

# Catalytic Conversion of Isopropanol and CO Oxidation in Presence of NiO Supported on Modified Cordierite

S.A. El-Molla<sup>\*1</sup>, G.A. El-Shobaky<sup>2</sup>, Y.M. Fahmy<sup>2</sup> and H.G. El-Shobaky<sup>3</sup>

<sup>1</sup>Chemistry Department, Faculty of Education, Ain Shams University, Roxy, Heliopolis, Cairo 11757, Egypt

<sup>2</sup>National Research Center, Dokki, Cairo, Egypt

<sup>3</sup>Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt

**Abstract:** A commercial cordierite sample showed a small catalytic activity in isopropanol conversion carried out at 150-350 °C and no measurable activity in CO oxidation by O<sub>2</sub>. On the other hand, supporting NiO on Al<sub>2</sub>O<sub>3</sub>-modified cordierite resulted in the formation of an active solid that having good catalytic activity in isopropanol conversion and CO oxidation by O<sub>2</sub>. These two reactions were carried out at 150-350 and 200 °C, respectively. The results revealed that the catalyst containing 5% (w/w) NiO showed the highest activity in the alcohol conversion and acted as selective dehydration catalyst. The catalyst sample containing 20% NiO (w/w) exhibited a good activity in CO oxidation by O<sub>2</sub> which decreased progressively by increasing its calcination temperature within 350-600 °C. Al<sub>2</sub>O<sub>3</sub>-treated cordierite dissolved a portion of NiO in its lattice, increasing the calcination temperature within 350-600 °C increases the dissolution of NiO in the matrix of Al<sub>2</sub>O<sub>3</sub>-modified cordierite system.

**Keywords:** EDX, Catalytic activity, NiO/Cordierite, Al<sub>2</sub>O<sub>3</sub>-treatment.

## INTRODUCTION

Supported transition metal oxides constitute an interesting class of catalytic materials. These materials are used in many important industrial and environmental applications such as CO oxidation [1], N<sub>2</sub>O decomposition [2], methane steam reforming [3], dehydration and dehydrogenation of alcohols [4]. The catalytic activity and selectivity of the oxide catalyst can be modified by loading on different support materials [5, 6]. The interaction between the support and transition metal oxide can take place *via* of formation metal aluminate in case of alumina- support, or solid solution in case of MgO support [7,8] having small catalytic activity if compared to metal oxide-supported solid. For this reason it is important to study the possibility of obtaining membranes which can not react with the catalytically active phase (transition metal oxide) and with low cost to be economic. Cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>) is a crystalline magnesium aluminosilicate and is one of the phases of MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [9]. This material has low cost, low pressure drop in the exhaust system, good thermal resistance and low expansion coefficient [10]. These properties characterize cordierite as a potentially available material employed in electronic industry [10]. Also, cordierite is commercial material for high temperature catalyst applications, specially for automotive catalysts due its high mechanical stability and low thermal expansion coefficient [11]. As a rule cordierite has a low specific surface area that could be increased by treatment with

alumina [12]. The big surface area is very desirable. It has been shown that the increase of the total surface area of the monolith is the most effective way to increase the conversion of automotive pollutants for a given loading of precious metals [13]. Cordierite has been successfully used as a catalyst support for Co<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, CuO, Fe<sub>2</sub>O<sub>3</sub> and NiO [1, 14, 15].

This work aims at studying the physicochemical surface and catalytic properties of NiO supported on cordierite support material. The effects of extent of NiO-loading, calcination temperature and treating cordierite with Al<sub>2</sub>O<sub>3</sub> using a washcoating technique on its physicochemical surface and catalytic properties have been investigated [16]. Different physicochemical surface and catalytic properties of NiO supported on Al<sub>2</sub>O<sub>3</sub>-modified cordierite support material were investigated using XRD, EDX, nitrogen adsorption at -196 °C and catalytic conversion of isopropanol at 150- 350 °C using the flow method and CO oxidation by O<sub>2</sub> at 200 °C.

## EXPERIMENTAL

### Sample Preparation

A commercial cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>) supplied by Baikowski Inc. company was treated with 25% Al<sub>2</sub>O<sub>3</sub> (w/w) using a washcoating technique. A given mass of aluminum ethoxide was dissolved in a convenient volume of ethanol and few drops of HCl (28%) and subjected to stirring for 60 min. A calculated amount of cordierite was then impregnated with alcoholic solution of aluminum ethoxide and stirred for 30 min. at 60 °C. The obtained solid was dried at 110 °C till constant weight. The dried solid was used as a catalyst support for NiO. The Al<sub>2</sub>O<sub>3</sub>-treated cordierite sample was then impregnated with calculated amounts of nickel nitrate

\*Address correspondence to this author at the Chemistry Department, Faculty of Education, Ain Shams University, Roxy, Heliopolis, Cairo 11757, Egypt; Tel: +202 24558087; Fax: +202 22581243; E-mail: saharelmolla@yahoo.com

dissolved in the least amounts of distilled water. The nominal compositions of the calcined impregnated solids were 5, 10 and 20% NiO (w/w). The obtained solids were dried at 110 °C then calcined at 350- 600 °C for 4h. All the chemicals employed were of analytical grade supplied by BDH Ltd.

### Characterization

Phase analysis of the pure and variously treated specimens calcined in air at 350, 450 and 600 °C was performed by X-ray powder diffraction employing a BRUKER Axs D8 Advance, Germany. Patterns were run using Ni-filtered copper radiation ( $\lambda = 1.5404 \text{ \AA}$ ) at 40 kV and 40 mA. The crystallite size of NiO phase in different catalysts was calculated using the Scherrer equation [17] from line broadening profile analysis of the main diffraction lines of NiO phase at a scanning rate of 0.2 degree in 2  $\theta$ /min. through TOPAZ2.Inc program.

Energy dispersive X-ray analysis (EDX) was carried out on Hitachi S-800 electron microscope with an attached keveX Delta system. The parameters were as follows: accelerating voltage 15 kV, accumulation time 100s, window width 8  $\mu\text{m}$ . The surface molar composition was determined by the Asa method, Zaf-correction, Gaussian approximation.

The specific surface areas of the pure and variously treated samples were determined from nitrogen adsorption isotherms measured at -196 °C using a conventional volumetric apparatus. All samples were degassed at 200 °C for 3 hours under a reduced pressure of  $10^{-5}$  Torr before undertaking such measurements.

