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

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A commercial cordierite sample showed a small catalytic activity in iso-propanol conversion carried out at 150-350 ºC and no measurable activity in CO oxidation by O_2. On the other hand, supporting NiO on Al_2O_3–modified cordierite resulted in the formation of an active solid that having good catalytic activity in iso-propanol conversion and CO oxidation by O_2. These two reactions were carried out at 150-350 and 200 ºC, respectively. The results revealed that the catalyst containing 5wt% NiO showed the biggest activity in the alcohol conversion and acted as selective dehydration catalyst. The catalyst sample containing 20wt% NiO exhibited a good activity in CO oxidation by O_2 which decreased progressively by increasing its calcination temperature within 350-600 ºC. Al_2O_3–treated cordierite dissolved a portion of NiO in its lattice which increased by increasing the calcination temperature within 350-600 ºC.

Keywords: EDX, Catalytic activity, NiO/Cordierite, Al_2O_3-treatment

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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_2O 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 took place via of formation metal aluminate in case of alumina- support, or solid solution in case of MgO support [7,8] that having small catalytic activity as compared to metal oxide-supported solid. For this reason it is important to study the possibility of obtaining membranes cannot react with the catalytically active phase (transition metal oxide) and with low cost to be economic. Cordierite ($Mg_2Al_4Si_5O_{18}$) is a crystalline magnesium alumosilicate and is one of the phases of $MgO-SiO_2-Al_2O_3$ [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 a available material employed in electronic industry [10]. Also, cordierite is commercial material for high temperature catalyst applications, especially 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_3O_4, Mn_2O_3, CuO, Fe_2O_3 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_2O_3 using a washcoating technique on its physicochemical surface and catalytic properties have been investigated. Different physicochemical surface and catalytic properties of NiO supported on Al_2O_3–modified cordierite support material were investigated using XRD, EDX, nitrogen adsorption at -196 ^{o}C and catalytic conversion of iso-propanol at 150- 350 ^{o}C using the flow method and CO oxidation by O_2 at 200 ^{o}C.

EXPERIMENTAL

Sample preparation

A commercial cordierite ($Mg_2Al_4Si_5O_{18}$) was supplied by Baikowski Inc. company was treated with 25 wt % Al_2O_3 using a washcoating technique. A given mass of aluminum ethoxide was dissolved in a convenient volume of ethanol and few drops of HCl (28%) were added to aluminum ethoxide solution 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 ^{o}C. The obtained solid was dried at 110 ^{o}C till constant weight. The dried solid was used as a catalyst support for NiO. The Al_2O_3-treated cordierite sample was then impregnated with calculated amounts of nickel nitrate dissolved in the least amounts of distilled water. The nominal compositions of the calcined impregnated solids were 5, 10 and 20 wt % NiO. The obtained solids were dried at 110 ºC then calcined at 350- 600 ºC 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 ^{o}C was performed by X-ray powder diffraction employing a BRUKER Axs D8

Advance, Germany. Patterns were run using Ni-filtered copper radiation ($\lambda = 1.5404$ Å) at 40 kV and 40 mA. The crystallite size of NiO phase in different catalysts was calculated using the Scherer equation[16] from line broadening profile analysis of the main diffraction lines of NiO phase at a scanning rate of 0.2 degree in 2 Θ /min. through TOPAZ2.Inc program.

Energy dispersive x-ray analysis (EDX) was carried out on Ltitachi S-800 electron microscope with a kevex Delta system attached. The parameters were as follows: accelerating voltage 15 kV, accumulation time 100s, window width 8 μm. 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 ^{o}C using a conventional volumetric apparatus. All samples were degassed at 200 ^{o}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_2 at 200°C and iso-propanol conversion at 150-300 ^{o}C. The catalytic activities in CO oxidation by O_2 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 ^{o}C for 2 h. under a reduced pressure 10^{-6} Torr. A stoichiometric mixture of CO and O_2 (CO+1/2O_2) at a pressure of 2 Torr was used. The reaction product (CO_2) 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 ^{o}C being 160 Torr makes its liquefaction at that pressure improbable under the employed conditions (2 Torr)[7].

