Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2016, 5 (1): 219-230

(International Peer Reviewed Journal)

Catalytic Oxidation of CO over Pure And Doped Cu-Ni-O System

A.M.Turky

Chemistry Department, Faculty of Science, Suez Canal University, Ismailia, **EGYPT**

Email: amturky1@yahoo.com

Accepted on 4th January 2016

ABSTRACT

Gas phase catalytic oxidation of CO by oxygen at temperature range 175-225^oC was studied over pure and Na_2O-doped binary CuO-NiO system. CuO content was varied between 20-50 mol% and dopant concentration was varied between 2-8 molpercent. All samples were prepared by wet impregnation method followed by thermal treatment at 400 and 600^oC. The techniques employed were XRD, EDX, nitrogen adsorption at -196^oC and gas phase oxidation of CO by oxygen adopting static method. Results revealed that the CuO-NiO system with chemical composition of CuO-4NiO was the most catalytically active one for CO oxidation. This system in particular was subjected to Na_2O-doping which resulted in further improvement of its catalytic activity. Doping process brought about a considerable change as to surface characteristic of the investigated system. Activation energy values indicated that doping process did not modify the energetic nature of this catalyzed reaction but rather changed the concentration of the active sites involved.

Keywords: CO oxidation, mixed Cu-Ni-O catalyst, Na_2O-doping.

INTRODUCTION

Catalytic oxidation is the process thought by many research studies to curb CO emissions of combustion engines into the atmosphere [1]. Therefore, there is a need to develop highly active catalysts for CO oxidation to remove it from local environment [2]. Developing satisfactory CO oxidation catalysts has received tremendous interest and become a subject of many investigations [3-5]. Noble metal catalysts have been found the most effectual for CO oxidation [6-9]. Nevertheless, the poor selectivity and high cost of noble metal catalysts greatly limited their applications. Alternatively, catalytic oxidation of CO over transition metal oxides is becoming of importance and interest [10]. The appropriateness of a metal oxide for catalytic oxidation of CO is gauged by: (i) tolerance to perfectly redox cycle (ii) stability for extended defective bulk and surface structures (iii) high capacity towards adsorption and activation of CO and O_2 molecules [11-14]. The intrinsic catalytic activity of CuO for CO oxidation was nearly similar to that of platinum [15]. So, CuO has been proposed as a promising catalyst for cO oxidation [16-19]. The activity of NiO for CO oxidation was extensively studied [20-25]. Yu *et al* [22] attributed to NiO an excellent activity close to that of CuO. Mixed oxide catalysts often have a catalytic properties that are superior to those of pure oxides [26, 27]. The improvement of catalytic activity upon combination of two or more metal oxide (synergism) was reported by many investigators [28-31]. It was reported that the activity of $NiCuO_2$ was almost four folds that of individual oxides [32, 33]. The effect of CuO content on the catalytic activity of mixed oxides was studied by many researchers [34-36]. According to these researchers, the catalytic activity attained a maximum at certain CuO content then fall down upon increasing the content above that value. Doping of metal oxides with small amounts of foreign oxides was found to influence the surface and catalytic properties of these oxides [37-40]. The present investigation reports the results of extensive study of the catalytic oxidation of CO over pure and Na_2O-doped mixed CuO-NiO oxide system. The effects of many factors including thermal treatment, CuO content, Na_2O- doping and dopant concentration are within the scope of the work aiming to determine the factors controlling the catalytic act, optimize the catalytic performance and improve the catalytic activity for CO oxidation as a contribution to the catalytic control of air pollution due to CO emissions.

MATERIALS AND METHODS

Materials: The chemicals employed were of analytical grade as supplied by Aldrich and Fluka companies. Mixed copper nickel oxides system with different CuO contents were prepared by wet impregnation method. The system will be denoted as follows throughout this text:

System	CuO-NiOI	CuO-NiOII	CuO-NiOIII	CuO-NiOIV
CuO content, mol%	20	25	33	50
Chemical formula	CuO-4NiO	CuO-3NiO	CuO-2NiO	CuO-NiO

A known weight of basic nickel carbonate was impregnated with copper nitrate solution of definite concentration to make a paste (copper nitrate: nickel carbonate =1:4,1:3, 1:2, 1:1 mol ratio for system I, II , III and IV respectively). The paste was stirred well, dried overnight at 110°C before being subjected to thermal treatment at 400 and 600°C for 4 hours. Pure NiO catalyst was prepared by processing of basic nickel carbonate paste in distilled water in the same method. Na_2O-doped solid was prepared by adding a known weight of sodium nitrate corresponding to 2, 4, 6 and 8 mole% (2, 4, 6, 8 mole of $NaNO_3$ for 100 mole of mixed oxide system respectively) to copper nitrate solution prior to impregnation process then proceeding as above.

