



Surface and catalytic properties of Li₂O--doped Co-Ni-O system

KEYWORDS

Co₃O₄-NiO, CO oxidation, Li₂O-doping

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ABSTRACT

A series of binary Co₃O₄-NiO with different Co₃O₄ contents ranging between 20-50 mol% were prepared by wet impregnation method followed by calcination at 400 and 600°C. The catalytic activity of obtained solids was checked towards gas phase oxidation of CO by oxygen. The most active system was doped with Li₂O with dopant concentrations between 2- 6 mol%. The surface and catalytic properties of pure and doped solids were investigated adopting many techniques including XRD, EDX, nitrogen adsorption at -196°C and catalytic oxidation of CO at 175-225°C.

The results revealed that binary Co-Ni oxides containing 33mol% Co₃O₄ was the most active for CO oxidation. Li₂O-doping of that system, followed by calcination at 400 and 600°C markedly influenced its surface and catalytic properties. Generally, the catalytic activity of binary oxides for CO oxidation was better than that of individual NiO and was further improved upon lithia-doping. Doping process did not change in the activation energy of catalyzed reaction but rather changed the concentration of active sites involved.

Introduction

Catalytic oxidation of CO, perhaps the most extensively studied reaction in the history of heterogeneous catalysis, is becoming of increasing importance in the context of air pollution control [1, 2]. Catalysts based on noble metals with high catalytic activity were used for this purpose. The high cost and rarity of these metals are disadvantages of such catalysts. Alternatively, catalysts based on transition metal oxides were developed with sufficient activity and stability for CO oxidation [3, 4]. Among transition metal oxides, Co₃O₄ is one of the most active catalysts for CO oxidation [5, 6]. Co₃O₄ has an ideal spinel structure containing Co³⁺ in the octahedral coordination and Co²⁺ in the tetrahedral one with some observed deviations in its particles [7, 8]. Most researchers assume that CO adsorbs on Co³⁺ site [9-11]. Yu et al.[12] reported that NiO is a highly active catalyst for CO oxidation. The catalytic activity of mixed transition metal oxides in most cases is higher than that of the individual oxides due to synergistic effect [13]. This effect arises due to either mixing of transition metal oxides involving bifunctional catalysis [14] or the formation of new active compounds as a result of interaction between the two oxides [15]. Catalytic oxidation of CO over binary transition metal oxide systems has long been the subject of many investigations [16-20]. Guo et al studied the catalytic oxidation of CO over binary Co₃O₄-NiO system of Co content between 5 and 80 percent [18]. The catalytic activity passed through a maximum at Co content of 20%. There was a decrease in the catalytic activity for Co content between 40-60%, this decrease was attributed to the formation of NiCo₂O₄. Doping of transition metal oxides with foreign cations of different valence was found to have significant influence as to the surface and catalytic properties of these oxides [21, 22]. It was reported that doping of NiO with a cation of lower valence induced a corresponding increase of Ni³⁺/Ni²⁺ ratio [22]. Li₂O was applied as a dopant for many catalysts including pure and mixed Co₃O₄ as well as NiO [23-25]. According to these investigators, Li₂O-doping brought about a considerable increase in both surface area

and catalytic activity towards CO oxidation. However, it seems that Co-Ni oxide system was not sufficiently studied as a catalyst for CO oxidation. The present work reports the results of an extensive study of this system involving mainly its surface characteristics and catalytic activity for gas phase oxidation of CO as being influenced by many factors. These factors include thermal treatment, Co₃O₄ content and doping with Li₂O aiming to improve its catalytic activity and optimize its catalytic performance for this reaction.

Experimental

Materials

The chemicals employed were of analytical grade as supplied by Aldrich and Merck companies.