The catalytic conversion of iso-propanol using various catalyst samples were determined at 150-350 ^{o}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 ± 1 ^{o}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 ^{o}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 wt% NiO/cordierite, 25wt%Al$_2$O$_3$-cordierite and 20wt%NiO/25wt%Al$_2$O$_3$-cordierite samples calcined at 350-600 ºC 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_2O_3. 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 20wt% NiO calcined at 350 ºC 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 ºC. 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 [17]. However, this speculation has not been observed experimentally in case of NiO/cordierite system. This discrepancy could be attributed to the dissolution of a portion of NiO in the matrix of cordierite sample and the increase of calcination temperature from 350 to 450 and finally to 600 ºC increases 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_2O_3, Fe_2O_3 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 bigger 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_2O_3-treated cordierite shows clearly that Al_2O_3-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

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dispersion power of Al_2O_3-treated solid towards nickel species. This influence might result from the possible appreciable increase in the specific surface area of the Al_2O_3-treated cordierite solid. This speculation will be confirmed later in the next section of the present work. Increasing the calcination temperature of al nickel containing solids from 350 to 600 ºC 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 wt % NiO oxide calcined at 350, 450 and 600 ºC were determined. X–Ray diffractograms of cordierite support material being treated with 25 wt% Al_2O_3 and 5, 10, 20 wt% NiO and calcined at 350, 450 and 600 ºC were carried out. Figures (1-3) depict the diffractograms of various solids calcined at 350, 450 and 600 ºC, respectively. Examination Figures (1-3) shows the following: (i) Al_2O_3-treatment of cordierite followed by calcination at 350- 600 ºC 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_2O_3 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 wt% 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

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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 wt% NiO in the Al_2O_3-treated cordierite calcined at 600 ºC seems to be beyond the detection limit of x-ray diffractometer, all diffraction lines of this phase were detected (c.f. figure 3, diffractogram3). 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_2O_3 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_{BET}) of cordierite support material and samples treated with Al_2O_3 and NiO oxides and being calcined at 350, 450 and 600 ºC were determined. The obtained results are given in Table (3). Inspection of table (3) reveals the following: (i) The S_{BET} of cordierite support material is very small which increases tremendously with treatment with 25 wt%Al_2O_3 calcined at 350-600 ºC. The increase in the S_{BET} of cordierite due to alumina treatment reaches to 30-fold. (ii) Increasing the calcination temperature from 350 to 450 ºC and from 450 to 600 ºC 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 wt% NiO followed by calcination at 350, 450 and 600 ºC led to a further small increase in the S_{BET} 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_2O_3 compared to that of cordierite but also because of the method of preparation which led to formation very fine crystallites form of Al_2O_3-coated the cordierite support material.

The significant increase in the specific surface areas of cordierite samples due to their treatment with Al_2O_3 and /or NiO oxides is expected to modify their catalytic properties.

Catalytic oxidation of CO by O_2 over different solids

Preliminary experiments showed that the employed untreated cordierite and the Al_2O_3-treated solids exhibited no measurable activity in CO oxidation by O_2 even by caring out the reaction at relatively high temperature reaching to 300 ^{o}C. So, the cordierite acted as a catalyst support for CO oxidation by O_2. The catalytic oxidation of CO by O_2 was carried out at 200 ^{o}C over nickel/ cordierite-alumina system containing 20 wt% NiO and calcined at 350, 450 and 600 ^{o}C. The catalytic reaction was found to follow 1st 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 x 10 $^{-2}$ min^{-1}. g^{-1} for the reaction carried out at 200 ^{o}C over the samples calcined at 350, 450 and 600 ^{o}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_2 because of increasing its calcination temperature from 350 to 450 ^{o}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_2. 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 ^{o}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 iso-propanol over different investigated solids

Effect of extent of NiO loading on the activity NiO/cordierite system towards iso-propanol conversion