Methods: X-ray powder diffractograms of the various investigated samples were carried out using a Bruker diffractometer (Bruker D8 advance target). The patterns were run with $CuK_{\alpha 1}$ with secondary monochromator (λ=0.1545nm).The crystallite size of crystalline phases present in the different investigated solids was calculated by line broadening of the main diffraction line of these phases using Scherrer equation: $d = k\lambda/\beta_{1/2}\cos\theta$, where d is the mean crystallite diameter, λ is the wave length of X-ray , k is Scherrer constant (0.89), θ is the diffraction angle and $\beta_{1/2}$ is the full width at half maximum (FWHM) of the diffraction peaks of crystalline phases . Lattice parameter "a" of NiO as major phase was calculated from the equation: $\mathbf{a=d(h^2 + k^2 + l^2)^{1/2}}$ where d is the d-spacing of the main diffraction line of NiO phase (2.41Å). The composition of surface layers was obtained by EDX analysis. EDX measurements were conducted on a Hitachi S-800 electron microscope with a Kevex Delta system attached. The surface molar composition was determined by Asa method (Zaf correction, Gaussian approximation. The specific surface area (S_{BET}), total pore volumes (V_p) and mean pore radii (r) of the various catalysts were determined from nitrogen adsorption isotherms measured at -196°C using a conventional volumetric apparatus and applying BJH model.

The catalytic activities of various prepared samples towards gas phase oxidation of CO by O_2 were determined by static method at the temperature range 175-225°C. The kinetics of CO oxidation by O_2 was followed up by measuring the total pressure of reacting gaseous mixture at different time intervals (P) for at least one h or until constant pressure was attained. Each catalyst sample (200 mg) was activated by heating at 300°C for 2 h under reduced pressure of 10^{-6} Torr prior to kinetic run. A stoichiometric mixture of CO and O_2 (CO + ½ O_2) at a total pressure of 2 Torr was used as the initial pressure of reactants (P^o). The reaction product (CO_2) was removed from reaction atmosphere by freezing at liquid nitrogen temperature. The saturation vapor pressure of CO at -196°C is 160Torr, a value that makes its liquefaction improbable at the given reaction pressure and temperature [41].

RESULTS AND DISCUSSION

XRD analysis: X-ray diffractograms of pure NiO, CuO and mixed CuO-NiO with different CuO calcined at 400 and 600°C contents are depicted in figs. 1.a and 1.b. The diffraction patterns of pure NiO and CuO contained many diffraction peaks characteristic of these phases specially, the main diffraction lines located at d=2.08, 2.4 Å for NiO phase and 2.31 Å for CuO one. The diffractograms of mixed oxides are consisted of many diffraction peaks of NiO and CuO phases depending on calcination temperature and CuO content. Increasing CuO content was accompanied by progressive increase in the intensity and number of diffraction lines characteristic of CuO phase together with a corresponding increase in crystallite size of both phases to an extent proportional to CuO content. Raising calcination temperature induced a corresponding increase in crystallite size of both phases. Thus, both of CuO content and calcination temperature influenced the degree of crystallinity and extent of dispersion of the investigated mixed oxides system that is expected to influence in turn the catalytic properties of this system.

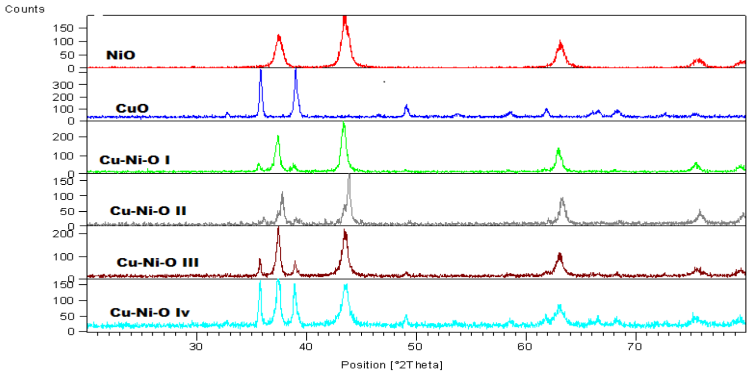


Fig.(1.a) XRD diffractograms of pure and mixed CuO-NiO system with different CuO content calcined at 400oC

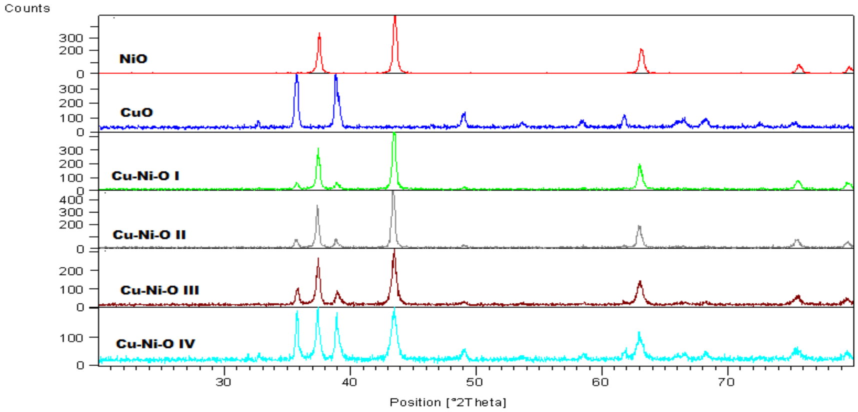


Fig.(1.b) XRD diffractogramms of pure and mixed CuO-NiO system with different CuO content calcined at 600oC

The diffraction patterns of Na_2O-doped CuO-4NiO system labeled as Cu-Ni-O I were nearly similar to that of pure one except for lower intensity of diffraction lines. The absence of diffraction lines characteristic of Na_2O phase may be attributed to two reasons, Na_2O content is below the detection limit of diffractometer and/or the possibility of dissolution of Na_2O in the lattice of NiO as major phase or CuO or both forming a solid solution. This possibility is favored as regard to two factors controlling the formation of solid solution, namely, the crystal form and ionic radii. Both of dopant and host cations are of cubic crystal form, moreover, the ionic radii of copper I, Ni II and Na ions are 0.96, 0.78 and 0.95Å, respectively, these values are allowed for the dissolution of dopant into the lattice of host cation with consequent formation of solid solution. The dissolution of Na_2O into CuO lattice is less probable as the radius of Cu II is 0.69Å. The effect of doping process on peak area, crystallite size of both NiO and CuO phases as well as the lattice parameter of NiO as major phase for the system Cu-Ni-OI calcined at 400 and 600^{o}C is presented in table 1. The crystallite sizes of NiO and CuO in all Cu-Ni-O systems with different CuO content are given in table 2.