Mixed cobalt nickel oxides system with different Co₃O₄ contents were prepared by wet impregnation method. The system will be denoted as follows throughout this text:

System	Co ₃ O ₄ -NiOI	Co ₃ O ₄ -NiOII	Co ₃ O ₄ -NiOIII
Co ₃ O ₄ content, mol%	20	33	50
Chemical formula	Co ₃ O ₄ -4NiO 0.25Co ₃ O ₄ -NiO	Co ₃ O ₄ -2NiO 0.5Co ₃ O ₄ -NiO	Co ₃ O ₄ -NiO

A known weight of basic nickel carbonate was impregnated with cobalt nitrate solution of definite concentration to make a paste (cobalt nitrate: nickel carbonate = 1:4, 1:2, 1:1 mol ratio for system I, II and III, respectively). The paste was stirred well, dried over night at 110°C before being subjected to thermal treatment at 400 and 600°C for 3 hours. Pure NiO catalyst was prepared by processing of basic nickel carbonate paste in distilled water in the same method. Li₂O-doped solid was prepared by adding a known weight of lithium nitrate corresponding to 2, 4 and 6 mol% (2, 4, 6 mol of LiNO₃ for 100 mol of system II, respectively) to cobalt

nitrate solution prior to impregnation process then proceeding as above. The amounts were designed to get 0.01mol of each system

Techniques

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 $\text{CuK}_{\alpha 1}$ with secondary monochromator ($\lambda=0.1545\text{nm}$). 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 [26]: $d = k\lambda/\beta_{1/2} \cos\theta$, 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: $a = d(h^2 + k^2 + l^2)^{1/2}$ 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. Surface non-stoichiometry was determined by chemical analysis of surface excess oxygen. About 0.1g of sample was mixed with a measured amount of 0.1N hydrazine sulphate solution. pH was adjusted to 8.4-8.6 with sodium carbonate and the solution was stirred under nitrogen atmosphere for 25 min, then filtered. pH was readjusted to 7-7.2 and the unreacted hydrazine was back-titrated against a standardized iodine solution under nitrogen atmosphere.

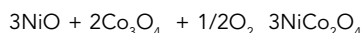
The catalytic activities of various prepared samples towards gas phase oxidation of CO by O_2 were determined by static method at the temperature range $175\text{-}225^\circ\text{C}$. The kinetics of CO oxidation by O_2 was followed up by measuring the total pressure of reacting gaseous mixture at different time intervals (P) for at least one h or until constant pressure was attained. Each catalyst sample (200mg) 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 ($\text{CO} + \frac{1}{2} \text{O}_2$) at a total pressure of 2 Torr was used as the initial pressure of reactants (P_0). 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 [19, 27].

Results and discussion

3.1. X-ray diffraction (XRD) analysis

The X-ray diffractograms of pure NiO, Co_3O_4 and mixed Co_3O_4 -NiO solids with different Co_3O_4 contents including Li_2O -doped samples were determined. Figs. (1.a and b) depict XRD diffractograms of the investigated pure and mixed oxides with a representative heavily Li_2O -doped one precalcined at 400 and 600°C , respectively. Table (1) summarizes some diffraction data of pure phases, pure and Li_2O -doped Co_3O_4 -NiO system. These data include main peak area of Co_3O_4 and NiO phases, their crystallite size and lattice parameter of NiO as major phase. Examination of the diffractograms and diffrac-

tion data shows the following: (i) Diffractograms of pure investigated solids are consisted of many diffraction peaks of NiO and Co_3O_4 phase depending on calcination temperature and Co_3O_4 content. (ii) Increasing calcination temperature from 400 to 600°C resulted in a measurable increase in crystallite size and the degree of crystallinity of both phases. (iii) Considerable decrease in the degree of crystallinity of Co_3O_4 and NiO phases in mixed systems upon doping process (iv) Gradual decrease in lattice parameter of NiO which ran parallel to dopant concentration and indicating lattice some contraction accompanying doping process. The peak area of diffraction lines was taken as a measure of the degree of crystallinity. At Co_3O_4 content mol %, a solid-solid interaction leading to the formation of nickel cobaltite spinel becomes likely [18]. The close similarity of diffraction data of Co_3O_4 and NiCo_2O_4 phases makes their distinction very difficult. So, one cannot exclude the possibility of nickel cobaltite phase formation in Co_3O_4 -NiOIII with Co_3O_4 content of 50 mol %. Furthermore, the possibility of formation of nickel cobaltite is favored by the appearance of some new diffraction peaks in this system (c.f. Fig1b). The formation of NiCo_2O_4 takes place according to:



This implies that the formation of nickel cobaltite is possible for Co_3O_4 content, which is applicable to Co_3O_4 - NiOIII system as mentioned above.