The catalytic activities of various investigated solids were determined by using each of oxidation of CO by O<sub>2</sub> at 200°C and iso-propanol conversion at 150-300 °C. The catalytic activities in CO oxidation by O<sub>2</sub> were determined using a static method and the kinetics of this reaction were monitored by measuring the pressure of the reacting gases at different time intervals until no change in pressure was attained. Each catalyst sample (200 mg) was activated by heating at 300 °C for 2 h. under a reduced pressure  $10^{-6}$  Torr. A stoichiometric mixture of CO and O<sub>2</sub> (CO+1/2O<sub>2</sub>) at a pressure of 2 Torr was used. The reaction product (CO<sub>2</sub>) was removed from the reaction atmosphere by freezing at liquid nitrogen temperature. So, the percentage decrease of the reacting gases at a given time interval determines the percentage conversion of catalytic reaction at that time. The saturation vapor pressure of CO at -196 °C being 160 Torr makes its liquefaction at that pressure improbable under the employed conditions (2 Torr) [7].

The catalytic conversion of isopropanol using various catalyst samples were determined at 150-350°C, the catalytic reaction being conducted in a flow reactor under atmospheric pressure. Thus, a 50 mg catalyst sample was held between two glass wool plugs in a Pyrex glass reactor tube 20 cm long and 1 cm internal diameter packed with quartz fragments 2-3 mm length. The temperature of the catalyst bed was regulated and controlled to within  $\pm 1$  °C. Argon gas was used as the diluent and the isopropyl alcohol vapor was introduced into the reactor through an evaporator/saturator containing the liquid reactant at constant temperature 35°C. The flow rate of the carrier gas was maintained at 25 ml/min.

Before carrying out such catalytic activity measurements, each catalyst sample was activated by heating at 300 °C in a current of argon for 2 hours then cooled to the catalytic reaction temperature. The reaction products in the gaseous phase were analyzed chromatographically using Perkin-Elmer Auto System XL Gas Chromatograph fitted with a flame ionization detector. The column used was fused silica glass capillary column type PE-CW length 15 m-1.0 UM Perkin-Elmer corp.

## RESULTS AND DISCUSSION

### EDX Investigation of Different Solids

Energy dispersive x-ray (EDX) investigation of untreated cordierite, 20% (w/w) NiO/cordierite, 25%Al<sub>2</sub>O<sub>3</sub>-cordierite and 20%NiO/25%Al<sub>2</sub>O<sub>3</sub>-cordierite samples calcined at 350-600 °C was carried out. The atomic abundance of nickel, aluminum, magnesium, silicon and oxygen species present in the uppermost surface layers of the calcined solids is given in Table 1. The atomic abundance of all cordierite constituents in its whole mass was calculated based on the formula of untreated cordierite samples and those treated with 20 wt% NiO and/or 25wt% Al<sub>2</sub>O<sub>3</sub>. The data obtained are also given in Table 1. Inspection of the results given in Table 1 reveals the following: (i) The calculated concentration of atoms constituting untreated cordierite in the bulk is similar to that found in the uppermost surface layers (from EDX data). This finding indicates the homogeneous structure of investigated cordierite sample. (ii) The concentration of Ni species present in the uppermost surface layers (determined by EDX) of cordierite samples treated with 20% NiO calcined at 350 °C are slightly smaller than those present in the bulk of solid(calculated). The difference is 16%. It is also found that the concentration of Ni species present in the uppermost surface layers determined by EDX decreases with increasing the calcination temperature from 350 to 600 °C. It is predicted that, the surface concentration of Ni species should be greater than that present in the bulk because the samples were prepared by wet impregnation method [18]. However, this speculation has not been observed experimentally in case of NiO/cordierite system. This discrepancy could be attributed to the dissolution of a significant portion of NiO present in the matrix of cordierite support material. In fact, the EDX investigation of NiO/cordierite-alumina system calcined at different calcination temperatures (Table 1) shows clearly that the rise in the calcination temperature for the catalyst sample from 350 to 450 °C led to an increases in the amount of Ni species dissolved in the matrix of the cordierite. In fact, it has been reported by El-Shobaky *et al.* that cordierite support material can dissolve different amounts of Mn<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CuO to an extent dependent mainly on the nature of transition metal species and calcination temperature [1,14, 15]. (iii) The concentration of Al species added to cordierite was found to be slightly higher than that present in the bulk, the difference attained 5%. (iv) The comparison between the surface concentration of Ni species in the untreated and Al<sub>2</sub>O<sub>3</sub>-treated cordierite shows clearly that Al<sub>2</sub>O<sub>3</sub>-treatment increases effectively the extent of Ni species present in the uppermost surface layers of the cordierite support material. This finding might be attributed to the possible effective increase in the dispersion power of

**Table 1. Surface Molar Composition of Cordierite, NiO/Cordierite, Al<sub>2</sub>O<sub>3</sub>-Cordierite and NiO/Al<sub>2</sub>O<sub>3</sub>-Cordierite Solids Determined by EDX**

Solid	Calcination Temperature °C	Element	Atomic Abundance (Atom %)	
			Calculated (Bulk)	Found (Surface)
Cordierite	350	Mg	6.9	6.3
		Al	13.8	13.9
		Si	17.2	17.6
		O	62.1	62.3
		Ni	0	0
20% NiO/Cordierite	350	Mg	6.1	6.5
		Al	12.2	12.9
		Si	15.2	15.0
		O	60.6	60.7
		Ni	5.9	5.0
25%Al <sub>2</sub> O <sub>3</sub> -Cordierite	350	Mg	5.2	4.6
		Al	20.3	21.1
		Si	13.0	12.6
		O	61.6	61.6
		Ni	0	0
20% NiO/ 25%Al <sub>2</sub> O <sub>3</sub> -Cordierite	350	Mg	4.6	4.5
		Al	17.9	17.8
		Si	11.4	11.3
		O	60.2	60.1
		Ni	6.0	6.4
20% NiO/Cordierite	450	Mg	6.1	5.4
		Al	12.2	13.2
		Si	15.2	16.0
		O	60.6	61.7
		Ni	5.9	3.7
20% NiO/ 25%Al <sub>2</sub> O <sub>3</sub> -Cordierite	450	Mg	4.6	5.0
		Al	17.9	18.1
		Si	11.4	11.5
		O	60.2	60.8
		Ni	5.9	4.5
20% NiO/Cordierite	600	Mg	6.1	6.1
		Al	12.2	13.3
		Si	15.2	16.0
		O	60.6	62.0
		Ni	5.9	2.6
20% NiO/ 25%Al <sub>2</sub> O <sub>3</sub> -Cordierite	600	Mg	4.6	5.1
		Al	17.9	18.5
		Si	11.4	11.7
		O	60.2	61.4
		Ni	5.9	3.1