Table1. Effect of thermal treatment and Na_2O-doping on peak area, crystallite size of different phases and lattice parameter of NiO as major phase

Solid	Calcination temperature, ^{o}C	Peak area, a.u.		Crystallite siz, nm		Lattice parameter NiO,Å
		NiO (d=2.08Å)	CuO (d=2.31Å)	NiO	CuO	
NiO	400	92.1		26.8		4.15839
CuO			46.4		83.4	
Ni-Cu-O I		86.8	8.3	41.7	46.2	4.16241
+2mol% Na_2O		71.3	7.5	39.6	43.9	4.16021
+4"		65.4	6.8	37.1	39.5	4.11173
+6"		58.3	6.2	34.2	35.0	4.06605
+8"		50.1	5.3	31.3	30.7	4.01402
NiO	600	39.2		98		4.15016
CuO			57.6		92.3	
Ni-Cu-O I		109.5	6.8	53.5	85.1	4.16372
+2mol% Na_2O		98.2	5.4	48.2	82.5	4.16182
+4"		81.1	4.9	45.1	74.9	4.16033
+6"		73.6	4.2	41.7	68.7	4.15812
+8"		61.2	3.1	37.5	61.2	4.15214

Table 2. Crystallite size of NiO and CuO in binary Cu-Ni-O with different CuO contents

System	Calination temperature,^{o}C	Crystallite size,nm NiO	Crystallite size,nm CuO
Cu-Ni-O I	400	41.7	46.2
Cu-Ni-O II		61.2	61.5
Cu-Ni-O III		65.6	75.3
Cu-Ni-O IV		73.7	82.1
Cu-Ni-O I	600	53.5	85.1
Cu-Ni-O II		81.2	87.6
Cu-Ni-O III		93.9	93.4
Cu-Ni-O IV		107.1	102.7

The data of tables 1 and 2 revealed the following:

i. Doping process brought about a progressive decrease in both peak area and crystallite size of both phases to an extent ran parallel with dopant concentration.
ii. Doping process effected a corresponding decrease in the lattice parameter of NiO which was more pronounced for the solids calcined at 400^{o}C.
iii. Increasing CuO content was accompanied by a gradual increase in crystallite size of both phases.

The observed decrease in crystallite size accompanying doping process reflected a lower degree of crystallinity and higher degree of dispersion of the investigated mixed oxides system.

The induced decrease in lattice parameter of NiO phase presented an evidence for dissolution of Na_2O into NiO lattice and the formation of solid solution according to Kroger's notation [42]:

$$2Na^{+} + 2Ni^{2+} + 1/2O_2 = 2Na^{+}(Ni^{2+}) + 2Ni^{3+} + O^{2-}$$

Where $2Na^{+}(Ni^{2+})$ denote two sodium ions located in the position of two nickel ions in NiO lattice with subsequent conversion of equal number of divalent nickel to trivalent one to keep the electro neutrality of doped NiO according to the theory of controlled valence[43,44]. Similar results were obtained by Antolini [45] upon doping of NiO with Li_2O. The ionic radii of Ni^{2+} and Ni^{3+} are 0.78 and 0.62Å, respectively. So, the conversion of Ni^{2+} to Ni^{3+} would be accompanied with lattice contraction with subsequent decrease in lattice parameter as monitored in table1. The induced changes in the degree of crystallinity and $Ni^{3+/}Ni^{2+}$ ratio are expected to be effective as regard to surface and catalytic properties of the investigated system.

Energy dispersive x-ray analysis (EDX): EDX investigation of different binary metal oxides calcined at 400 and 600°C was performed aiming to confirm the chemical structure of prepared solids assuming a homogeneous distribution of the present oxides among the bulk and surface layers. The relative atomic abundance of Ni, Cu and oxygen species in the uppermost surface layers for CuO-NiO system with CuO contents of 20, 25, 33 and 50 mol% denoted as Cu-Ni-O I, II, III and IV, respectively calcined at 400 and 600°C are listed in Table 3. Inspection of this Table indicated that the values of calculated and found atomic abundance for the three elements are nearly the same and the differences are within the experimental error. This finding stands for the complete transformation of copper nitrate and basic nickel carbonate to the corresponding CuO and NiO at the temperature range 400-600°C according to the stoichiometric equations and serves as a confirmation of the chemical composition of the prepared mixed oxides system .