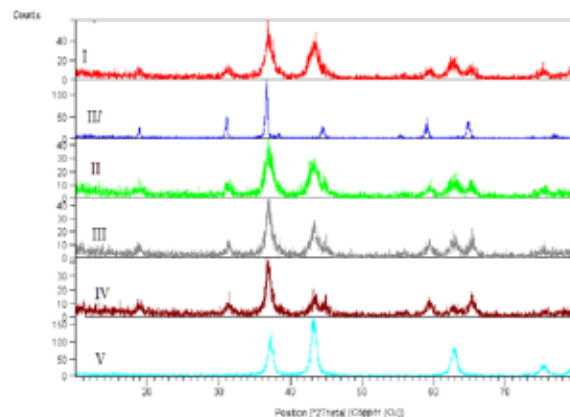


Fig.1(a) XRD diffractograms of pure, mixed and heavily doped Co_3O_4 -NiO solids calcined at 400°C
I: Co-Ni-OI, II: Co-Ni-OII, III: Co-Ni-OIII+6% Li_2O , III: Co-Ni-OIII, IV: pure Co_3O_4 , V: pure NiO

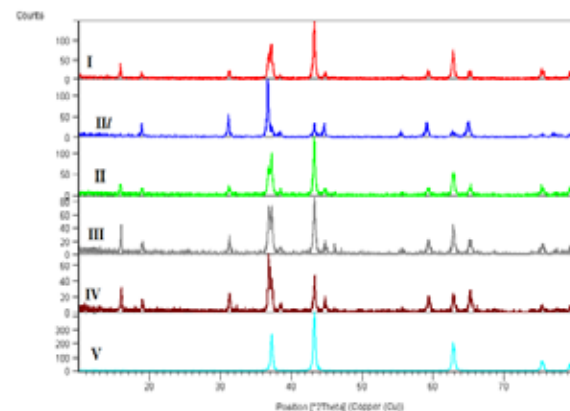


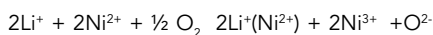
Fig.1(b) XRD diffractograms of pure, mixed and heavily doped Co_3O_4 -NiO solids calcined at 600°C
I: Co-Ni-OI, II: Co-Ni-OII, III: Co-Ni-OIII+6% Li_2O , III: Co-Ni-OIII, IV: Pure Co_3O_4 , V: Pure NiO.

Table (1): Effect of thermal treatment and Li₂O-doping on peak area, crystallite size of different phases and lattice parameter of major phase

Solid	Calc. temp , °C	Peak area (a.u.)NiO d=2.09Å	Peak area (a.u.)Co ₃ O ₄ d=2.44 Å	Crystal size of NiO, nm	Crystal size of Co ₃ O ₄ , nm	Lattice parameter of NiO, Å
Pure NiO	400	66.19		31.27		4.1797
PureCo ₃ O ₄			20.42		25.82	
Co-Ni-OII*		29.73	36.28	31.30	29.41	4.2414
+2%Li ₂ O		23.84	27.40	25.43	25.33	4.2315
+4%Li ₂ O		16.11	18.75	19.84	21.75	4.2252
+6%Li ₂ O		10.31	10.06	13.10	17.20	4.2190
Pure NiO	600	123.21		46.83		4.1826
PureCo ₃ O ₄			13.78		34.48	
Co-Ni-OII*		31.68	26.03	74.95	68.82	4.2473
+2%Li ₂ O		23.17	20.15	68.34	60.15	4.2465
+4%Li ₂ O		14.93	16.45	61.14	52.31	4.2431
+6%Li ₂ O		5.71	12.78	53.55	45.93	4.2397

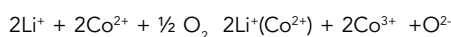
With Co₃O₄ content of 33 mol%.

The diffractograms of lithia-doped Co₃O₄-NiO II were nearly similar to those of pure one except for lower crystallinity leading to an appreciable decrease in peak area for characteristic lines of both phases especially for NiO as indicated by sharp decrease in its characteristic peak located at 2.09Å together with an observed shift to lower d-spacing (c.f.Fig.1b). Thus, the diffraction data of doped solids are better presented as a table. A representative diffractogram of 6mol% Li₂O-doped Co₃O₄-NiO is included in Fig. (1). The absence of diffraction lines characteristic of Li₂O is possibly attributed to the dissolution of Li₂O in NiO and Co₃O₄ as discussed below. On the other hand, doping of Co₃O₄-NiOII with Li₂O resulted in a progressive decrease in crystallite size of both phase implying a corresponding increase in the degree of dispersion as evident from Table (1). Moreover, doping process brought about a progressive decrease in the lattice parameter "a" of cubic NiO as major phase as supported by the induced shift of its diffraction line located at 2.09Å to lower d-spacing. The ionic radii of Li⁺, Ni³⁺ and Ni²⁺ are 0.60, 0.62 and 0.78Å, respectively. The close values of ionic radii of Li⁺ and Ni²⁺ enables the dissolution of Li₂O in NiO lattice, a process which leads to oxygen uptake with consequent conversion of some Ni²⁺ to non-stoichiometric Ni³⁺ according to Kröger's notation [28], the theory of controlled valence [29,30] and in accordance with Antolini[24]:



Where 2Li⁺(Ni²⁺) denote two Li⁺ ions located in the position of two Ni²⁺ host cation in NiO lattice with subsequent conversion of two Ni²⁺ to Ni³⁺ to keep the electro neutrality of doped NiO. This process is accompanied with a decrease in ionic radii from 0.78 to 0.62Å with a consequent decrease in lattice parameter "a" due to lattice contraction. According to Antolini [24], the structure of Li-Ni-O is based on cubic rock salt structure of the parent nickel oxide, where Li⁺ substitute randomly for Ni²⁺ in the rock salt lattice. In view of the similar ionic radii of Ni²⁺ and Co²⁺, one can not overlook the possibility of dissolution of Li₂O in Co₃O₄ lattice, according to the above solid state inter-

action, with an expected conversion of some Co²⁺ to Co³⁺ and oxygen uptake as :



Where 2Li⁺(Co²⁺) are two Li⁺ replacing two Co²⁺ in the tetrahedral positions of Co₃O₄ spinel with subsequent appearance of two Co³⁺ to keep electro neutrality. Further evidence for these solid-solid interactions was presented from the data of surface non-stoichiometry expressed as concentration of surface excess oxygen as discussed below.

3.2. Energy dispersive x-ray analysis of various solids

EDX investigation of different binary metal oxides calcined at 400 and 600°C was carried out. The relative atomic abundance of Ni, Co and oxygen species in the uppermost surface layers for Co-Ni-OI and Co-Ni-OII with Co₃O₄ contents of 20 and 33 mol %, respectively, are given in Table 2. Assuming a homogeneous distribution of the oxide phases between bulk and surface layers, it can be shown from the table that the composition thus obtained is nearly the same as calculated one within the experimental error. This provided an evidence for complete transformation of metal nitrates and carbonates to the corresponding oxides according to the stoichiometric equations and confirmed the chemical composition of the investigated systems.

Table 2: Surface molar composition of Co₃O₄-NiO system determined by EDX

Solid catalyst	Calcination temperature, °C	Element	Atomic abundance	
			Calculated	Found
Co ₃ O ₄ -NiO-I (20mol%Co ₃ O ₄)	400	O	53.4	53.9
		Ni	26.6	26.1
		Co	20.0	19.4
Co ₃ O ₄ -NiO-II (33mol%Co ₃ O ₄)	400	O	54.5	55.1
		Ni	18.2	17.8
		Co	27.3	26.9

Co₃O₄-NiO-I (20mol%Co ₃ O ₄) 600	O	53.4	53.8
	Ni	26.6	26.0
	Co	20.0	19.5
Co₃O₄-NiO-II (33mol%Co ₃ O ₄) 600	O	54.5	54.8
	Ni	18.2	17.7
	Co	27.3	26.8

3.3. Surface characteristics and non-stoichiometry of pure and doped adsorbents

3.3.1. Surface characteristics

The different surface characteristics of pure and Li₂O-doped Co₃O₄-NiOII calcined at 400 and 600°C were determined from nitrogen adsorption isotherms conducted at -196°C. These characteristics include the specific surface area (S_{BET}), total pore volume (V_p) and pore size expressed as mean pore radius (\bar{r}). Pore size and pore volumes were determined using BJH model. The values of (\bar{r}) for different adsorbents were calculated from the equation: $\bar{r} = 2V_p/S_{BET} \times 10^{-4}$ Å. Pore volume is the volume of liquid adsorbate near saturation pressure, i.e, $P/P_0=0.98$. For nitrogen, it is given by:

$V_p = V_s \times 28/22414 \times d_l$ where V_s is the volume adsorbed at $P/P_0=0.98$ and d_l is the density of liquid nitrogen. Representative N₂-adsorption isotherms for Co₃O₄-NiO II system with Co₃O₄ content of 33% and of chemical formula 0.5Co₃O₄-NiO calcined at 400 and 600°C are presented in Fig.(2). Both isotherms of pure and variously doped Co-Ni-O II followed type II of Brunauer classification. Another series of specific surface area (St) were computed from volume thickness curves (V_{it} plots) of the investigated adsorbents. These curves were constructed using the DeBoor-t curve [28].