The catalytic conversion of iso-propanol was carried out over 10 and 20 wt% NiO/cordierite solids calcined at 350, 450 and 600 ^{o}C. The same catalytic reaction was also carried out over cordierite material calcined at the same temperatures. Figure (4) shows the effect of extent of NiO loading of NiO/cordierite system calcined at 350-600 ^{o}C on its catalytic activity expressed as the total conversion. The same figure shows the selectivities towards propene and acetone formation for the reaction carried out at 275 ^{o}C. It is noticed from figure (4) that: (i) the cordierite exhibited a measurable catalytic activity, which increased by increasing the calcination temperature from 350 to 450 ^{o}C and then decreased with increasing the calcination temperature to 600 ^{o}C. (ii) Supporting 10 wt% NiO on cordierite material increased the catalytic activity and dehydrogenation selectivity but it decreased the dehydration selectivity especially for the solids calcined at 350 ^{o}C. (iii) Increasing the calcination temperature from 350 to 450 ^{o}C increased the catalytic activity of NiO/cordierite which deceased by increasing the calcination temperature to 600 ^{o}C without much affecting the dehydration selectivity. (iv) The increase of NiO content from 10 wt % to 20 wt% in the solids calcined at 350 ^{o}C led to a measurable decrease in their catalytic activity expressed as, total conversion, with a noticeable increase in the dehydrogenation selectivity. The increase in calcination temperature to 450 ^{o}C increased the catalytic activity

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and did not much affect the dehydrogenation 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 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 ^{o}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 ^{o}C could be attributed to an effective decrease in the surface acidity [18].

The observed increase in the catalytic activity of NiO/cordierite system due to increasing its calcination temperature from 350 to 450 ^{o}C expressed a corresponding increase in the concentration of active sites involved in iso-propanol conversion. EDX investigation (Table 1) revealed that the rise in calcination temperature from 350 to 450 ^{o}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 iso-propanol (surface alumina) present in the 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 ^{o}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 wt% 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 iso-propanol.

Effect of Al_2O_3 treatment on the activity NiO/Cordierite system towards iso-propanol conversion

The effect of treating cordierite material with Al_2O_3, by washcoating method, on the activity and selectivity of both cordierite and NiO/cordierite systems, towards dehydration and dehydrogenation of iso-propanol, were investigated. The NiO contents present were 5, 10 and 20 wt%. Figures 5 and 6 show the effect of Al_2O_3–treatment on the activity and selectivity of cordierite and NiO/cordierite systems and extent of NiO loading in NiO/ Al_2O_3-cordierite system calcined at 350, 450 and 600 ^{o}C. It is noticed from figures 5 and 6 that: (i) Al_2O_3 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 ^{o}C for the employed cordierite due to its treatment with Al_2O_3 attained 182 and 244% for the catalysts calcined at 350 and 600 ^{o}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 25wt% Al_2O_3. (ii) The presence of the smallest amount of NiO (5wt%) in the Al_2O_3– treated NiO/cordierite being calcined at 350 or 600 ^{o}C much increased the catalytic activity, the increase attained 29 and 87% for the catalyst at 350 and 600 ^{o}C, respectively. The

catalytic activity decreased progressively by increasing the extent of NiO to 10 and 20 wt%. The observed decrease in the catalytic activity of Al_2O_3–treated NiO/cordierite above 5wt% 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 ^{o}C brought about a considerable decrease in its catalytic activity (c.f. Fig. 6). However alumina treatment of cordierite followed by calcination at 600 ^{o}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.

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 and having no measurable catalytic activity in CO oxidation by O_2. However, it showed relatively small catalytic activity in iso-propanol conversion. Al_2O_3-treatment of the cordierite sample and NiO-cordierite solids using washcoating method brought about a considerable increase in their S_{BET} 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 being treated or not with alumina and calcined within 350-600 ºC 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 wt%) 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_2O_3–treated cordierite acted as

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dehydration catalyst with selectivity above 90%. The increase of NiO content within (5-20 wt%) in NiO/ Cordierite-Al_2O_3 followed by calcination at 350 to 600 ºC resulted in a progressive increase in the selectivity towards dehydrogenation of alcohols. Al_2O_3 – treated NiO-cordierite containing 20 wt% NiO showed measurable catalytic activity in CO oxidation by O_2 carried out at 200 ºC. The activity suffered a serious drop in the catalytic activity upon increasing calcination temperature from 350 to 600 ºC.

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Table 1. Surface molar composition of cordierite, NiO/cordierite, Al_2O_3-cordierite and NiO/Al_2O_3-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
20wt% 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_2O_3-75%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
20wt% NiO /25 %Al_2O_3-75%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
20wt% 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
20wt% NiO /25 %Al_2O_3-75%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
20wt% 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
20wt% NiO /25 %Al_2O_3-75%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

Table 2. The crystallite size and degree of crystallinity of NiO phase in different investigated solids.