Al<sub>2</sub>O<sub>3</sub>-treated solid towards nickel species. This influence might result from the possible appreciable increase in the specific surface area of the Al<sub>2</sub>O<sub>3</sub>-treated cordierite solid. This speculation will be confirmed later in the next section of the present work. Increasing the calcination temperature of all nickel containing solids from 350 to 600 °C resulted in a progressive decrease in surface concentration of nickel. This decrease might result from an enhanced diffusion of nickel species from top surface layers towards the bulk of calcined solids. This process should be accompanied by an effective dissolution of nickel species in the matrix of the support material.

### XRD Investigation of Different Investigated Solids

X-Ray powder diffractograms of cordierite support material treated with 10 and 20% NiO oxide calcined at 350, 450 and 600 °C were determined. X-Ray diffractograms of cordierite support material being treated with 25% Al<sub>2</sub>O<sub>3</sub> and 5, 10, 20% NiO and calcined at 350, 450 and 600 °C were carried out. Figs. (1-3) depicts the diffractograms of various solids calcined at 350, 450 and 600 °C, respectively. Examination of Figs. (1-3) shows the following: (i) Al<sub>2</sub>O<sub>3</sub>-treatment of cordierite followed by calcination at 350-600 °C led to a drop in the degree of crystallinity of the cordierite i.e. the relative intensity of all diffraction lines of the cordierite suffered a drastic decrease. This finding indicates clearly that Al<sub>2</sub>O<sub>3</sub> brought about a significant structure collapse of cordierite structure more than 50% as evidenced from the significant drop (50%) in the relative intensity of all diffraction lines of cordierite solid. (ii) All diffraction lines of NiO were detected in the diffractograms of NiO containing solids even those treated with 5% NiO. (iii) The relative intensity of diffraction lines of NiO increases progressively by increasing the NiO content. The crystallite size and degree of crystallinity of NiO present in different solids calcined at different temperatures were calculated and the results obtained are given in Table 2. This table shows clearly that NiO phase existed as nanocrystalline material. (iv) Although the concentration of 5% NiO in the Al<sub>2</sub>O<sub>3</sub>-treated cordierite calcined at 600 °C seems to be beyond the detection limit of x-ray diffractometer, all diffraction lines of

this phase were detected (c.f. Fig. 3). This finding might suggest an enriched existence of this phase on top surface layers of the calcined solid. This conclusion has been reached at by EDX investigation previously given in the present work. (v) Examination of Table 2 shows also that Al<sub>2</sub>O<sub>3</sub> treatment of NiO-containing cordierite brought about a significant drop in the degree of crystallinity of NiO with subsequent decrease in its crystallite size.

### Specific Surface Areas of Different Investigated Solids

The specific surface area (S<sub>BET</sub>) of cordierite support material and samples treated with Al<sub>2</sub>O<sub>3</sub> and NiO oxides and being calcined at 350, 450 and 600 °C were determined. The obtained results are given in Table 3. Inspection of Table 3 reveals the following: (i) The S<sub>BET</sub> of cordierite support material is very small increasing tremendously with treatment with 25% Al<sub>2</sub>O<sub>3</sub> calcined at 350-600 °C. The increase in the S<sub>BET</sub> of cordierite due to alumina treatment reaches to 30-fold. (ii) Increasing the calcination temperature from 350 to 450 °C and from 450 to 600 °C for alumina-cordierite solids decreases their surface areas with 9 and 19%, respectively. These results show the high thermal stability of alumina-cordierite samples. (iii) Treating alumina-cordierite samples with 10 and 20% NiO followed by calcination at 350, 450 and 600 °C led to a further small increase in the S<sub>BET</sub> of the treated samples. The observed increase in the specific surface area of cordierite due to alumina treatment is expected not only because of the relatively big surface area of Al<sub>2</sub>O<sub>3</sub> compared to that of cordierite but also because of the method of preparation which led to the formation of very fine crystallites.

The significant increase in the specific surface areas of cordierite samples due to their treatment with Al<sub>2</sub>O<sub>3</sub> and/or NiO oxides is expected to modify their catalytic properties.