The data obtained are listed in Table (3). Inspection of data shows the following:

S_{BET} and St values of the investigated solids are very close justifying the choice of standard t-curve.

Li₂O-doping of Co₃O₄-NiOII led to a progressive increase in S_{BET} with a corresponding increase in V_p and a slight decrease in (\bar{r}).

Rising calcination temperature to 600°C resulted in a considerable decrease in S_{BET} and a slight decrease in V_p with marked increase in (\bar{r}).

The values of mean pore radius reflected the mesoporous nature of all adsorbents.

The observed increase in S_{BET} to an extent proportional to dopant concentration was in consistency with the corresponding decrease in the degree of crystallinity and crystallite size evident from XRD data (Table 1). Pore volume increase could be attributed to the creation of new pores due to liberation of gases upon thermal decomposition of LiNO₃. Both of pore narrowing and pore volume increase contributed markedly in the observed S_{BET} increment. Alternatively, the considerable reduction of S_{BET} upon rising calcination temperature could be attributed to the induced increase in the degree of crystallization and crystallite size as a result of sintering process. Besides, pore widening and pore volume decrease effectively reduced the value of S_{BET} .

Table (3): Surface characteristics of pure and Li₂O-doped Co₃O₄-NiOII .

Adsorbent	Calcination temperature, °C	S_{BET} , m ² /g	St, m ² /g	V_p , ml/g	\bar{r} , Å
Co₃O₄-NiOII	400	110	107	0.209	38
+2mol% Li ₂ O		121	120	0.223	37
+4mol% Li ₂ O		132	135	0.237	36
+6mol% Li ₂ O		143	141	0.250	35
Co₃O₄-NiOII	600	65	64	0.202	62
+2mol% Li ₂ O		71	69	0.214	60
+4mol% Li ₂ O		78	79	0.230	59
+6mol% Li ₂ O		84	83	0.242	58

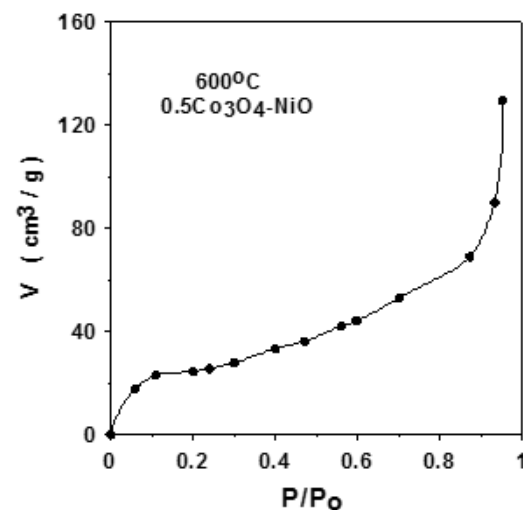
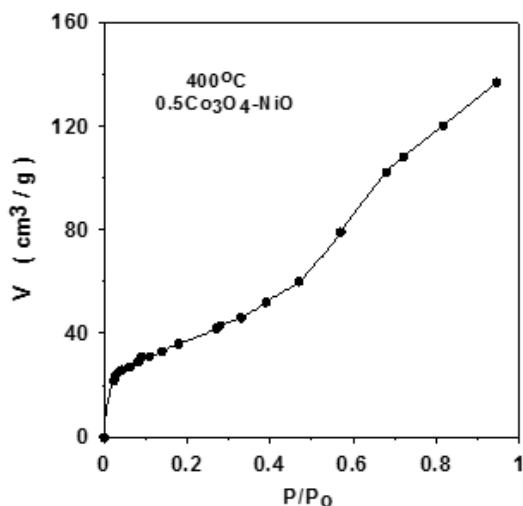
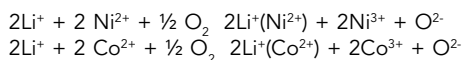