Table 3. Surface molar composition of binary Cu-Ni-O system with different CuO content Calcined at 400°C

Solid catalyst	Element	Atomic abundance	
		Calculated	Found
CuO-4NiO (Cu-Ni-O I)	O	21.1	21.5
	Ni	62.1	61.9
	Cu	16.8	16.5
CuO-3NiO (Cu-Ni-OII)	O	21.1	21.7
	Ni	58.0	57.8
	Cu	20.9	20.5
CuO-2NiO (Cu-Ni-OIII)	O	21.0	21.3
	Ni	51.3	51.0
	Cu	27.7	27.5
CuO-NiO (Cu-Ni-OIV)	O	20.8	21.0
	Ni	38.1	38.0
	Cu	41.1	40.9

Surface characteristics of pure and doped Cu-Ni-O I: The different surface characteristics of pure and Na_2O-doped Cu-Ni-O-I were determined from nitrogen adsorption isotherms conducted at -196°C. These characteristics include specific surface area (S_{BET}), total pore volume (V_p) and pore size expressed as mean pore radius ($\overline{r}$). Pore size and pore volume were determined using BJH model . The values of pore radius for different adsorbents were calculated from the equation: $\overline{r} = 2V_p/S_{BET} x10^{-4}$ Å. Pore volume was taken as the volume of liquid adsorbate near saturation pressure, $P/P^o = 0.98$. For nitrogen, it is given by: $V_p = V_a x28/22414xd_l$, where Va is the volume of adsorbed at $P/P^o = 0.98$ and d_l is the density of liquid nitrogen. The data obtained are monitored in table 4 and shows the following:

i- Doping process exerted a progressive increase in both specific surface area and pore volume with a limited decrease in pore radius to an extent proportional to dopant concentration. The values of pore radius indicated that all the investigated adsorbents were of mesoporous type.

ii- Raising the calcination temperature from 400 to 600^{o}C effected considerable changes as regard to the surface characteristics that can be summarized as decreasing both of specific surface area and pore volume and some increase in pore radius.

Table 4. Surface characteristics of pure and Na_2O-doped Cu-Ni-O I calcined at 400 and 600^{o}C

Catalyst	Calcination temperature, ^{o}C	S_{BET},m^2/g	Vp, ml/g	$\bar{r}$, Å
Cu-Ni-O I	400	70	0.174	50
+2mol% Na_2O		75	0.190	51
+4		84	0.210	50
+6		95	0.229	48
+8		108	0.248	46
Cu-Ni-O I	600	55	0.156	57
+2mol% Na_2O		66	0.181	55
+4		73	0.200	55
+6		81	0.218	54
+8		93	0.241	52

Increasing specific surface area accompanying doping process came in consistency with the results of XRD and could be accounted for in terms of the observed lowering in the degree of crystallinity due to lattice contraction resulting from the conversion of some divalent nickel ions to trivalent cations as discussed above. Another factor contributing to increasing specific surface area is the observed increase in pore volume that could be attributed to the creation of new pores as a result of liberation of gaseous products during thermal treatment. Thirdly, pore narrowing indicated by decreasing the pore radius is another factor for the increment in $S_{BET.}$ Alternatively, the induced decrease in specific surface area together with lowering the pore volume upon raising the calcination temperature is regarded as a consequence of sintering process. Besides, pore widening indicated by pore radius increment cannot be overlooked among the factors contributing to the S_{BET} decrease thus obtained. Consequently, the above mentioned changes in surface characteristic due to doping process are expected to bring about a corresponding change in the catalytic properties of doped Cu-Ni-O I as will be discussed below.

Catalytic activity towards CO oxidation by oxygen

Catalytic activity of pure Cu-Ni-O with different CuO contents: The catalytic activity of pure NiO and Cu-Ni-O with different CuO contents was checked towards gas phase oxidation of CO by oxygen at the temperature range 175-225^{o}C using static method. First-order kinetics was observed in all cases for a plot of lnP^o/P vs. time, where P^o and P denote the initial total pressure of reactants and that at different time intervals, respectively. The corresponding conversion percent can be calculated as $(P^o-P)x100/P^o$ and the slope of first-order plots gives directly the reaction rate constant (k) at a given temperature, which was taken as a measure of the catalytic activity at that temperature. Fig.(2) depicts representative first-order plots of CO oxidation over pure NiO and Cu-Ni-O system with different CuO content calcined at 400^{o}C in the temperature range 175-225^{o}C. The catalytic activity expressed as reaction rate constant per unit mass (specific rate, k, $min^{-1}g^{-1}$) as a function of CuO content is presented in table 5. The role of CuO in the catalytic activity of NiO is better investigated by comparing the values of k as a function of CuO content for the catalysts calcined at 400 and 600^{o}C. The variation of k for the catalytic reaction conducted at 175-225^{o}C as a function of CuO content is graphically illustrated in fig 3 a & b. Considering the data obtained in figs.2 &3 and table 5, the following remarks could be observed:

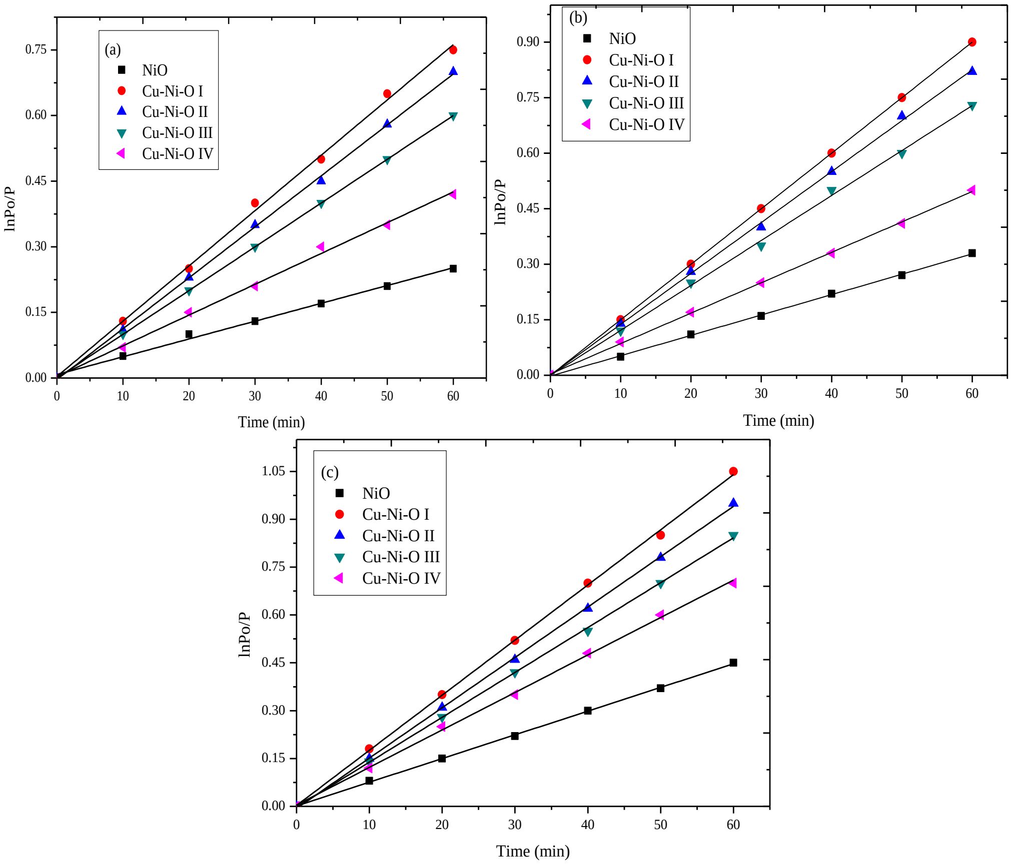
i. All binary Cu-Ni-O systems were devoted with higher catalytic activity compared to pure NiO one.

ii. The catalytic activity of binary Cu-Ni-O system with chemical composition CuO-4NiO of CuO content 20mol% and labeled as Cu-Ni-O I was maximum, Increasing CuO above that value resulted in a progressive decrease in the catalytic activity but was still higher than that of pure NiO.

iii. Raising calcination temperature from 400 to 600°C resulted in a considerable decrease in the catalytic activity of all systems but still following the same trend regarded at 400°C.

Table 5. Specific rate (k $x10^2$, $min^{-1}g^{-1}$) for the catalytic oxidation of CO by O_2 over NiO and Cu-Ni-O system with different CuO content

System	Calcination temperature,°C	k_{175}	k_{200}	k_{225}
NiO	400	2.1	2.7	3.7
Cu-Ni-OI		6.4	7.5	8.7
Cu-Ni-OII		5.8	6.9	7.8
Cu-Ni-OIII		5.2	6.1	7.1
Cu-Ni-OIV		3.5	4.1	5.9
NiO	600	1.4	2.0	3.3
Cu-Ni-OI		4.6	5.7	7.4
Cu-Ni-OII		3.5	4.7	6.7
Cu-Ni-OIII		2.7	3.8	4.1
Cu-Ni-OIV		2.1	3.0	3.5



Reaction temperature, °C: (a) 175, (b) 200, (c) 225.

Fig. (2) First-order plots of CO oxidation over pure NiO and mixed CuO-NiO system with different CuO content calcined at 400°C.

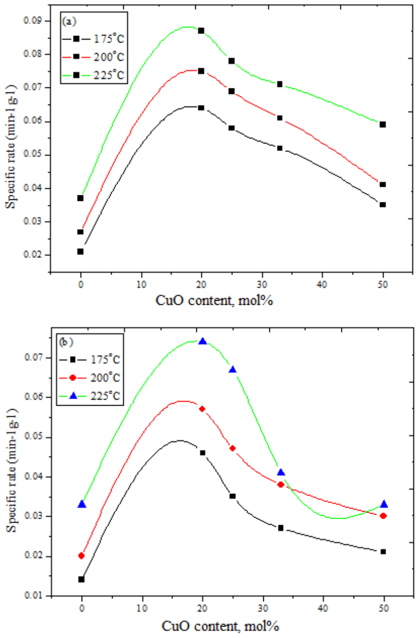


Fig.(3) Variation of specific rate for CO oxidation as a function of CuO content

(0 mol% = pure NiO)

