

Structural and Surface Characteristics of Cordierite Treated with a Mixture of NiO-Mn₂O₃

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Abstract: Structural and surface characterization of untreated commercial cordierite and that treated with a mixture of 10% wt of NiO and 10 wt % Mn₂O₃ were investigated. The technique employed were XRD, EDX and nitrogen adsorption at -196°C. The results revealed that the employed cordierite sample existed as very well crystallized phase. Its composition has been confirmed by EDX technique which revealed that the surface and bulk composition are almost identical and having the formula Mg₂Al₄Si₅O₁₈. The degree of crystallinity of the cordierite phase was found to decrease effectively by treating with a mixture of NiO and Mn₂O₃. XRD investigation revealed the absence of free NiO and Mn₂O₃ as separate phases. However, EDX investigation showed that the presence of a portion of NiO as a separate phase and the other portion dissolved in cordierite matrix. However, manganese oxide added dissolved completely in the bulk of the cordierite lattice. So, cordierite can dissolve 10.0 wt% Mn₂O₃ and 4.6 wt% NiO. The S_{BET} of the cordierite measured 3.2 m²/g and remained almost unchanged by treating with Ni, Mn oxides. Pure and treated cordierite show the same pore volume distribution curve, that having unimodal distribution.

Key words: Cordierite • Nickel oxide • Manganese oxide • EDX

INTRODUCTION

Cordierite (2MgO·2Al₂O₃·5SiO₂) is a crystalline magnesium aluminosilicate with hexagonal framework. Cordierite is widespread commercial material for high temperature catalyst applications. Cordierite used for automotive catalysts due to its high mechanical stability and low thermal expansion coefficient [1]. Cordierite is promising materials for electronic applications because of their low dielectric constant, high resistivity, high thermal and chemical stability and very low thermal expansion coefficient. Cordierite is an alternative material to be used as substrate in replacement of alumina employed in the electronic industry [2-4]. Cordierite is an attractive coat for high temperature applications; it has been examined thoroughly with regard to industrial processing [5-8] and to some extent as plasma sprayed coatings [9]. Magnesium cordierite (Mg₂Al₄Si₅O₁₈) exists under three polymorphic forms; a hexagonal high temperature form (α-cordierite), an orthorhombic low temperature form (β-cordierite) and a metastable form (μ-cordierite). The physicochemical, surface and catalytic properties of cordierite samples treated with 10 wt % NiO and 10 wt% CuO calcined at 350-700°C were investigated [10].

The results showed that the formation of nickel cuprate on top surface layers of the cordierite support which acted as active catalyst for CO oxidation by O₂. Physicochemical, surface and catalytic properties of Al₂O₃-treated cordierite and being impregnated with 5 wt% NiO [11]. The authors claimed that a huge increase in the specific surface area of the cordierite by treating with Al₂O₃ using wash coat method. The present work aimed at investigating the effect of treating a cordierite sample with a mixture of NiO and Mn₂O₃ on its structural and surface characteristics. The techniques employed for characterization were of various solids XRD, EDX and nitrogen adsorption at -196°C.

Experimental

Materials: A given mass of a finely powdered cordierite Mg₂Al₄Si₅O₁₈ supplied by Baikowski international Corporation was impregnated with a solution containing calculated amount of nickel and manganese nitrates dissolved in the least amount of distilled water, then dried at 110°C and heated in air at 500°C for 4h. The amounts of nickel or manganese expressed as 10 wt. % NiO and 10 wt. % Mn₂O₃.

Techniques: X-ray powder diffractograms of different solids investigated calcined at 500 °C were determined using a Bruker diffractometer (Bruker D 8 advance Cu target). The patterns were run with copper K α with secondly monochromator ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 40 mA. The scanning rate was 8° and 0.8° in 0.2° in 2 θ . min⁻¹ for phase identification and line broadening profile analysis, respectively. Energy dispersive x-ray analysis (EDX): EDX measurements were carried out on a Hitachi S-800 electron microscope with a Kevex Delta system attached. The parameters were as follows: 15 kV accelerating voltage, 100 s accumulation time, 8 μm window width. The surface molar composition was determined by the Asa method (Zaf-correction, Gaussian approximation). The surface properties, namely, specific surface area (S_{BET}), total pore volume (V_p) and mean pore radius (r) of various solid samples were determined from nitrogen adsorption isotherms at -196°C using Quantachrome NOVA Automated Gas sorption system.

RESULTS AND DISCUSSION

XRD Investigation of Different Solids:

X-ray diffractograms of untreated cordierite sample and cordierite sample treated with 10 wt% NiO and 10 wt% Mn₂O₃ being calcined at 500°C were carried out. The cordierite treated with a mixture NiO and Mn₂O₃ calcined at the same temperatures were also carried out. The diffractograms of the two solids are illustrated in Fig. 1. The diffractogram of untreated cordierite sample shows that the investigated solid is cordierite, Mg₂Al₄Si₅O₁₈ that having big sized crystallites and an excellent degree of crystallinity.