Sample	Calcination temperature	Crystallite size of NiO(nm)	[a] Degree of crystallinity(a.u)
10wt%NiO /cordierite	350 °C	20.7	40.8
20wt%NiO /cordierite	350 °C	22.3	92.7
10wt%NiO /cordierite	450 °C	16.5	36
20wt%NiO /cordierite	450 °C	25.6	75.5
10wt%NiO /cordierite	600 °C	20.8	36
10wt%NiO /cordierite- Al_2O_3	350 °C	23	20.4
10wt%NiO /cordierite- Al_2O_3	450 °C	3	13
5wt%NiO /cordierite- Al_2O_3	600 °C	17.7	29.1
10wt%NiO /cordierite- Al_2O_3	600 °C	20	20
20wt%NiO /cordierite- Al_2O_3	600 °C	36.7	22.2

(a)The areas of the main diffraction lines of NiO phase were taken as a measure of degree of crystallinity of this phase.

Table 3. The specific surface areas of different investigated adsorbents

Sample	Calcination temperature	S_{BET} , (m^2/g)
untreated cordierite	350 °C	4
+25wt% Al_2O_3	350 °C	127
+ 25wt% Al_2O_3+10wt%NiO	350 °C	131.8
+ 25wt% Al_2O_3+20wt%NiO	350 °C	135.8
+25wt% Al_2O_3	450 °C	115
+ 25wt% Al_2O_3+10wt%NiO	450 °C	117
+ 25wt% Al_2O_3+20wt%NiO	450 °C	120
+25wt% Al_2O_3	600 °C	92.9
+ 25wt% Al_2O_3+10wt%NiO	600 °C	93.4
+ 25wt% Al_2O_3+20wt%NiO	600 °C	94.2