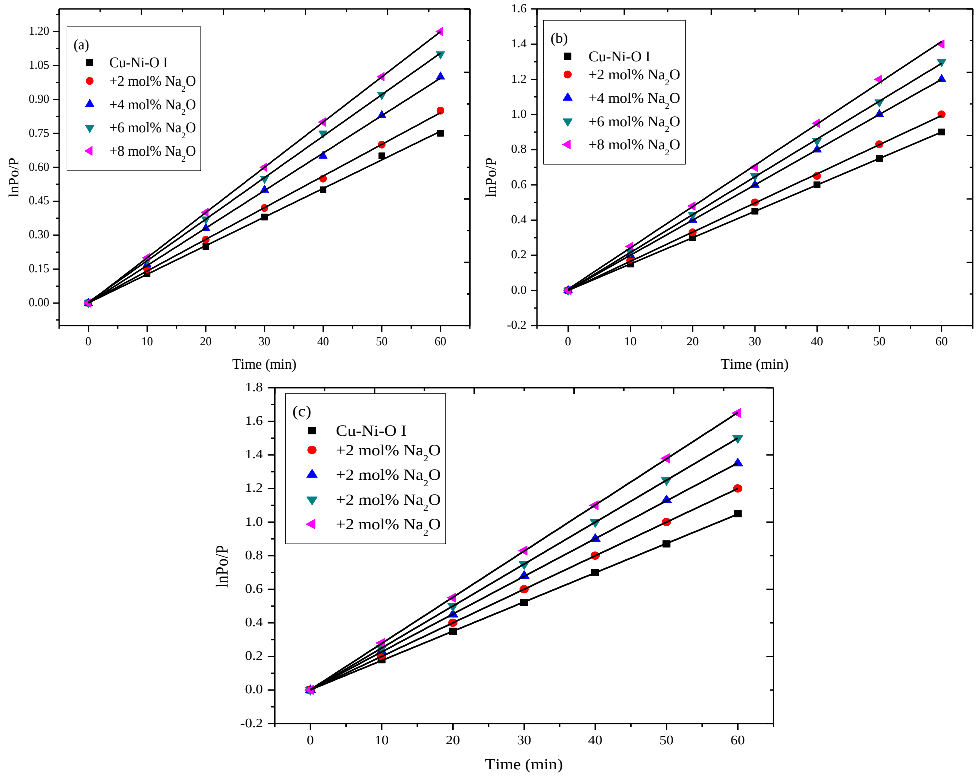
Calcination temperature,°C: (a) 400, (b) 600.

The observed increasing trend in catalytic activity for all binary systems came in good correlation with the calculated crystallite size for these system presented in table 2. From this table, Cu-Ni-O I system was characterized by its minimum crystallite size for both phases and hence the lowest degree of crystallinity. Consequently, it is expected to have more active sites accessible to reacting mixture. The obtained results are consistent with that of many investigators who reported that the catalytic activity of catalysts containing different CuO contents increased, passed through a maximum then decreased with further CuO content above certain limit [46-48]. The higher activity observed for all the investigated binary oxides systems compared to that of pure NiO is worth mentioning and extensively reported as a synergistic effect [28-31].

Catalytic activity of pure and Na_2O-doped Cu-Ni-O system: The most active system with chemical formula CuO-4NiO denoted as Cu-Ni-O I was subjected to Na_2O-doping adopting dopant concentration in the rang 2-8 mol%. The catalytic activity of pure and doped samples was checked towards Co oxidation under the same conditions mentioned above. Representative first-order plots of CO oxidation over pure and Na_2O- doped Cu-Ni-OI calcined at 400°C are shown in fig. 4.The data of fig. 4 indicated a progressive improvement of the catalytic activity to an extent proportional to to dopant concentration. Moreover, samples fired at 400°C were more active than those thermally treated at 600°C.

The presence of Ni^{2+} / Ni^{3+} ion pair is necessary for the Catalytic oxidation of CO by oxygen, CO is chemisorbed on Ni^{3+} as an electron acceptor site whereas O_2 is chemisorbed on Ni^{2+} as an electron donor one. According to Xu *et al.* [49], CO oxidation over transition metal oxide ion pair followed Mars-Van Krevelen Mechanism at which CO chemisorbed on the ion with higher oxidation state was oxidized by the adjacent lattice oxygen with the creation of oxygen vacancy site which was refilled by gas phase oxygen being chemisorbed on the lower valence ion with subsequent reform of lattice oxygen. The concentration of Ni^{3+} constituting the active center for CO chemisorption can be increased by doping with monovalent cation leading to increasing the p-type semiconducting character [50-52]. The presence of Ni^{3+} in NiO was confirmed by Ni2p XPS spectra [53, 54]. Furthermore, the presence of non-stoichiometric Ni^{3+} as lattice defect in NiO was reported by Kostad [55] who explained the electrical conductivity of NiO in terms of hoping mechanism via electron transfer between Ni^{3+} and Ni^{2+} ions. In view of the above discussion, CO oxidation by oxygen followed first –order independent of gas phase oxygen concentration. Therefore, the above mentioned mechanism seems to be applicable to this reaction. Gas phase oxygen being chemisorbed on divalent nickel is used to refill the resulting oxygen vacancy and reform the lattice oxygen consumed during the course of CO oxidation. Na_2O-doping would increase the concentration of trivalent nickel, the active site for CO chemisorption with an expected enhancement of the reaction rate. This assumption came in good agreement with the results of XRD analysis and surface characteristics. Recalling that doping process resulted in the conversion of some divalent nickel ions to trivalent ions, moreover, the conversion of some divalent nickel to trivalent one as a consequence of doping process led to a corresponding lattice contraction with subsequent increase in specific surface area leading to increasing the surface concentration and accessibility of active sites responsible for the catalytic reaction investigated. Accordingly, the observed drop of catalytic activity for the samples fired at 600°C could be interpreted in terms of the reported lowering of surface area and subsequent decrease of the surface active sites accessible to reacting mixture.

Determination of activation energy (ΔEa) for CO oxidation over pure and Na_2O –doped Cu-Ni-OI was performed applying Arrhenius equation. The computed values for ΔEa and lnA for all catalysts calcined at 400 and 600°C are listed in table 6. The values of ΔEa were in the range 12.0-13.5 kJ mol^{-1} and 20.0-21.32 kJ mol^{-1} for the catalysts calcined at 400 and 600°C, respectively. These values are approximately the same for each calcination temperature within the experimental error. Consequently, it is believed that doping process did not modify the mechanism or energetic nature of catalyzed reaction but rather changed the concentration of active sites involved.



