEM & TEM),

2. Experimental

2.1. Materials

Acetone, ethanol and oxalic acid dihydrate were of analytically pure reagent and were used without further purification. Copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were supplied by WINLAB company for laboratory chemicals (>99 %), India.

2.2. Catalysts Preparation

Pure Nano CuO and NiO were prepared by precipitation

method as described previously [35, 43] with some modifications. In a typical process, analytical grade of copper and nickel nitrates (0.2M) and 1.0M oxalic acid were separately dissolved in absolute ethanol at 50°C. In the course of magnetically stirred of each metal nitrate solution, the same concentration of warm oxalic acid was added as precipitator dropwise with constant stirring in one direction. Kind of light blue sediments were formed, these precipitates were filtered and washed with ethanol and finally washed with small amount of acetone. The washed precipitates were dried in air overnight at room temperature to get the precursors.

CuO-NiO mixed oxide systems were prepared by co-precipitation method. The calculated amounts of copper and nickel nitrates were dissolved in ethanol at 50°C, after stirring the mixtures of metal nitrate solutions; ethanolic oxalic acid solution was added dropwise with constant stirring as described above. The precipitates are then filtered off, washed with ethanol and then with acetone and dried in air overnight at room temperature to obtain the precursors. Pure CuO, Pure NiO and CuO-NiO mixed systems with different ratios of NiO (1- 50 wt. %) were obtained by annealing these precursors at 400 and 600°C in muffle furnace under air atmosphere for 3 h.

2.3. Apparatus and Techniques

2.3.1. Thermal Analysis

Thermogravimetry (TG) and Differential thermal analysis (DTA) were carried out using a computerized Shimadzu Thermal analyzer (TGA 60 Japan) apparatus. The samples were studied under air atmosphere with flowing rate of 30 mL min⁻¹. Constant weights of samples (~ 5.5 mg) were used in order to avoid the effect of sample weight on peak shape and temperature. α -Al₂O₃ was used as a reference material in this technique. The heating rate was fixed at 10°C min⁻¹.

2.3.2. Fourier transform infrared (FT-IR)

FT-IR spectra of the original and the calcined samples at 400 and 600°C for 3h were recorded in the 4000-400 cm⁻¹ region with a Nicolet (Madison, WI, USA) 710 FT-IR equipped with data station. Dried samples of about 20 mg each were mixed with 100 mg of dry spectral grade KBr and pressed into disk under hydraulic pressure.

2.3.3. X-ray diffraction (XRD)

An x-ray investigation of the individual and mixed solids precalcined at 400 and 600°C in air for 3 h was conducted using a Philips diffractometer (Model PW 2103, $\lambda=1.5418\text{\AA}$, 35 KV and 20 mA) with a source of CuK α 1 radiation (Ni Filtered). An on-line data acquisition and handling system facilitated automatic JCPDS library search and match for phase identification purpose.

Crystallite size can be estimated from the full width at half maximum (FWHM) of the X-ray diffraction liner. The broadening of the FWHM is inversely proportional to the

average crystallite size (D) as predicted by the well-known Scherer's formula [44] the grain size D is calculated from the following relation:

$$D = \frac{K \lambda}{\beta \cos \theta}$$

Where β is the observed angular width at half maximum intensity of the peak and calculated from:

$$\beta^2 = \beta_s^2 - \beta_o^2$$

where β_s is the measured line width at half maximum and β_o is the instrumental broadening [45]. $\beta_o = 0.16$ with the apparatus used. K is dimension less number, which is equal to 0.89, λ is the X-ray wavelength (1.548 Å for Cu K α 1) and θ is the diffraction angle.

2.3.4. Nitrogen adsorption

Nitrogen adsorption-desorption isotherms were measured at -196°C by Quantachrom Instrument Corporation, USA (Model Nova 3200). Test samples were thoroughly out gassed for 2h at 250°C to a residual pressure of 10⁻⁴ torr and the weight of the out gassed sample was that used in calculations. The porosity of the catalysts was determined from the desorption curve using Nova enhanced data reduction software (Version 2.13). Highly pure nitrogen was used as adsorbent.