Fig. (2) N₂-adsorption isotherms for Co₃O₄-NiOII (0.5Co₃O₄-NiO) system with Co₃O₄ content of 33 mol% calcined at 400 and 600°C

3.3.2. Surface non-stoichiometry

Surface non-stoichiometry of pure and doped samples was determined by chemical analysis of surface excess oxygen (SEO) using hydrazine method reported by Kobayashi et.al [29]. The results obtained are summarized in Table (4). Li₂O-doping of Co₃O₄-NiOII brought about a corresponding increase in SEO which was more pronounced for sam-

ples calcined at 400°C. Rising calcination temperature to 600°C resulted in lowering the concentration of SEO. The observed increase in SEO which ran parallel to dopant concentration presented further evidence for the solid-solid interaction in terms of dissolution of Li^+ in both NiO and Co_3O_4 lattice with a consequent oxygen uptake and surface enrichment with chemisorbed oxygen as previously mentioned in section 3.1:



Recalling that the ionic radii of Li^+ , Ni^{2+} and Co^{2+} (0.60, 0.78 and 0.78Å, respectively) facilitates these interactions [28-30]. On the other hand, the encountered decrease in SEO upon rising calcination temperature to 600°C was consistent with the decrease in S_{BET} due to sintering process and pore widening together with the removal of some chemisorbed oxygen at elevated temperature.

Table(4): Concentration of surface excess oxygen for pure and Li_2O -doped Co_3O_4 -NiO II.

Catalyst	Surface excess oxygen, mg/g	
	Calcined at 400°C	Calcined at 600°C
Co_3O_4 -NiOII	16.6	10.1
+2mol% Li_2O	18.3	11.1
+4mol% Li_2O	19.9	12.2
+6mol% Li_2O	21.6	13.4

3.4 Catalytic activity of pure and Li_2O -doped binary Co-Ni oxides systems.

3.4.1. Catalytic activity of pure and Co_3O_4 -NiO with different Co_3O_4 content

The catalytic activity of pure NiO and Co-Ni-O system with different Co_3O_4 contents was checked towards gas phase oxidation of CO by O_2 at temperature range 175-225°C. First-order kinetics was observed in all cases for a plot of $\ln(P_0/P)$ vs. time, where P_0 and P denote the initial reactants pressure and that at different time intervals, respectively. The conversion percent is given by $(P_0 - P/P_0) \times 100$ and the slope of first-order plots gives directly the reaction rate constant (k) at given temperature, which monitors the catalytic activity of studied sample. Fig. (3) depicts representative first-order plots of CO oxidation conducted at 175-225°C over pure NiO and binary Co_3O_4 -NiO systems calcined at 400°C. It can be shown from Fig.(3) that all binary systems were devoted with better activity compared to pure NiO passing through a maximum value for the system Co_3O_4 -NiOII having Co_3O_4 content of 33 mol%. Alternatively, a drop in the catalytic activity for all samples was regarded upon rising calcination temperature to 600°C with the same trend of relative activities for pure NiO and binary oxides of different Co_3O_4 content. It was reported by Gou et.al [18] that the composite Co-Ni bimetal oxides show a better activity than the corresponding individual metal oxides. The observed improvement of catalytic activity with increasing Co_3O_4 content up to 33 mol % could be correlated to the corresponding increase in the concentration of Co^{3+} constituting the active center for CO chemisorption and catalytic conversion [9,10,18,33,34].

In addition, the presence of binary Co_3O_4 -NiO system would enhance the mobility and release of lattice oxygen responsible for CO oxidation as discussed in the next part of this section. Furthermore, the increased degree of dispersion in binary oxides system, as compared to pure NiO, monitored by lowering the degree of crystallinity as evident from XRD analysis would result in a corresponding increase in the active centers accessible to catalytic reaction. Alternatively, the lowering of catalytic activity induced by increasing Co_3O_4 content to 50 mol % could be attributed to the formation of NiCo_2O_4 spinel according to the stoichiometric equation in section (3.1). The similarity of ionic radii of Ni^{2+} and Co^{2+} (0.78Å) favored the formation of nickel cobaltite of lower catalytic activity [18]. The drop in catalytic activity at elevated calcination temperature came because of the lowering of surface area due to sintering process and pore widening with consequent decrease in the surface active sites accessible to catalyzed reaction.