### Catalytic Oxidation of CO by O<sub>2</sub> Over Different Solids

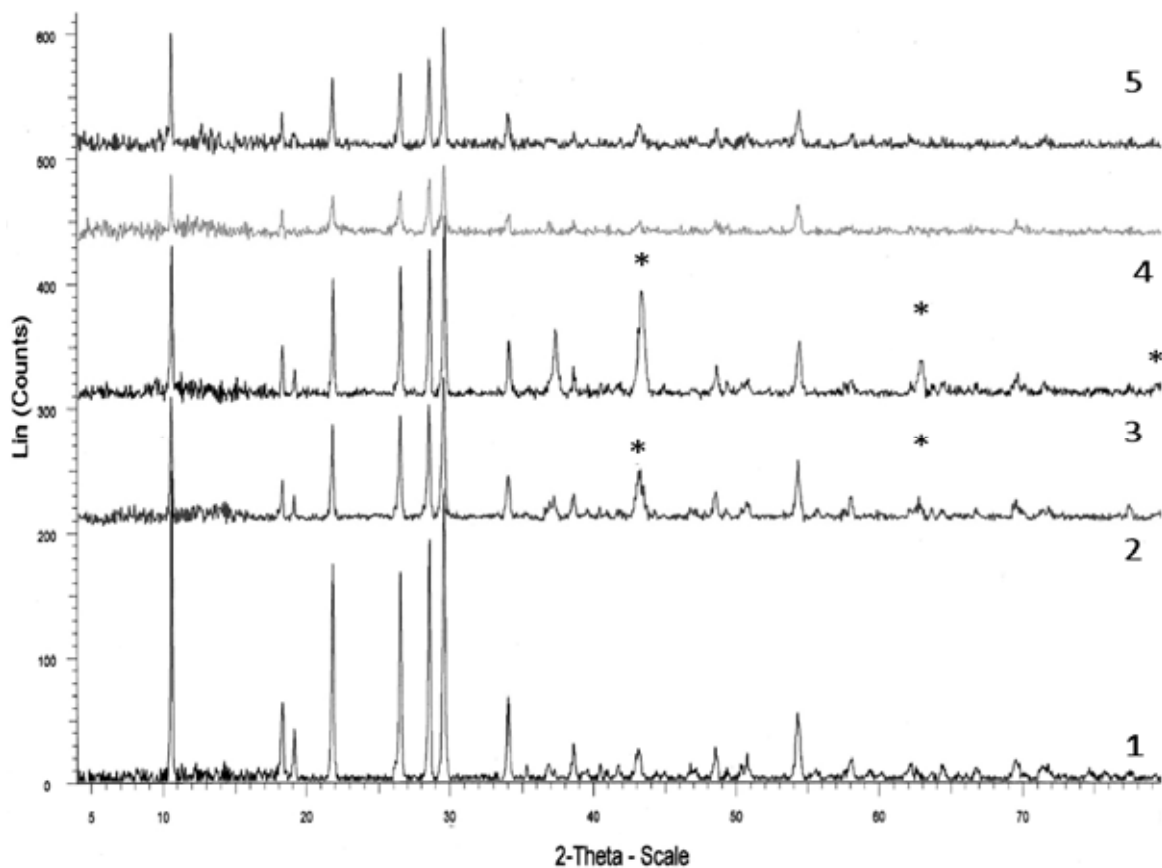
Preliminary experiments showed that the employed untreated cordierite and the Al<sub>2</sub>O<sub>3</sub>-treated solids exhibited no measurable activity in CO oxidation by O<sub>2</sub> even by carrying out the reaction at relatively high temperature reaching to

**Table 2. The Crystallite Size and Degree of Crystallinity of NiO Phase in Different Investigated Solids**

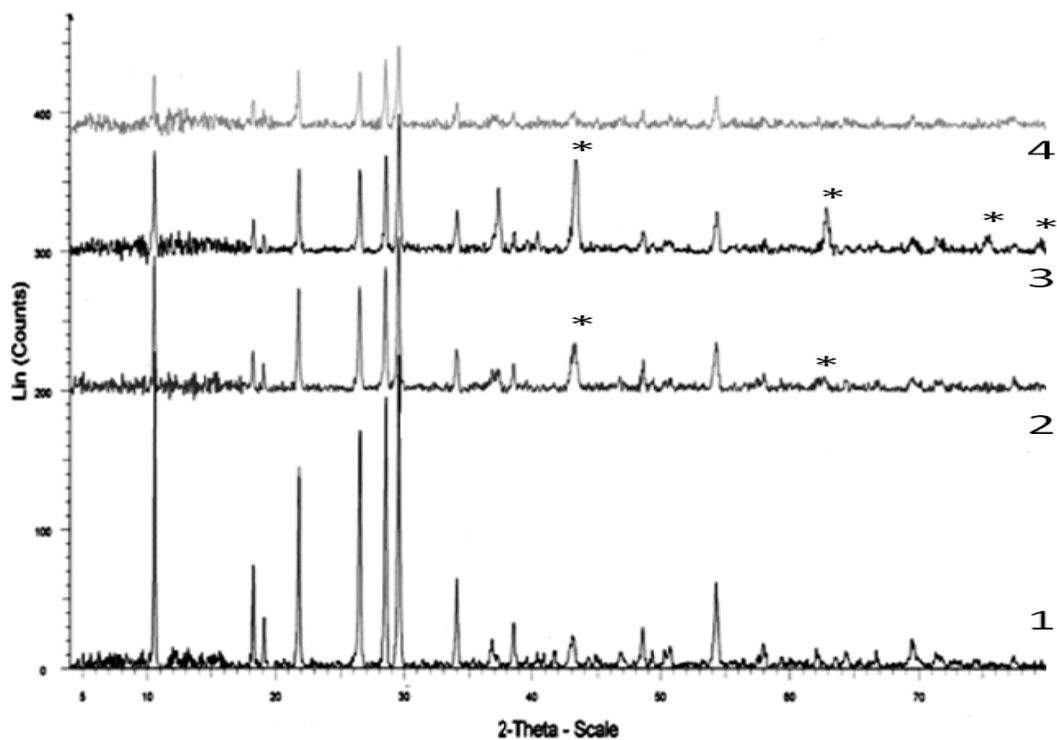
Sample	Calcination Temperature	Crystallite Size of NiO (nm) <sup>b</sup>	Degree of Crystallinity (a.u) <sup>a</sup>
10%NiO/cordierite	350 °C	20.7	40.8
20%NiO/cordierite	350 °C	22.3	92.7
10%NiO/cordierite	450 °C	16.5	36
20%NiO/cordierite	450 °C	25.6	75.5
10%NiO/cordierite	600 °C	20.8	36
10%NiO/cordierite-25% Al <sub>2</sub> O <sub>3</sub>	350 °C	23	20.4
10%NiO/cordierite- 25% Al <sub>2</sub> O <sub>3</sub>	450 °C	3	13
5%NiO/cordierite- 25% Al <sub>2</sub> O	600 °C	17.7	29.1
10%NiO/cordierite- 25% Al <sub>2</sub> O <sub>3</sub>	600 °C	20	20
20%NiO/cordierite-25% Al <sub>2</sub> O <sub>3</sub>	600 °C	36.7	22.2

<sup>a</sup>The areas of the main diffraction lines of NiO phase were taken as a measure of degree of crystallinity of this phase.