2.3.5. Surface excess oxygen measurement

The surface excess oxygen was measured by the method described in reference [46]. This method consists in reducing the surface excess oxygen on the oxide catalyst surface with hydrazine and measuring the amount of nitrogen gas evolved with the aid of gasometric technique which early described by Deren et al. [47].

2.3.6. Electron microscopy (SEM&TEM)

The size and morphology of the investigated solids were characterized by Scanning electron microscope (SEM) and Transmittance electron microscop (TEM) JEOL Model JSM-5400 LV (Jeol, Tokyo, Japan). For SEM imaging, the samples were prepared by the gold sputtering technique [69]. Micrographs were obtained in a secondary electron imaging mode using a potential difference of 25KV. Representative sections from the surface were recorded and developed on monochrome paper. For TEM imaging, the sample powder dispersed in ethanol using ultrasonic radiation for 20 min and a drop of that suspension was place onto the carbon-coated grids. The degree of magnification of TEM images was the same for all the different investigated solids.

3. Results and Discussion

3.1. Thermal Analysis of Pure Cu₂O₄, Ni₂O₄.2H₂O and Their Mixtures

TG and DTA curves of pure copper oxalate, pure nickel oxalate and their mixtures with different ratios (5-50 wt. %

NiO) are shown in Fig. (1). TG curve of pure copper oxalate, Fig. (1a), shows one decomposition step in the range of 270-350°C with a weight loss of 47.8%. This weight loss is attributed to the decomposition of copper oxalate to copper oxide (CuO) which agrees, approximately, with the theoretical value (47.52%). DTA curve shows a sharp exothermic peak maximized at 325°C which is again corresponding to the decomposition of copper oxalate to CuO. No other peaks were observed either in TG or DTA on increasing the heating temperature up to 1000°C which confirm that the produced CuO is thermally stable and does not undergo any phase-phase transitions. These results are in agreement with the results obtained by many authors [16, 25, 26, 46]. From the above results, copper oxalate can decompose to copper oxide according to the following equation [25]:

TG and DTA curves of pure nickel oxalate dihydrate $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ are shown in Fig. (1g). TG curve exhibits two steps. The first step is in the range of 180-250°C with a weight loss of ~ 19.8 % and is accompanied with an endothermic peak on the DTA curve centered at 233°C. Such process was attributed to the removal of the two crystalline water molecules to give the anhydrous oxalate form. The weight loss (~19.8 %) in this step is very closely to the theoretical value (19.7%). The second step in the range of 307-370°C exhibits a 39.7 % weight loss and is accompanied with a sharp exothermic peak maximized at 354°C. This stage may correspond to the decomposition of anhydrous NiC_2O_4 to NiO [50, 51]. In addition the weight loss (39.7 %) is in good agreement with the theoretical value (39.9 %)

From the above results, nickel oxalate can thermally decompose to NiO via the following equations [50].

TG and DTA curves of CuC_2O_4 mixed with $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ are shown in Fig. 1(b-f). The TG and DTA curves show that the thermal decomposition of these samples to give the corresponding oxides proceeds via two stages. The first one observed in the range of 170-250°C with a weight loss of 3.79, 8.9, 10.4, 12.1 and 17.2 % for the samples 5, 10, 20, 30 and 50 wt. % NiO, respectively. The samples are also exhibit endothermic peaks appear on the DTA curves minimized at (168, 176, 185, 193 and 200°C) for NiO loadings of (5, 10, 20, 30 and 50 wt. %) respectively. These peaks attributed to the removal of crystalline water molecules from the samples which originally come from nickel oxalate. The elimination of the crystalline water molecules become more easily as the enhancement observed on the DTA curves as illustrated in the Fig. (1). The second thermal stage occurs in the range of 220-370°C with weight loss of (49.1, 45.2, 41.3, 39.8 and 37.66 %) is accompanied with exothermic peaks maximized at (320, 317 and 322°C) for the samples containing 5, 10 and 20 wt. % NiO, respectively. It is observed that, on increasing the ratio of nickel oxalate above (20 wt. % NiO), the

exothermic peak is splitted into two peaks, the first peak maximized at (317 and 315°C) and the second peak maximized at (328 and 332°C). These two peaks are attributed to the simultaneous decomposition of copper and nickel oxalates to the corresponding oxides.