Reaction temperature, °C: (a) 175, (b) 200, (c) 225

Fig. 4 First-order plots of CO oxidation over pure and doped Cu-Ni-O I calcined at 400°C

Table 6. Activation energy and frequency factor for the catalytic oxidation of CO by O_2 over pure and Na_2O-doped Cu-Ni-OI conducted at 175-225°C

Catalyst	Calcination temperature,°C	Ea, kJ mol^{-1}	lnA
Cu-Ni-OI	400	12.79	0.66
+2mol%Na_2O		13.36	0.76
+4		13.00	0.93
+6		13.50	1.02
+8		12.00	1.11
Cu-Ni-OI	600	20.75	2.42
+2mol%Na_2O		20.00	2.52
+4		21.32	2.68
+6		19.81	2.77
+8		20.58	2.87

APPLICATIONS

CuO-4NiO system is devoted with the maximum catalytic activity for CO oxidation, its activity was further improved by doping with Na_2O. This catalyst is applicable to catalytic minimization of air pollution due to CO emissions from internal ignition engines.

CONCLUSIONS

1. Binary CuO-NiO of CuO content in the range 20-50 mol% acquired better activity for gas phase oxidation by oxygen compared to that of pure NiO.
2. Cu-Ni-O system with chemical formula CuO-4NiO was devoted with the maximum catalytic activity towards the investigated catalyzed reaction.
3. Na_2O-doping of Cu-Ni-OI induced a considerable changes to the surface characteristics.
4. The catalytic activity of Cu-Ni-O was markedly improved as a result of Na_2O-doping.
5. Doping process did not modify the energetic nature of mechanism of catalyzed reaction but rather changed the concentration of active sites involved.

ACKNOWLEDGEMENT

The author is forever grateful to G.A.El-Shobaky, Late Professor of Physical Chemistry.

REFERENCES

[1] E. S. Lox, B. H. Engler, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.),” Handbook of Heterogeneous Catalysis”, Vol. 4, Wiley-VCH, Weinheim, **1997** p:1595.
[2] G. Glassbell, L. Fuoco, M.S. El-Shall, *J. Phys.Chem. B*, **2005**, 109, 17350-17355.
[3] O. Pozdnyakova, D. Teschner, A. Wooktesch, J. Krohnert, B. Steinhauer, L.Toth, F.Gentoft, A.Knopgericke, Z. Paal, *J. Catal*., **2006**, 237, 1-16.
[4] Y.Yoshida, Y.Mitani, T.Itoi, Y.Izumi, *J.Catal*., **2012**, 287, 190-202.
[5] E.V.Ramos-Fernandez, C.Pieters, B. vanderLinden, J.Juan-Alcaniz, P.Serra, Crespo, M.W.Verhoeven, H. Niemantsverdriet, G. Gascon, F. Kapteijn, *J.Catal*., **2012**, 289, 42-52.
[6] C.S.Polster, R.Zhang, M.T.Cyb, J.T.Miller, C.D.Baretsch, *J. Catal*., **2010**, 273, 50-58.
[7] L.H.Chang, N.Sasirekha, Y.W.Chen, *Catal. Commun*., **2007**, 8, 1702-1710.
[8] H.Wang, H.Zhu, Z.Qin, F.Liang, G.Wang, J.Wang, *J.Catal*., **2009**, 264, 154-162.
[9] Y.Huang, A.Wang, L.Li, X.Wang, D.Su, T.Zhang, *J.Catal*., **2008**, 255, 144-152.
[10] S.Royer, D.Duprez, *Chem Cat Chem*., **2011**, 3(1), 24-65.
[11] A.Bielanski, J.Haber, “Oxygen in Catalysis”, Marcel Dekker, New York, **1991**, p: 211.

[12] R.Prassad, L.A. Kennedy, E.Rukenstein, *Catal. Rev.Sci. Eng.***, 1984**, 26, 1-58.

[13] P.J.Gellings, H.J.M.Bauwmeester, *Catal. Today*, **1992**, 12, 1-101.

[14] H.H.Kung," Transition Metal Oxides: Surface Chemistry and Catalysis, Studies in Surface Science and Catalysis", Vol.45, Elsevier, Amstrdam, **1989**.

[15] J.K.Kummer, *Prog. Energy Combust. Sci*., **1980**, 6, 177-199.

[16] D.Gammara, C.Belver, M. Fernandez-Garcia, A.Martinez-Arias, *J.Am.Chem.Soc***., 2007,** 129, 12064-12065.

[17] M.Turco, G.Bagnasco, C.Cammarano, L.Micoli, M.Lenarda, E.Moretti, L.Storavo, A.Talon, *Appl. Catal. B*, **2011**, 102, 387-394.

[18] C.S.Polster, H.Nair, C.D.Baertsch, *J.Catal*., **2009**, 266, 308-319.

[19] F.Zhang, C.Chen, W.M.Xiao, L.Xu, N.Zhang, *Catal.Commun*., **2012**, 26, 25-29.

[20] D.Mehandgiev, A.Naydenov, G.Ivanov, *Appl. Catal. A*, **2003,** 206(1), 13-18.