Fig.1. XRD diffractograms of: (1) Cordierite, (2) 10% NiO/Cordierite, (3) 20% NiO/Cordierite, (4) Cordierite- alumina and (5) 10% NiO/Cordierite-alumina solids precalcined at 350 ºC. Dotted lines are related to NiO phase and the other lines are related to cordierite phase.
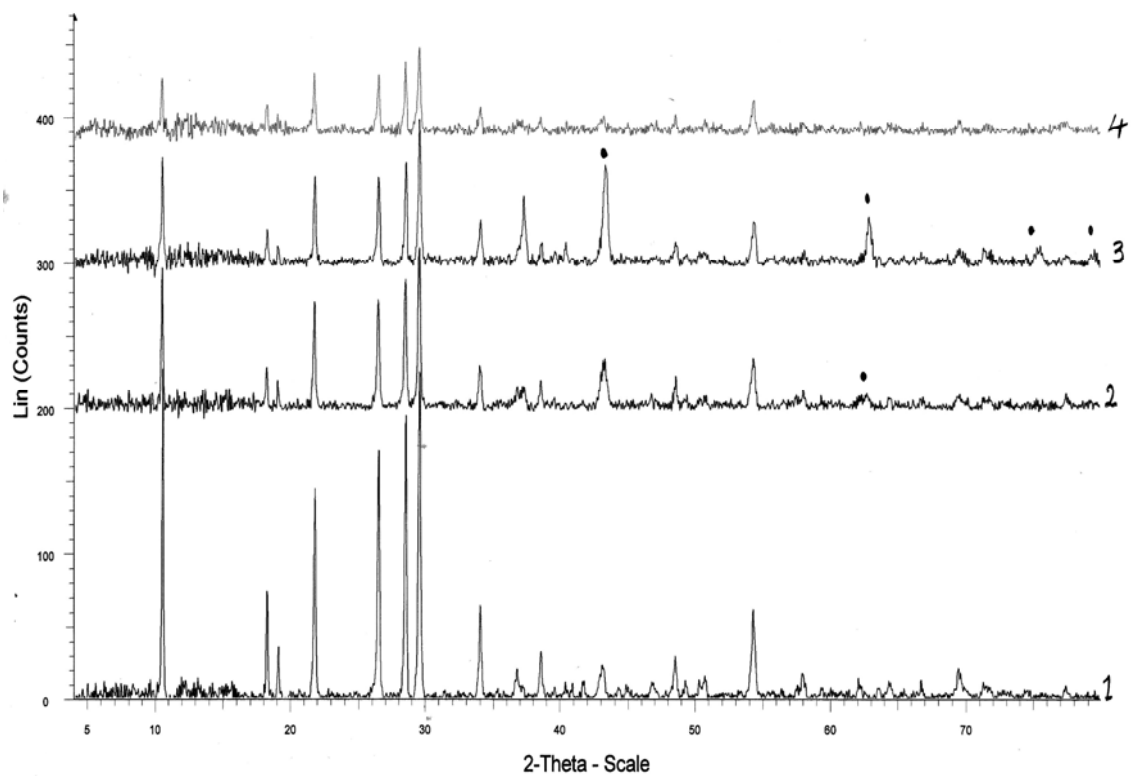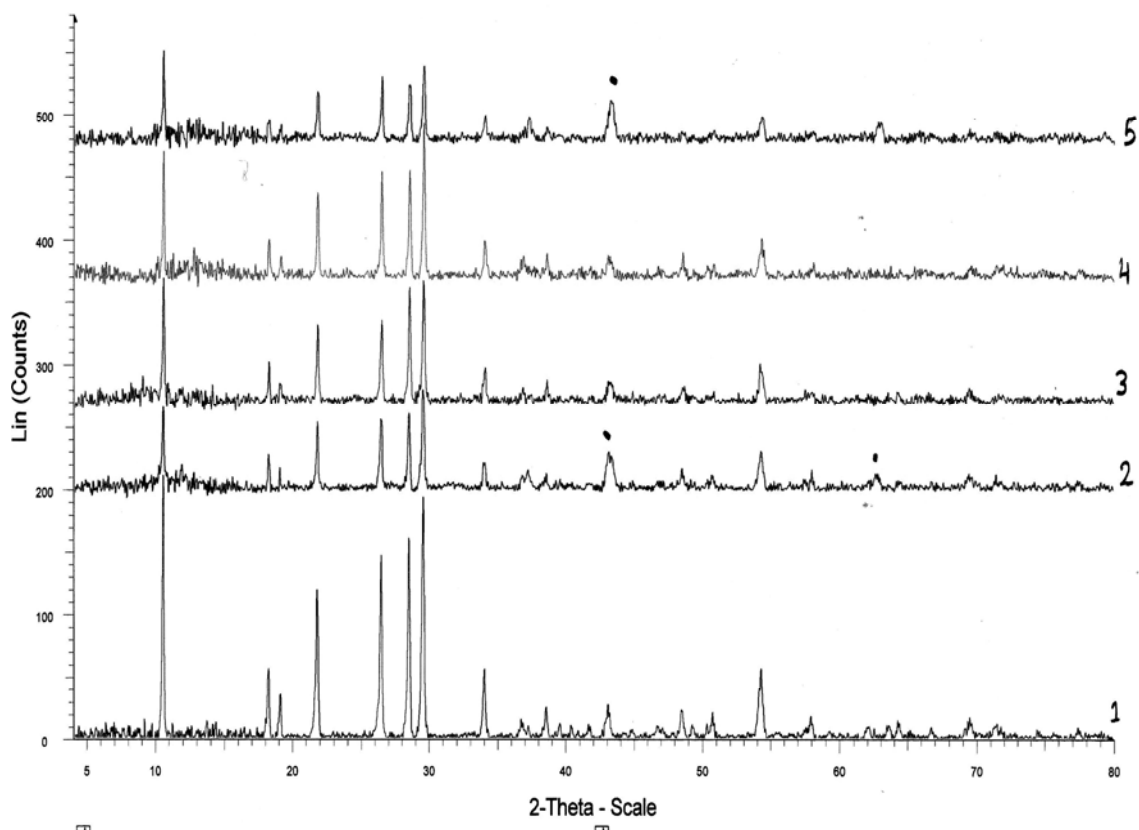
Fig.2. XRD diffractograms of: (1) Cordierite, (2) 10% NiO/Cordierite, (3) 20% NiO/Cordierite and (4) 10% NiO/Cordierite-alumina solids precalcined at 450 ºC. Dotted lines are related to NiO phase and the other lines are related to cordierite phase.