Figure 1. TG and DTA curves of pure copper oxalate (a), pure nickel oxalate (g) and copper mixed with nickel oxalate with corresponding ratios of NiO 5% (b), 10% (c), 20% (d), 30% (e) and 50% (f).

3.2. Fourier Transform Infrared (FT-IR)

Fourier transform infrared (FTIR) analysis of the original and the calcined products of pure copper oxalate, pure nickel oxalate and copper- nickel oxalate mixtures was carried out. Figures (2-4) represent the FTIR spectra obtained for the original and the calcined samples at 400° and 600° C in air for

3 h atmosphere. Spectra of the original samples presented in Fig. (2) displayed bands at 3400-3450, 1628, 1360-1364, 1315, 830, 760, 615-620, 530 and 475-480 cm^{-1} . These bands assigned to

$\nu_s(\text{H}_2\text{O})$, $\nu_{as}(\text{C}=\text{O})$, $\nu_s(\text{C}-\text{O})+\nu(\text{C}-\text{C})$, $\nu_s(\text{C}-\text{O})+\delta(\text{O}-\text{C}=\text{O})$,
 $\nu_s(\text{C}-\text{O})+\delta(\text{O}-\text{C}=\text{O})$, $\delta(\text{O}-\text{C}=\text{O})+\nu(\text{M}-\text{O})$, $\nu(\text{O}-\text{M}-\text{O})$,
 $\nu(\text{M}-\text{O})+\nu(\text{C}-\text{C})$ and $\nu(\text{M}-\text{O})$ respectively, [35, 52].

Figure 2. FTIR Spectra of original pure copper oxalate (a), pure nickel oxalate (g) and copper oxalate mixed with nickel oxalate with corresponding ratios of NiO of 5% (b), 10% (c), 20% (d), 30% (e) and 50% (f) (wt. %), as precipitated and dried at 100°C.

Spectra of pure copper oxalate calcined at 400 and 600°C are shown in Figs. (3&4). The spectra show a broad band at 480-486, 530 and at 580 cm^{-1} . These bands are corresponded to the Cu-O bond in the monoclinic structure of CuO [53]. The weak bands in the region of 700-1000 cm^{-1} appeared especially in the samples calcined at 400°C, may be attributed to the different vibrations modes of CO_3^{2-} . The CO_3^{2-} anions are formed due to the exposure of the samples to ambient after calcination and adsorption of CO_2 [54, 55] to form CO_3^{2-} . The band which appeared at the range

(1050-1110 cm^{-1}) may be attributed to the chemisorptions of O_2 on the surface of the catalysts [56].

Figure 3. FTIR Spectra of pure CuO, pure NiO and CuO-NiO mixed oxide systems calcined at 400°C in air atmosphere for 3h.

The FTIR spectra of pure nickel oxalate calcined at 400 and 600°C are shown in Figs. (3&4). The spectra show a broad band exists in the range of 440-470 cm^{-1} , this band is assigned to the Ni-O bond stretching vibrations [57-59]. The broadness of the absorption band indicates that NiO powder is nanocrystalline [51, 60]. The other bands present in the spectra which assigned at the same wave number are explained in the CuO spectra.

The spectra of CuO mixed with NiO and calcined at 400 and 600°C indicate that no bands are assigned corresponding to the formation of new spinel. The observed broad band assigned at 440-530 cm^{-1} of the mixed oxides may be attributed to the M-O vibration. In addition, this broadness is a proof of the existence of nano-particles exists in the mixed system [60]. The broad band assigned at 3200-3500 cm^{-1} in all samples may be attributed to vibration of physically adsorbed water. This band is completely different from coordinated water in compounds [51]. The other band which

appeared at 1635 cm^{-1} is due to the bending vibration of H_2O . This means that the plain band at $3200\text{--}3500\text{ cm}^{-1}$ and the sharp band at $1635\text{--}1640\text{ cm}^{-1}$ assigned to the stretching and bending vibration of OH group of H_2O [61].