[21] G. Parravano**,** *J. Am. Chem. Soc*., **1953**, *75* (6), pp 1452–1454

[22] Y.Yu, T.Takei, H.Ohash, H.He, X.Zhang, M.Haruta, *J.Catal*, **2009,** 267, 121-128.

[23] B.M.Reddy, K.N.Rao, P.bharali, *Ind.Eng Chem.Res*., **2009,** 48, 8478-8486.

[24] Y.F.Yu Yao, J.T.Kummer, *J.Catal*, **1973**, 28,124-138.

[25] G.Parravano, *J.Am.Chem.Soc*., **1953**, 75, 1448-1451.

[26] E.A.El-Shrkawy, S.E.El-Hakam, S.E.Samra, *Mater. Lett*, **2000**, 42, 333-338.

[27] S.S.Ashour, *Oxford Research Fourm J*., **2007,** 2(4), 17-26.

[28] M.Haruta, N.Yamada, T.Kobayashi, S.Ishida, *J.Catal*., **1989**, 115, 301-309.

[29] S.Imamura, H.Sawada, K.Uemura, S.Ishida, *J.Catal*., **1988**, 109, 198-205.

[30] M.Haruta, H.Sano, G.Paneclet, P.Grange, P.A.Jacob," Preparation of Catalysts, III", Elsevier, Amstrdam, **1983**, p:225.

[31] S.Imamura, Y.Tsuji, Y.Miyake, T.Ito, *J.Catal*.,**1995**, 151, 279-284

[32] H.G. El-Shobaky, *Appl.Catal A, **2004**,* 278,1-9.

[33] H.G.El-Shobaky, Y.M.Fahmy, *Appl. Catal B*, **2006**, 63,168-177.

[34] Y.Zhigiang, M.Dongsen, G.Xiaoming, L. Gaunzhong, *J.Rare Earths*, **2014**, 32(2) ,117-123.

[35] P.Aunbamrung, A.Wongkaew, *Advances. Chem Eng. Sci*., **2013**,(3), 15-19

[36] J.L. Ayastuy, A. Gurbani, M.P. Gonzales-Marcus, M.A.Gutierrez-Oritz, *Intern. J. Hydrogen Enegy*, **2010,** 35 (3), 1232-1244.

[37] G.A. El-Shobaky, A.N. Al-Noaimi, A.Abd El-Aal, A.M. Ghozza, *Mat.Lett*, **1995**, 22, 39-45.

[38] G.A.El-Shobaky, M.A.Shuman, S.M.El-Khouly, *Mat.Lett*., **2003**, 58,184-190.

[39] S.A. El-Molla, M.N. Hammed, G.A. El-Shobaky, *Mat. Lett.*, **2004**, *58* (6), 1003-1011.

[40] S.S.Ashour, *J.Saudi Chem.Soc*., **2014**, 18,69.

[41] G.A.El-Shobaky, S.M.El-Kholy, A.M.Ghozza, G.M. Mohamed, *Appl. Catal.A*, **2006**, 302, 296-304.

[42] F.A. Kröger, Chemistry of Imperfect crystals, North-Holland, Amsterdam **(1964)**.

[43] E.G.Verwey, J.H. DeBoor, *Rec. Trav. Chem. Pays-Bas*, **2006**, 55, 531-540.

[44] N.N. Greenwood, Inorganic Crystal Lattice Defects and Non-Stoichiometry, vol.37, Butterworth, London **(1964)**.

[45] E.Antolini, *Mater. Lett*., **2001**, 51, 385-588.

[46] S.P.Wang, X.Y.Wang, X.C.Zheng, S.R.Wang,S.M.Zhang, W.P.Haung, S.H.Wu, *Reac. Kinet. Cata. Lett.*, **2006**, 89,37-44.

[47] J.L.Cao, Y.Wang, T.Y.Zhang, S.H.Wu, Z.Y.Yuan, *Appl.Catal.B,* **2008**, 78,120-128.

[48] J.Zhu, L.L.Chang, Y.Deng,B.Lui, L.H.Dong, F.Gao, K.Q.Sun, L.Dong, Y.Chen, *Appl.Catal.B*, **2010**, 96, 449-457.

[49] X.L.Xu, E.Yang, J.Q.Li, Y.Li, W.K.Chen, A DFT Study of CO Catalytic Oxidation by N_2O or O_2 on the Co_3O_4(110) Surface, *Chem Cat Chem*., **2009,** 1,384-392.

[50] A.E. Cherkashin, A.N.Goldobin, V.I.Savkenko,N.P.Keir, G.L.Semin, *Reac. Kinet. Catal. Lett*. **1974**, 1(4), 411-415.

[51] V.F.Kiselev, O.V.Krylov, Adsorption and Catalysis on Transition Metals and Their Oxides Springer, New York, **(1989).**
[52] A.M.Turky, *Appl. Catal. A*, **2003**, 247, 83-93.
[53] M. Tomellini, *J. Electron. Spectrosc. Relat. Phenom.*, **1992**, 58, 75-78.
[54] C.J. Lui, B.Cui, H. Lin, *J. Phys. Chem. C.*, **2009**, 113, 14083-14087.
[55] P. Kostad, Non-stoichiometry, Diffusion and Electrical Conductivity in Binary metal Oxides. Wiley-Interscience, New York **(1972)** 426.

AUTHORS' ADDRESS

1. **A.M.Turky**
Chemistry Department,
Faculty of Science,
Suez Canal University,
Ismailia, EGYPT
Email: amturky1@yahoo.com