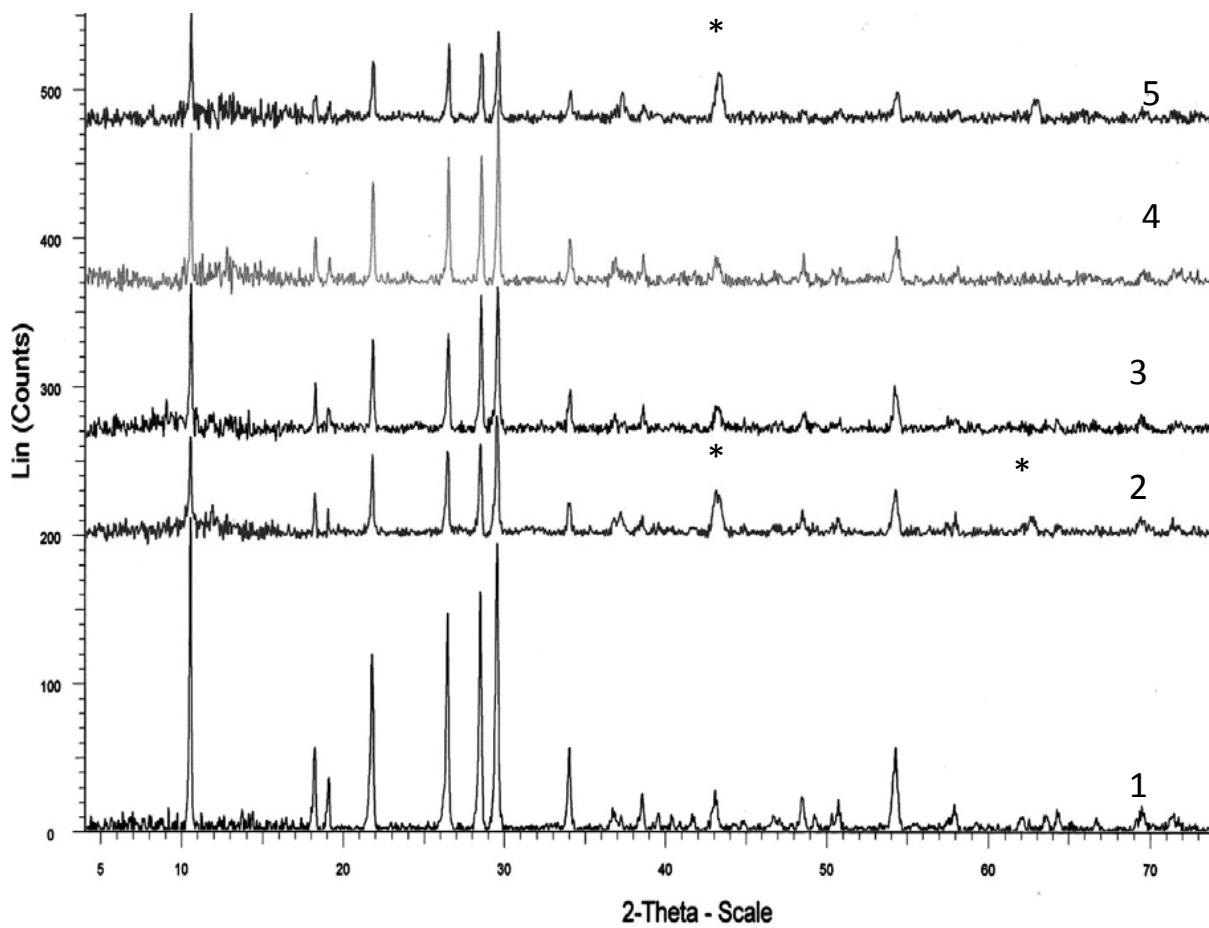
<sup>b</sup>The hkl of the main diffraction lines of NiO phase (012) was considered in calculating the crystallite size of NiO phase.



**Fig. (1).** XRD diffractograms of: (1) Cordierite, (2) 10% NiO/Cordierite, (3) 20% NiO/Cordierite, (4) Cordierite- 25%alumina and (5) 10% NiO/Cordierite-25% alumina precalcined at 350 °C. \* For NiO phase and the other lines are related to cordierite phase.



**Fig. (2).** XRD diffractograms of: (1) Cordierite, (2) 10% NiO/Cordierite, (3) 20% NiO/Cordierite and (4) 10% NiO/Cordierite-25% alumina precalcined at 450 °C. \* For NiO phase and the other lines are related to cordierite phase.



**Fig. (3).** XRD diffractograms of: (1) Cordierite, (2) 10% NiO/Cordierite, (3) 5% NiO/Cordierite-25%alumina, (4) 10% NiO/Cordierite-25%alumina and (5) 20% NiO/Cordierite-25% alumina precalcined at 600 °C. \* For NiO phase and the other lines are related to cordierite phase.

300 °C. So, the cordierite acted as a catalyst support for CO oxidation by O<sub>2</sub>. The catalytic oxidation of CO by O<sub>2</sub> was carried out at 200 °C over nickel/ cordierite-alumina system containing 20% NiO and calcined at 350, 450 and 600 °C. The catalytic reaction was found to follow first-order kinetics in all cases. The slope of the first order plots (not given) determines the reaction rate constant *k* at a given temperature over a given catalyst sample. The computed *k* values were found to be 7, 2.4 and 0.7 × 10<sup>-2</sup> min<sup>-1</sup>. g<sup>-1</sup> for the reaction carried out at 200 °C over the samples calcined at 350, 450 and 600 °C, respectively. This finding indicates clearly that the rise in precalcination temperature of nickel/cordierite-alumina system suffered a drastic decrease in its activity towards catalytic oxidation of CO by O<sub>2</sub> because of increasing its calcination temperature from 350 to 450 °C. The rise in the precalcination temperature above this limit brought about a limited decrease in its catalytic activity. The observed remarkable decrease in the catalytic activity might indicate a significant decrease in the concentration of active sites involved in chemisorption and catalysis of CO oxidation by O<sub>2</sub>. This decrease could be attributed to a significant decrease in surface concentration of NiO (catalytically active constituent in CO oxidation reaction). This decrease could result from the dissolution of a significant portion of NiO present in the matrix of the cordierite support material. In fact, the EDX investigation of

NiO/cordierite–alumina system calcined at different temperatures (Table 1) shows clearly that the rise in the calcination temperature for the catalyst sample from 350 to 450 °C led to a considerable decrease in surface concentration of Ni species present in the top surface layers of the treated solids.