Figure 4. FTIR Spectra of pure CuO, pure NiO and CuO-NiO mixed oxide systems calcined at 600°C in air atmosphere for 3h.

3.3. X-Ray Diffraction (XRD)

The x-ray diffraction patterns (XRD) obtained for the parent materials, pure copper oxalate (CuC_2O_4) and nickel oxalate ($\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), are graphically represented in Figs. (5). Matching the XRD patterns of copper oxalate with the reported data in the (JCPDS No. 00-021-0297), results show that the prepared sample is well crystalline and the predominate diffraction lines correspond to CuC_2O_4 lattice are at $d(\text{\AA})=3.896, 2.484, 2.32, 2.139, 1.946$ and 1.773 . On the other hand, matching the XRD patterns of nickel oxalate with that identified in the (JCPDS No. 01-073-2580) show also that the synthesized sample is well crystalline and the diffraction lines correspond to $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ lattice are at $d(\text{\AA})=4.727, 3.914, 2.957, 2.523, 2.064$ and 1.865 .

Figure 5. X-ray patterns of the as-synthesized copper oxalate (CuC_2O_4) (a) and nickel oxalate ($\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) (b).

These results are in good agreement with the results previously obtained [25,35,43,49].

The XRD diffractograms of pure copper oxide, pure nickel oxide and their mixtures containing 10, 20, 30 and 50 wt. % NiO calcined at 400 and 600°C were graphically represented in Figs. (6&7). From these figures, matching the XRD patterns of pure copper oxalate calcined at 400 and 600°C with that identified in the (JCPDS No. 04-012-7238), results show that the predominant diffraction lines correspond to CuO lattice are at $d(\text{\AA})=2.753, 2.75, 2.527, 2.323, 1.867, 1.408$ and 1.265 . The XRD patterns of pure nickel oxalate calcined at 400 and 600°C were matched with the (JCPDS No.04-012-6347) and the results show that the diffraction lines correspond to NiO lattice are at $d(\text{\AA})=2.413, 2.089, 1.477, 1.259$ and 1.206 .

Figure 6. X-ray diffractograms of pure CuO, pure NiO and CuO-NiO mixed systems (wt. %) calcined at 400°C in air atmosphere for 3h.

The diffraction patterns for the copper-nickel oxalate mixtures calcined at 400, 500, 600 and 700°C were matched with that identified in the JCPDS cards. The results show that at lower NiO mixing ratio (up to 10 wt. % NiO) the predominant diffraction lines are corresponding to CuO.

Above 10 wt. % NiO, the lines corresponding to NiO start to appear and their intensities increase with increasing the percentage content of NiO up to 50 %. Examination of these patterns illustrate that no new peaks corresponding to the solid-solid interactions were observed between the thermally produced NiO and CuO. These results are in good agreement with those obtained from thermal analysis DTA Fig. (1), which shows that, no peaks observed due to the solid-solid interaction between CuO and NiO. The crystallite size of crystalline phases present in the different investigated samples was calculated from the line broadening of the main diffraction lines of these phases using Scherrer equation [44].

The diffraction peaks at 2θ values of 35.55, 38.66 and 48.84° corresponding to (-1 1 1), (1 1 1) and (-2 0 2) Miller planes were selected for calculating the crystallite size for

CuO phase. On the other hand, the diffraction peaks at 2θ values of 37.28, 43.32 and 62.9° corresponding to (1 1 1), (2 0 0) and (2 2 0) Miller planes were selected for calculating the crystallite size for NiO phase as these peaks are well isolated and with high intensity. The average of these measurements was reported as crystallite size for each phase. The crystallite sizes for CuO and NiO phases for the samples calcined at 400 and 600°C are cited in Tables 1. It is clear that, mixing of CuO with different ratios of NiO followed by calcination at 400 and 600°C led to a significant increase in the crystallite size of CuO and NiO phases. Moreover, the observed increase in the value of the crystallite size of NiO upon loaded to the CuO surface may be attributed to the agglomeration of NiO particles.