Fig.3. XRD diffractograms of: (1) Cordierite, (2) 10% NiO/Cordierite, (3) 5% NiO/Cordierite-alumina, (4) 10 % NiO/Cordierite-alumina and (5) 20% NiO/Cordierite-alumina solids precalcined at 600 ºC. Dotted lines are related to NiO phase and the other lines are related to cordierite phase.
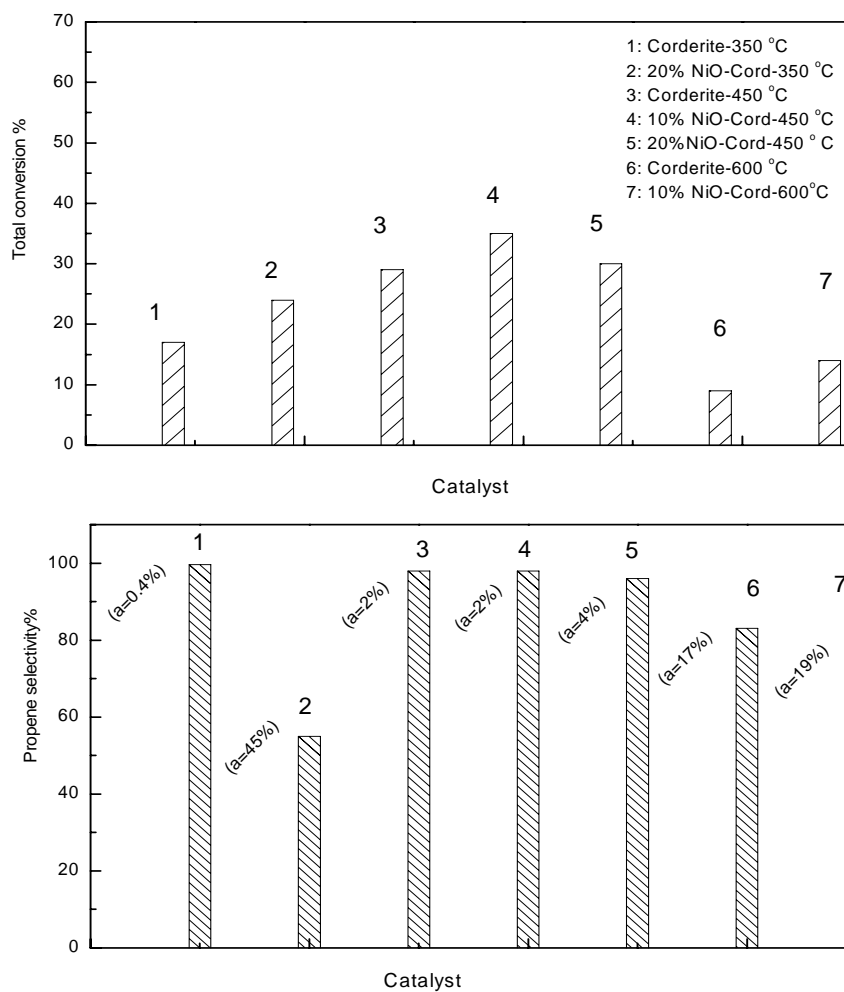
Fig.4. Effect of extent of NiO loading and calcination temperature on the total conversion and selectivity towards propene formation using different catalysts for the reaction carried out at 275ºC.
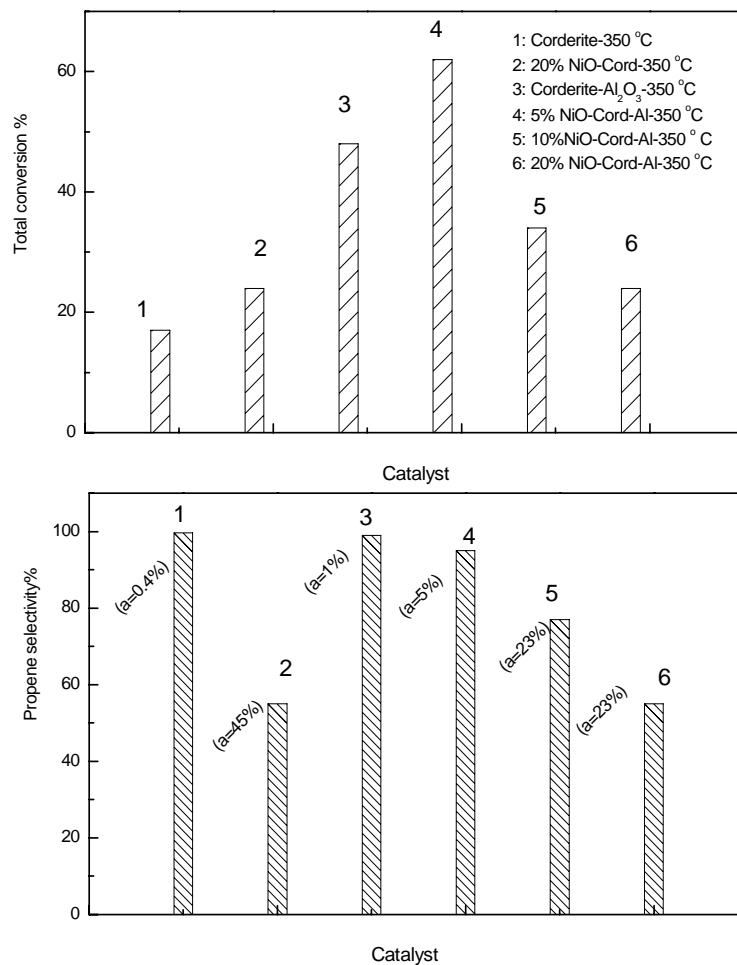Note: a= selectivity towards acetone formation.