### Catalytic Conversion of Isopropanol Over Different Investigated Solids

#### *Effect of Extent of NiO Loading on the Activity NiO/Cordierite System Towards Isopropanol Conversion*

The catalytic conversion of isopropanol was carried out over 10 and 20% NiO/cordierite solids calcined at 350, 450 and 600 °C. The same catalytic reaction was also carried out over cordierite material calcined at the same temperatures. Fig. (4) shows the effect of extent of NiO loading of NiO/cordierite system calcined at 350–600 °C on its catalytic activity expressed as the total conversion. The same figure shows the selectivity towards propene formation for the reaction carried out at 275 °C. It is noticed from Fig. (4) that: (i) the cordierite exhibited a measurable catalytic activity, which increased by increasing the calcination temperature from 350 to 450 °C and then decreased with increasing the calcination temperature to 600 °C. (ii) Supporting 10% NiO on cordierite material calcined at 450 and 600 °C increased

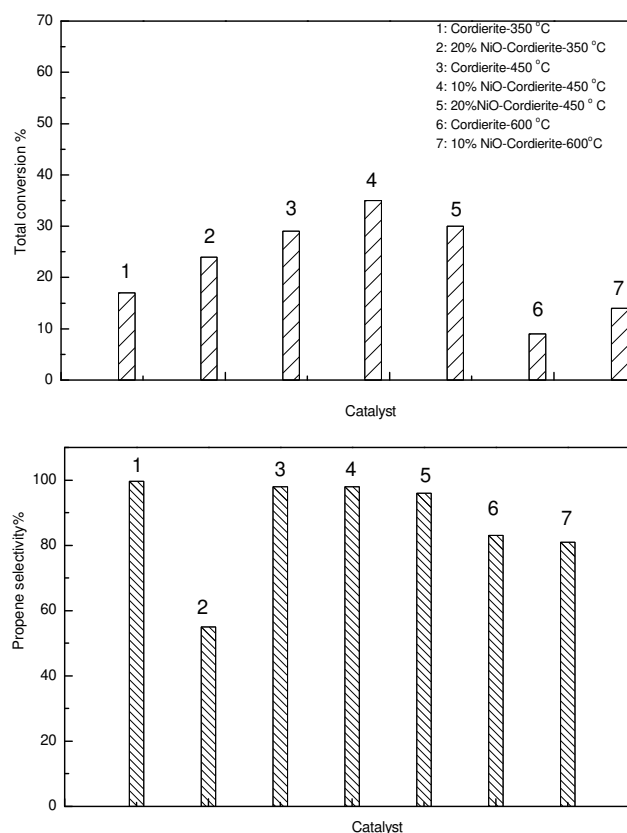
**Table 3. The Specific Surface Areas  $S_{\text{BET}}$  of Different Investigated Adsorbents at Different Calcination Temperatures**

Sample	Calcination Temperature	$S_{\text{BET}}$ , ( $\text{m}^2/\text{g}$ )
untreated cordierite	350 °C	4
+25% $\text{Al}_2\text{O}_3$	350 °C	127
+ 25% $\text{Al}_2\text{O}_3$ +10%NiO	350 °C	131.8
+ 25% $\text{Al}_2\text{O}_3$ +20%NiO	350 °C	135.8
+25% $\text{Al}_2\text{O}_3$	450 °C	115
+ 25% $\text{Al}_2\text{O}_3$ +10%NiO	450 °C	117
+ 25% $\text{Al}_2\text{O}_3$ +20%NiO	450 °C	120
+25% $\text{Al}_2\text{O}_3$	600 °C	92.9
+ 25% $\text{Al}_2\text{O}_3$ +10%NiO	600 °C	93.4
+ 25% $\text{Al}_2\text{O}_3$ +20%NiO	600 °C	94.2

the catalytic activity (expressed as a total conversion %) and decreases the dehydration selectivity. Also, Supporting 20% NiO on cordierite material calcined at 350 °C increased the catalytic activity and decreases the dehydration selectivity (iii) Increasing the calcination temperature from 350 to 450 °C increased the catalytic activity of NiO/cordierite decreased by increasing the calcination temperature to 600 °C without much affecting the dehydration selectivity. (iv) The increase of NiO content from 10% to 20% in the solids calcined at 350 °C led to a measurable decrease in their catalytic activity with a no effect in the dehydration selectivity.

So, NiO/cordierite system acted as multi component catalyst where the cordierite material itself has a measurable catalytic activity in alcohol conversion while it acted as a catalyst support in CO oxidation by  $\text{O}_2$ . The observed catalytic activity of unloaded cordierite solid which acted as selective catalyst for the dehydration of the investigated alcohol could be attributed to the presence of alumina-silica-magnesia components. These components behave normally as dehydration catalyst. The observed increase in the catalytic activity of unsupported cordierite by increasing its calcination temperature from 350 to 450 °C could be attributed to an effective increase in the concentration of active sites involved in dehydration reaction while the significant drop in its activity upon heating to 600 °C could be attributed to an effective decrease in the surface acidity [19].

The observed increase in the catalytic activity of NiO/cordierite system due to increasing its calcination temperature from 350 to 450 °C expressed a corresponding increase in the concentration of active sites involved in isopropanol conversion. EDX investigation (Table 1) revealed that the rise in calcination temperature from 350 to 450 °C led to a measurable decrease in the concentration of surface Ni-species, not involved in the dehydration process. This decrease is expected to be accompanied by an increase in the concentration of the active sites involved in the dehydration of isopropanol (surface alumina) present in the

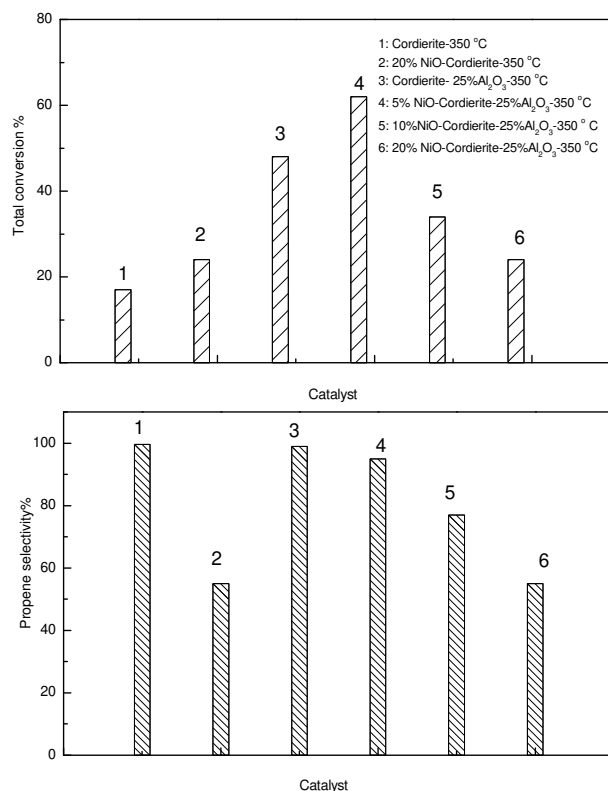


**Fig. (4).** Effect of extent of NiO loading and calcination temperature on the total conversion and selectivity towards propene formation using different catalysts for the reaction carried out at 275°C.

cordierite material. In other words, NiO might block a portion of active sites taking part in the dehydration process, the removal of which is expected to increase the portion of active sites participating in the dehydration reaction. The measurable decrease in the activity of NiO/cordierite system by increasing the calcination temperature up to 600 °C might be attributed to both an effective removal of surface OH groups, involved in the dehydration reaction and an effective increase in the degree of crystallinity and crystallite size of the catalyst constituents. The decrease in the catalytic activity expressed as total conversion by increasing NiO content from 10 to 20% could be attributed to blocking of some surface active sites (alumina constituents of the cordierite material) by NiO not directly involved in the dehydration process of isopropanol.