Figure 7. X-ray diffractograms of pure CuO, pure NiO and CuO-NiO mixed systems (wt.%) calcined at 600 °C in air atmosphere for 3h.

It is important to mention here that, the effective increase in crystallite sizes of both NiO and CuO could be attributed to conversion of some NiO to Ni_2O_3 and also some CuO to Cu_2O phases via a synergistic mechanism [37, 62-64] between the nickel and copper oxides as follows:

It is important to mention here from the above equations

that the synergistic effect leads to the existence of Cu^+ and Ni^{3+} in the host oxides together with Cu^{2+} and Ni^{3+} . The presence of dual in the oxide mixtures valences should modify their textural, morphological, electrical and catalytic properties.

Table 1. Variation of crystallite sizes of CuO and NiO phases in the investigated solids calcined at 400 and 600°C.

Catalyst	400 °C		600 °C	
	D_{CuO} (nm)	D_{NiO} (nm)	D_{CuO} (nm)	D_{NiO} (nm)
Pure CuO	12.6	-	18.9	-
10 % NiO	16.2	4.1	22.8	11.1
20 % NiO	20.0	8.7	26.7	14.4
30 % NiO	22.5	11.5	29.6	17.5
50 % NiO	23.6	15.5	30.2	20.1
Pure NiO	-	18.6	-	24.3

3.4. Nitrogen Adsorption

The adsorption-desorption isotherms of nitrogen gas at liquid nitrogen temperature (-196°C) were measured for pure CuO, NiO and their mixtures calcined at 400 and 600°C.

All isotherms (not given) of pure and mixed calcined samples are of type II of Brunauer's classification [65]. In addition, the adsorbents under investigation are characterized by being irreversible and exhibit hysteresis loop close in the low relative pressure range. The hysteresis loop belongs to type H4 with little of type E of de Bore classification [66]. The specific surface area S_{BET} was obtained by applying the BET equation in its normal range of applicability ($p/p^0 = 0.05 - 0.35$) with cross-sectional area of $\text{N}_2 = 16.2 \text{ \AA}^2$. Another series of specific surface area S_t was calculated from the V_{a-t} plots. These plots were constructed using standard t-curves depending on the magnitudes of C-constant in the BET-equation (second column of Tables (2&3)). The computed S_{BET} values of pure and mixed oxide samples calcined at 400 and 600 °C are cited in Table (2,3). Examination of Tables (2&3), the following conclusions can

be drawn:

- At all calcination temperatures, pure CuO possesses the highest value of S_{BET} compared to pure NiO. The S_{BET} value of pure CuO due to mixing with NiO was found to suffer a progressive decrease to an extent that proportional to the amount of NiO added up to 50 wt.. The decrease was, however, more pronounced with the low ratios of NiO (1-10 wt. %). The S_{BET} value decreased from 25.5 to 13.9 $\text{m}^2 \text{ g}^{-1}$ on doping of CuO with 5 wt. % NiO for the solids calcined at 400°C. This reflects that about 45.5 % reduction in the S_{BET} value of pure CuO occurred. Further increase in NiO ratio up to 10 wt. % causes a reduction in the S_{BET} value of pure CuO from 25.5 to 7.8 $\text{m}^2 \text{ g}^{-1}$ which is equal to 69.4 %. Above these ratios, the S_{BET} values are steadily decreased with increasing the amount of NiO added up to 50 %. This decrease in the S_{BET} value might be discussed in terms of (i) the lower value of S_{BET} of NiO added which consequently reduces the surface area of the CuO, (ii) the continuous decrease in the total pore volume with the increase in the NiO content and (iii) blocking of some pores of the host oxide by NiO additions. This blocking may be attributed to the cationic substitution of CuO by NiO. Furthermore, the decrease in S_{BET} due to NiO additions can be discussed in terms of the particle size. In fact, X-ray analysis of the samples calcined at different temperatures indicated a significant increase in the particle size of the solids by mixing with NiO. This increase in the particle size of the calcined samples should be accompanied by a significant decrease in the surface areas of the mixed solids.
- Raising the calcination temperatures from 400 to 600°C, resulted in a significant and continuous decrease in the S_{BET} values of pure and mixed oxides. This behavior may be attributed to the high temperature sintering process.
- The values of S_{BET} and S_t are close to each other which justify the correct choice of t-curve for analysis and indicate the absence of ultramicropores.