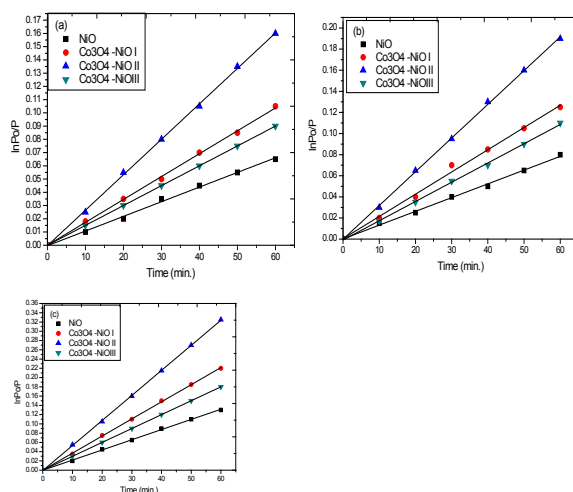


Fig.(3) first-order plots of CO oxidation by O_2 over binary Co_3O_4 -NiO with different Co_3O_4

contents calcined at 400°C. Reaction temperature, °C (a) : 175, (b): 200, (c): 225.

Co_3O_4 content, mol%: I: 20, II: 33, III: 50

P_0 , P are the reactants initial pressure and that at different time intervals, respectively

3.4.2. Catalytic activity of pure and Li_2O -doped Co_3O_4 -NiOII.

The most active system Co_3O_4 -NiOII was subjected to Li_2O -doping with dopant concentration 2-6 mol%. The catalytic activity of doped samples compared to that of pure one was checked towards CO oxidation at the same conditions mentioned above. Representative first-order plots of CO oxidation over pure and doped Co_3O_4 -NiOII calcined at 400°C are shown in Fig. (4). The catalytic activity expressed as reaction rate constant per unit mass (k) as a function of dopant concentration for catalysts calcined at 400 and 600°C are monitored in Table (5). Both Fig. (4) and Table (5) indicated a progressive improvement in catalytic activity to an extent proportional to dopant concentration. Moreover, Samples fired at 400°C were devoted with higher activity compare to that thermally treated at 600°C.

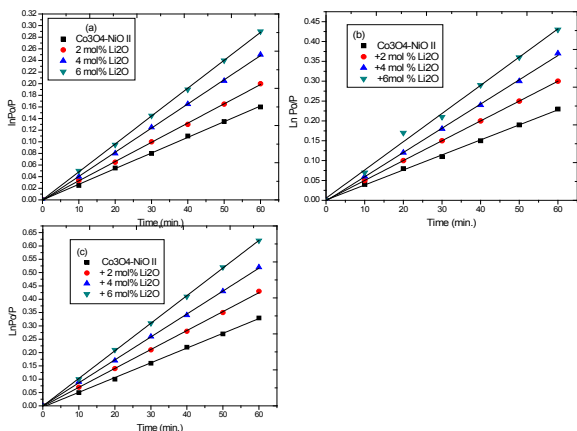


Fig. (4) First-order plots of catalytic oxidation of CO by O₂ over pure and Li₂O-doped Co₃O₄-NiOII calcined at 400°C. Reaction temperature : (a) 175°C, (b) 200°C, (c) 225°C

Table (5): Reaction rate constant per unit mass (k, min⁻¹g⁻¹) for the catalytic oxidation of CO by O₂ conducted at 175-225°C over pure and Li₂O-doped Co₃O₄- NiOII .

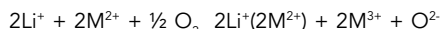
Catalyst	Calcination temp., °C	k ₁₇₅ , min ⁻¹ g ⁻¹	k ₂₀₀ , min ⁻¹ g ⁻¹	k ₂₂₅ , min ⁻¹ g ⁻¹
Co ₃ O ₄ -NiOII	400	2.68x10 ⁻³	3.81x10 ⁻³	5.46x10 ⁻³
+2mol%Li ₂ O		3.30	4.95	7.12
+4mol%Li ₂ O		4.11	6.10	8.71
+6mol%Li ₂ O		4.82	7.11	10.37
Co ₃ O ₄ -NiOII	600	1.18x10 ⁻⁴	2.10x10 ⁻⁴	3.41x10 ⁻⁴
+2mol%Li ₂ O		1.40	2.51	4.11
+4mol%Li ₂ O		1.72	2.90	4.82
+6mol%Li ₂ O		1.91	3.42	5.41