#### **Effect of $\text{Al}_2\text{O}_3$ Treatment on the Activity NiO/Cordierite System Towards Isopropanol Conversion**

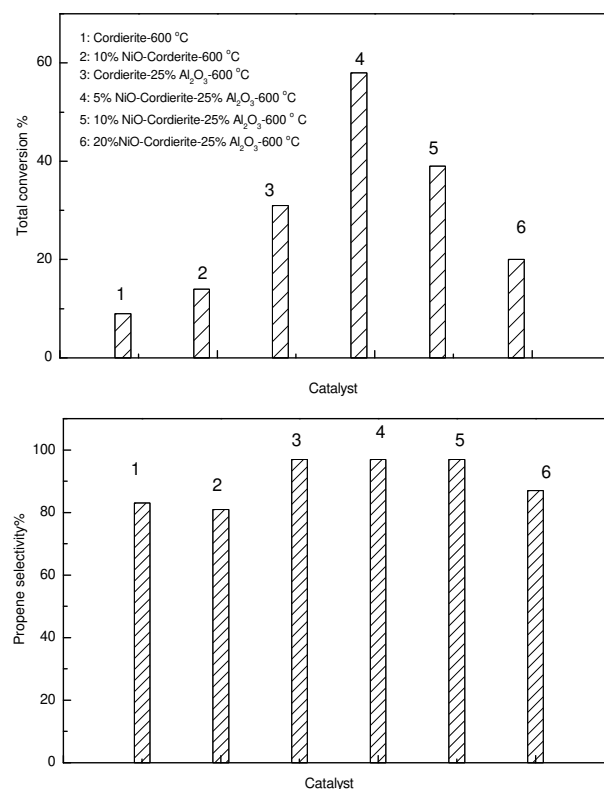
The effect of treating cordierite material with  $\text{Al}_2\text{O}_3$ , by washcoating method, on the activity and selectivity of both cordierite and NiO/cordierite systems, towards dehydration and dehydrogenation of isopropanol, were investigated. The NiO contents present were 5, 10 and 20%(w/w). Figs. (5, 6) show the effect of  $\text{Al}_2\text{O}_3$ -treatment on the activity and selectivity of cordierite and NiO/cordierite systems and extent of NiO loading in NiO/  $\text{Al}_2\text{O}_3$ -cordierite system calcined at 350, 450 and 600 °C. It is well-known that alumina acts as an active dehydration catalyst [20]. It is



**Fig. (5).** Effect of alumina treatment and amount of NiO added on the total conversion and selectivity towards propene formation for the reaction carried out at 275°C over various solids calcined at 350 °C.

noticed from Figs. (5, 6) that: (i) Al<sub>2</sub>O<sub>3</sub> treatment much increased the catalytic performance of both cordierite and NiO/cordierite systems. The increase was, however, more pronounced in case of the cordierite solid. The % increase in the catalytic activity measured at 275 °C for the employed cordierite due to its treatment with Al<sub>2</sub>O<sub>3</sub> attained 182 and 244% for the catalysts calcined at 350 and 600 °C, respectively. The observed significant increase in the catalytic activity of cordierite and NiO-cordierite solids due to treating with alumina can be directly attributed to the significant and considerable increase in the specific surface area of the treated catalyst (*c.f.* Table 3). This increase could also be attributed to the presence of free alumina on top surface layers of the treated catalyst. This behavior could be evidenced from EDX investigation of alumina-treated solids (*c.f.* Table 1). In fact the surface concentration of aluminum species increased from 13.9 to 21.1 atom % upon treating the cordierite solid with 25% Al<sub>2</sub>O<sub>3</sub>. (ii) The presence of the smallest amount of NiO (5%) in the Al<sub>2</sub>O<sub>3</sub>-treated NiO/cordierite being calcined at 350 or 600 °C much increased the catalytic activity, the increase attained 29 and 87% for the catalyst at 350 and 600 °C, respectively. The catalytic activity decreased progressively by increasing the extent of NiO to 10 and 20%. The observed decrease in the catalytic activity of Al<sub>2</sub>O<sub>3</sub>-treated NiO/cordierite above 5% NiO might be attributed to a possible blocking of some active sites (surface alumina) by NiO which may contribute directly in the dehydrogenation of the investigated alcohol. (iii) Increasing the calcination temperature of untreated

cordierite up to 600 °C brought about a considerable decrease in its catalytic activity (*c.f.* Fig. 6). However alumina treatment of cordierite followed by calcination at 600 °C led to a limited decrease in its catalytic activity. This finding justified the use of alumina treatment by washcoating method in increasing the thermal stability of the treated cordierite.



**Fig. (6).** Effect of alumina treatment and amount of NiO added on the total conversion and selectivity towards propene formation for the reaction carried out at 275°C over various solids calcined at 600 °C.