Table 2. Texture data of the CuO-NiO mixed oxide systems (wt./wt.) calcined at 400°C in air for 3 h.

Mixing (%)	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	S_t ($\text{m}^2 \text{ g}^{-1}$)	Total pore volume (cc g^{-1})	Average pore diameter ($\text{\AA}$)	S_t/S_{BET} (%)
Pure CuO	25.5	25.5	0.0309	48.5	100
1 % NiO	22.7	22.6	0.02688	47.3	99.5
3 % NiO	18.6	18.5	0.02336	50.1	99.1
5 % NiO	13.9	13.7	0.0156	44.8	98.6
7 % NiO	11.2	11.1	0.01461	52.9	99.3
10 % NiO	7.8	7.7	0.01185	69.6	98.6
20% NiO	5.6	5.5	0.00832	53.3	97.9
30% NiO	4.3	4.3	0.00476	57	99.1
40 % NiO	3.6	3.5	0.00355	55.2	98.3
50 % NiO	3.5	3.4	0.00502	81.8	98.6
Pure NiO	12.4	12.2	0.01606	52	99.1

Table 3. Texture data of the CuO-NiO mixed oxide systems (wt./wt.) calcined at 600 °C in air for 3 h.

Mixing (%)	S _{BET} (m ² g ⁻¹)	S _t (m ² g ⁻¹)	Total pore Volume (cc g ⁻¹)	Average pore diameter (Å)	S _t /S _{BET} (%)
Pure CuO	15.6	15.5	0.00968	45.2	99.7
1 % NiO	12.6	12.5	0.00678	35.9	99.9
3 % NiO	9.2	9.2	0.00622	55.1	99.9
5 % NiO	6.5	6.4	0.00525	46.9	98.4
7 % NiO	5.4	5.3	0.00649	58.8	98.1
10 % NiO	3.7	3.6	0.00513	56.1	99.7
20% NiO	2.6	2.6	0.00418	50.8	99.6
30% NiO	2.3	2.3	0.0038	59.2	99.6
40 % NiO	2.1	2.1	0.0035	68.2	98.6
50 % NiO	1.8	1.8	0.00293	65	98.3
Pure NiO	5.4	5.3	0.00608	45	99.1

3.5. Determination of Surface Excess Oxygen

The results of experiments carried out for determining the amount of surface excess oxygen for pure CuO, pure NiO and CuO-NiO mixed oxide systems calcined at 400 and 600°C are cited in Table (4).

Table 4. Concentration of surface excess oxygen (mg g⁻¹) for CuO-NiO mixed oxide systems calcined at 400 and 600°C.

Catalyst	Surface excess oxygen (mg g ⁻¹)	
	400 °C	600 °C
Pure CuO	17.5	14.9
1% NiO	16.2	14.0
3% NiO	15.1	12.7
5% NiO	14.1	11.1
7% NiO	12.5	9.6
10% NiO	11.1	8.6
20% NiO	7.2	4.9
30% NiO	5.7	3.6
40% NiO	4.7	2.6
50% NiO	3.4	1.9
Pure NiO	3.2	1.4

Examination of the results in Table (4) shows the following observations:

- Pure CuO possesses the highest value of surface excess oxygen than pure NiO at all calcination temperatures.
- The amount of surface excess oxygen of pure CuO was found to suffer a progressive decrease with the additions of NiO at different calcination temperatures. The decrease was found, however, more pronounced for the lower additions (1-10 wt. %) and extended up to 20 wt. % NiO. Above this ratio, the amount of surface excess oxygen was steadily decreased with the additions of NiO up to 50 wt. % NiO. The additions of

7, 10, 20, 30, 40 and 50 wt. % NiO were found to reduce the amount of surface excess oxygen by 28.5, 36.5, 58.5, 67, 72.8, and 80.7 %, respectively, for the catalysts calcined at 400°C.