Fig.5. Effect of extent of NiO loading and alumina treatment on the total conversion and selectivity towards propene formation for the reaction carried out at 275ºC over different solids calcined at 350 ºC.
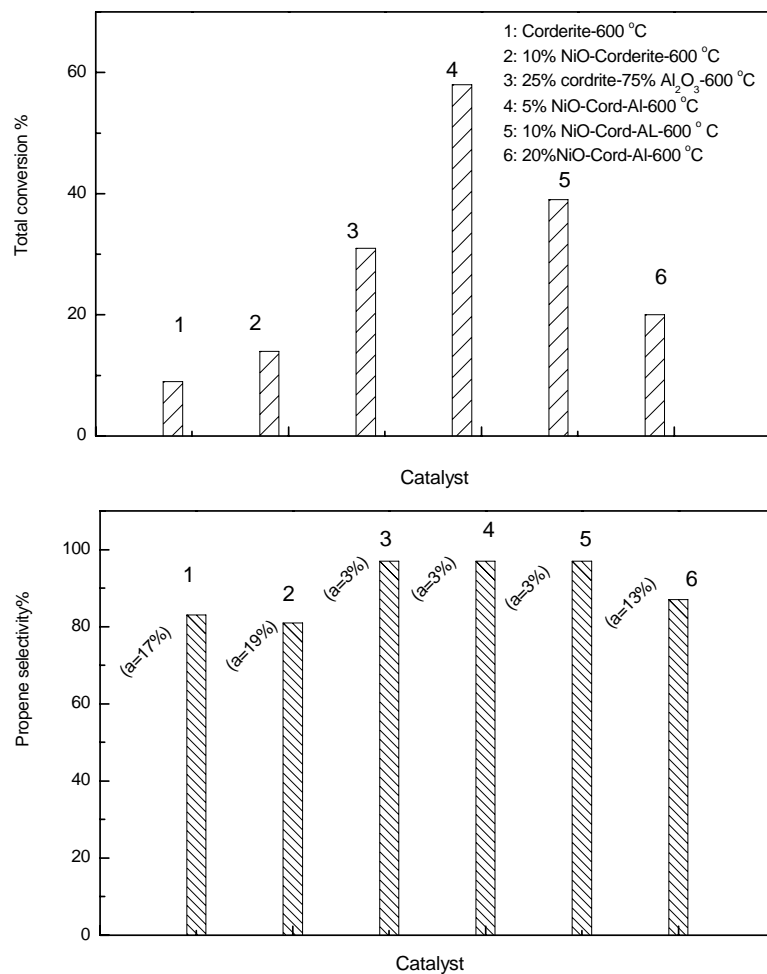Note: a= selectivity towards acetone formation.

Fig. 6. Effect of extent of NiO loading and alumina treatment on the total
conversion and selectivity towards propene formation for the
reaction carried out at 275ºC over different solids calcined at 600
ºC. Note: a= selectivity towards acetone