## CONCLUSIONS

The following are the main conclusions that may be drawn from the obtained results:

A commercial cordierite sample measured very small specific surface area had no measurable catalytic activity in CO oxidation by O<sub>2</sub>. However, it showed relatively small catalytic activity in iso-propanol conversion. Al<sub>2</sub>O<sub>3</sub>-treatment of the cordierite sample and NiO-cordierite solids using washcoating method brought about a considerable increase in their S<sub>BET</sub> which reached about 30-fold. This treatment brought about a significant increase in the catalytic activity of both cordierite and NiO-cordierite solids. Untreated cordierite, alumina-treated cordierite, and NiO-cordierite solids acted as selective dehydration catalysts. The activity of cordierite and NiO-cordierite with or without alumina treatment and calcined within 350-600 °C decreased progressively. The decrease was, however, more pronounced in case of the solids not treated with alumina. The presence of the smallest amount of NiO (5%) in the alumina treated solids much increased the catalytic activity which decreased



by increasing the extent of NiO loading above this limit. The cordierite support material and Al<sub>2</sub>O<sub>3</sub>-treated cordierite acted as dehydration catalyst with selectivity above 90%. The increase of NiO content within (5-20%) in NiO/Cordierite-Al<sub>2</sub>O<sub>3</sub> followed by calcination at 350 to 600 °C resulted in a progressive increase in the selectivity towards dehydrogenation of alcohol. Al<sub>2</sub>O<sub>3</sub> – treated NiO-cordierite containing 20% NiO showed measurable catalytic activity in CO oxidation by O<sub>2</sub> carried out at 200 °C. The activity suffered a serious drop in the catalytic activity upon increasing calcination temperature from 350 to 600 °C.

## REFERENCES

- [1] Radwan, N. R. E.; El-Shobaky, G. A.; Fahmy, Y. M. Cordierite as catalyst support for cobalt and manganese oxides in oxidation-reduction reactions. *Appl. Catal. A*, **2004**, *274*, 87-99.
- [2] Liu, Z.; Woo, S. I. Recent advances in catalytic de NO<sub>x</sub> science and technology. *Catal. Rev. Sci. Eng.* **2006**, *48*, 43-89.
- [3] Parmaliana, A.; Arena, F.; Frusteri, F.; Coluccia, S.; Marchese, L.; Martra, G.; Chuvili, A. L. Magnesia-supported nickel catalysts : ii. surface properties and reactivity in methane steam reforming. *J. Catal.* **1993**, *141*, 34-47.
- [4] El-Molla, S. A. Dehydrogenation and condensation in catalytic conversion of iso-propanol over CuO/MgO system doped with Li<sub>2</sub>O and ZrO<sub>2</sub>. *Appl. Catal. A*, **2006**, *298*, 103-108.
- [5] Andreini, A.; DeBoer, M.; Vuurman, M. A.; Deo, G.; Waches, I.E. Selective catalytic reduction of nitric oxide with ammonia on vanadia/alumina catalysts. Influence of vanadia loading and secondary metal oxide additives. *J. Chem. Soc., Faraday Trans.*, **1996**, *92*, 3267-3272.
- [6] Lemenidou, A. A.; Stambouli, A. E. Catalytic and non-catalytic oxidative dehydrogenation of n-butane. *Appl. Catal. A*, **1998**, *171*, 325-332.
- [7] El-Shobaky, G. A.; EL-Khouly, S. M.; Ghozza, A. M.; Mohamed, G. M. Surface and catalytic investigations of CuO-Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> system. *Appl. Catal. A*, **2006**, *302*, 296-304.
- [8] El-Molla, S. A.; Hamed, M. N.; El-Shobaky, G. A. Catalytic conversion of isopropanol over NiO/MgO system doped with Li<sub>2</sub>O. *Mater Lett.* **2004**, *58*, 1003-1011.
- [9] Khezrabadi, M. N.; Naghizadeh, R.; Assadollah, P.; Mirhosseini, S. H. An investigation on the properties and microstructure of mullite-bonded cordierite ceramics. *J. Ceram. Process. Res.*, **2007**, *8*, 431-434.
- [10] Subramanian, M. A.; Corbin, D.R.; Chowdhry, U. Better ceramic substrates through zeolites. *Bull. Mater Sci.*, **1993**, *16*, 665-678.
- [11] Trimm, D. L. Materials selection and design of high temperature catalytic combustion units. *Catal Today*, **1995**, *26*, 231-238.
- [12] Skoglundh, M.; Johansson, H.; Löwendahl, L.; Jansson, K.; Dahl, L.; Hirschauer, B. Cobalt-promoted palladium as a three-way catalyst. *Appl. Catal. B*, **1996**, *7*, 299-319.
- [13] Shigapov, A. N.; Graham, G. W.; McCabe, R.W.; Peck, M.P.; Jr, H.K.P. The preparation of high-surface-area cordierite monolith by acid treatment. *Appl. Catal. A*, **1999**, *18*, 137-146.
- [14] El-Shobaky, H.G.; Fahmy, Y.M. Cordierite as catalyst support for nanocrystalline CuO/Fe<sub>2</sub>O<sub>3</sub> system. *Mater. Res. Bull.* **2006**, *41*, 1701-1713.
- [15] El-Shobaky, H.G.; Fahmy, Y.M. Nickel cuprate supported on cordierite as an active catalyst for CO oxidation by O<sub>2</sub>. *Appl. Catal. B*, **2006**, *63*, 168-177.
- [16] Liu, O.; Liu, Z.; Zhu, Z.; Xie, G.; Wang, Y. Al<sub>2</sub>O<sub>3</sub>-Coated Honeycomb Cordierite-Supported CuO for Simultaneous SO<sub>2</sub> and NO Removal from Flue Gas: Effect of Na<sub>2</sub>O Additive. *Ind. Eng. Chem. Res.*, **2004**, *43*, 4031-4037.
- [17] Cullity, B.D. "Elements of x-ray diffraction", 2<sup>nd</sup> Ed , Addison-Wesley Publishing Co, Reading, MA, USA, **1978**.
- [18] El-Shobaky, G.A.; Ghozza, A.M.; El-Warraky, A.A.; Mohamed, G.M. Surface and catalytic investigations of Co<sub>3</sub>O<sub>4</sub>-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> system. *Colloids Surf.* **2003**, *219*, 97-111.
- [19] Youssef, A.M.; El Kherbawy, M.A.; Samra, S.E. Effect of irradiation with gamma-rays on the surface and catalytic properties of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O-impregnated SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> systems. *Radiat. Phys. Chem.* **1992**, *40*, 559-563.
- [20] Youssef, A.M.; El-Hakam, S.A.; El-Shobaky, G.A. Effect of gamma-irradiation on catalytic activity and selectivity of CuO-Al<sub>2</sub>O<sub>3</sub> solids . *Radiat. Phys. Chem.* **1992**, *40*, 575-578.

Received: April 19, 2010

Revised: July 18, 2010

Accepted: July 19, 2010

© El-Molla et al.; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.