It was reported that Co³⁺ located at the octahedral positions of Co₃O₄ spinel constituted the active center for CO chemisorption as evident from DFT calculations [11, 35]. According to Xu et. al [35], CO oxidation over Co₃O₄ followed a Mars-Van Krevelen mechanism at which CO chemisorbed on Co³⁺ site was oxidized by adjacent lattice oxygen with the creation of oxygen vacancy site which was refilled by gas phase oxygen with subsequent reform of lattice oxygen. According to this mechanism, lattice oxygen withdrawal is slow while the reoxidation of catalyst surface is fast and hence CO oxidation is the rate-determining step. So, the reaction should follow first-order kinetics, a condition that was realized in this work.

Extending this argument to NiO, CO would preferentially adsorbed on Ni³⁺ as an electron acceptor site. The presence of Ni³⁺ in NiO was confirmed by Ni2p XPS spectra [36, 37]. Furthermore, the presence of non-stoichiometric Ni³⁺ as lattice defect in NiO was reported by Kostad [38] who explained the electrical conductivity of NiO in terms of hopping mechanism via electron transfer between Ni³⁺ and Ni²⁺ ions.

The results of XRD and surface non stoichiometry analyses indicated that lithia -doping of Co₃O₄-NiOII resulted in successive increase in both Co³⁺ and Ni³⁺ concentration as evident from NiO lattice parameter decrease implying lattice contraction together with increasing the concentration of surface excess oxygen as reported in the preceding discussion section(3.1) and (3.3.2). Both Co₃O₄ and NiO are p-type semiconductors that can dissolve Li₂O in their

lattice [38-40]. The dissolution of lithia in both oxides was better simplified by Kröger's mechanism [28] and reported by El-Shobaky et.al [40, 41] as follows:



Where 2M are two divalent Co or Ni ions being replaced by two Li⁺ with simultaneous conversion of two divalent cation to trivalent state to retain the electro neutrality with oxygen uptake process. Therefore, the accelerating effect of CO oxidation over Lithia-doped Co₃O₄-NiOII could be correlated to the corresponding increase in the concentration of Co³⁺ and Ni³⁺ constituting the active sites for CO chemisorption. It is worth mentioning that the observed drop in catalytic activity of all solids fired at 600°C could be attributed to the indicated lowering of S_{BET} resulting from sintering process with an expected decrease in surface active sites accessible to CO chemisorption.

Determination of activation energy (ΔEa) for CO oxidation over pure and lithia -doped Co₃O₄-NiOII 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 29.69- 30.76 kJ/mol and 43.13-44.06 kJ/mol 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 was believed that doping process did not modify the mechanism or energetic nature of catalyzed reaction but rather changed the concentration of active sites involved.

Table (6): Activation energy and frequency factor for the catalytic oxidation of CO over pure and Li₂O-doped Co₃O₄-NiOII .

Catalyst	Calcination temp., °C	lnA	ΔEa, kJ/mol
Co ₃ O ₄ -NiOII	400	5.09	29.69
+2mol%Li ₂ O		4.87	31.17
+4mol%Li ₂ O		4.62	33.25
+6mol%Li ₂ O		4.46	30.76
Co ₃ O ₄ -NiOII	600	5.57	43.13
+2mol%Li ₂ O		5.39	44.06
+4mol%Li ₂ O		5.24	43.03
+6mol%Li ₂ O		5.11	43.23

Conclusions

- Binary Co₃O₄-NiO showed better activity for oxidation of CO by oxygen in all Co₃O₄ proportions than pure NiO.
- The solid Co₃O₄-NiOII with Co₃O₄ content of 33 mol% was devoted with maximum catalytic activity for CO oxidation.
- Lithia-doping of Co₃O₄-NiOII resulted in considerable change as regard to surface characteristics and surface stoichiometry as well.
- The catalytic activity of Co₃O₄-NiOII was markedly improved by Li₂O-doping.
- Doping process did not modify the energetic nature or mechanism of catalyzed reaction but rather changed the concentration of active sites involved.

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To the Spirit of Prof. G.A.El-Shobaky who left but his name still alive.

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