- Raising the calcination temperatures from 500 to 700°C, resulted in a significant decrease in the amount of surface excess oxygen for the pure CuO and mixed oxide systems.

However, it is well known that, CuO is a nonstoichiometric and p-type semiconductor. According to Jeong and Choi [67], CuO was confirmed to be a metal deficient p-type semiconductor with copper vacancies at low temperatures. On the other hand, adsorption of oxygen and change in electrical conductivity of NiO [68,69-71] have shown that, at room temperature, chemisorption of oxygen occurs in the form of negatively charged species. As regards with the nature of negatively charged adsorbed species, the formation of O₂⁻, O⁻, O²⁻ ions has been postulated [68].

It is worth mentioning that, the formation of charged chemisorbed oxygen species is accompanied by the promotion of an appropriate number of cations in the oxide crystal lattice to a higher oxidation state. In the case of NiO, this will be the oxidation of Ni²⁺ to Ni³⁺ [68], which from the viewpoint of the semiconducting properties of the oxides is equivalent to the formation of positive holes [72]. Therefore, the oxidation power of nonstoichiometric NiO can be plausibly ascribed to the creation of surface Ni³⁺. The formation of chemisorbed O⁻ species on NiO has been reported [68] to take place at 150-250°C, at 250°C chemisorbed oxygen species was found to predominant as O²⁻.

For CuO-NiO mixed oxide systems, a synergism [73,62-64] between the two oxides will be occurred. As a result of the syngestic effect, the decrease in the amount of excess oxygen may be attributed to the synergistic effect. The above equations (4&5) revealed that the addition of NiO to CuO is accompanied with consumption of oxygen released from CuO. Moreover, the observed decrease in the

specific surface area on mixing CuO with NiO may correspond to such decrease in the surface excess oxygen. The fact that the changes in the values of surface excess oxygen ran almost parallel to the values of specific surface areas of the various adsorbents. This parallelism might suggest the idea that oxygen is uptaken on top of surface layers of the investigated adsorbents [37,73].

Figure 8. SEM photographs of CuO-NiO mixed oxide nanoparticles.

3.6. Electron Microscopy (SEM&TEM)

The surface morphological study of the pure CuO, pure NiO and CuO mixed with 30 wt.% of NiO catalysts nano-particles calcined at 400 and 600°C was carried out using SEM and TEM and the images are shown in Figs. (8&9). Fig. (8) shows the SEM images of the solids under investigation. From the SEM analysis, one can conclude the formation of aggregates of semi-spherical structure with almost uniform distribution. Inspection of these images revealed that:

- i. At all calcination temperatures, Pure CuO catalyst has small aggregates size compared to that of pure NiO and 30 wt. % NiO-CuO solids.
- ii. The aggregates size increases with increasing the addition of NiO.
- iii. The aggregates size increases on increasing the calcination temperature from 400 to 600°C, this agglomeration resulted in an increase of the crystallite size of the particles.

The transmittance electron microscopic (TEM) photographs of the solids have been given in Fig. (9). The size of nano-particles obtained from TEM images show sizes of 12-20 nm for the pure CuO and NiO catalysts and 25-40 nm for the mixed oxides (30 wt. % NiO) calcined at 400 and 600°C, respectively. These results are in a close agreement with the results that obtained from the XRD diffraction pattern see Table (1).

Figure 9. TEM photographs CuO-NiO mixed oxides nanoparticles

4. Conclusion

The main conclusions derived from the results obtained can be summarized as follows:

1. Pure and mixed solids of nano CuO and NiO have been synthesized via oxalic acid rout.
2. CuO, NiO and their mixtures are thermally stable on No solid-solid interaction was detected between the NiO and CuO oxides.
3. The addition of NiO to CuO resulted in increasing the particle size and decreasing the surface area and surface excess oxygen over the investigated solids.

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