It is clearly shown from Fig. 1 that treatment of cordierite solid sample with a mixture containing 10 wt% NiO and 10 wt% Mn₂O₃ followed by calcinations at 500 °C decreases slightly the relative intensity of all diffraction peaks of the cordierite phase. This decrease might reflect a limited structure collapse as evidenced by the observed decrease in the degree of crystallinity of the treated cordierite. Fig 1 shows also the absence of all diffraction peaks of NiO and Mn₂O₃ phases. This finding might suggest a possible dissolution of transition metal oxides added in the matrix of cordierite lattice forming solid solutions. The possible dissolution of NiO and Mn₂O₃ in the matrix of cordierites could be examined by determination of nickel and manganese species present in the outermost surface layers of the cordierites by using EDX investigation. This technique enable us to determine the relative atomic abunds of nickel, manganese and all elements of the cordierites present in the outermost surface layers of treated cordierites [12].

Energy Dispersive X-ray Analysis (EDX) of Supported

Cordierite: EDX investigation of manganese and nickel treated cordierite catalysts calcined at 500°C was carried out. These solids contained 10 wt % NiO and 10 % Mn₂O₃. The atomic abundance of nickel and manganese 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 on the basis of the formula of untreated cordierite samples and those treated with 10 wt % NiO and Mn₂O₃. Data obtained are also given in Table 1. Cordierite untreated sample has been confirmed by EDX technique which revealed that the surface and bulk compositions are almost identical and having the formula Mg₂Al₄Si₅O₁₈.

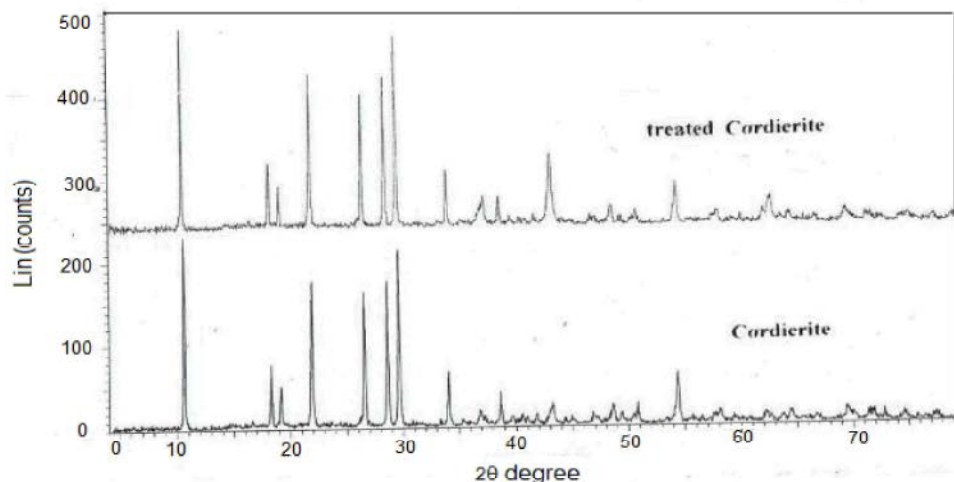


Fig. 1: X-ray diffractogram of untreated and treated cordierite samples calcined at 500°C

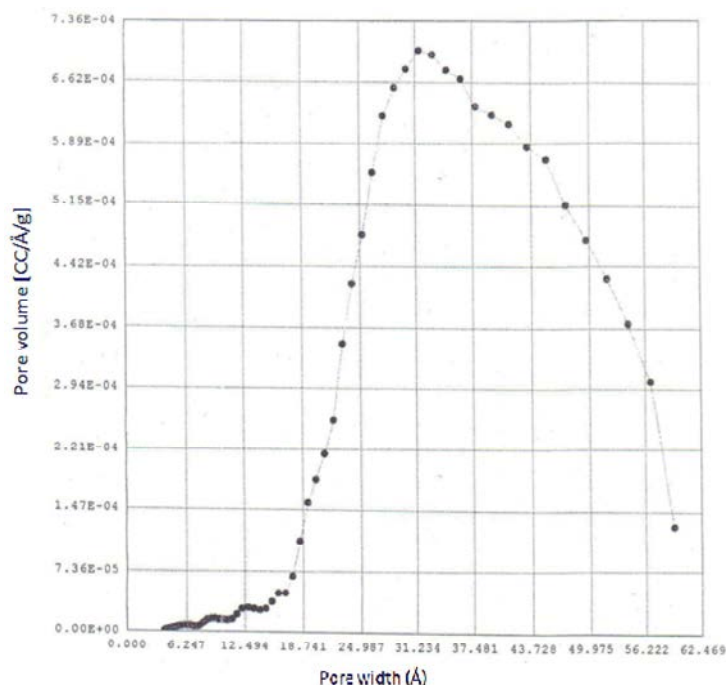


Fig. 2: Pore volume distribution of treated cordierite sample

Table 1: Surface molar composition of NiO and Mn₂O₃/cordierite calcined at 500°C determined by EDX

Solid catalysts	Element	Atomic abundance	
		Calculated	Found
10wt.% NiO and 10% Mn ₂ O ₃ /cordierite	O	54.30	76.847
	Mg	4.51	5.45
	Al	12	8.043
	Si	3.32	8.18
	Ni	2.95	1.533
	Mn	2.77	--
Cordierite	O	62.56	62.40
	Mg	6.408	6.44
	Al	13.10	13.86
	Si	17.93	17.29

It is well known that the EDX technique supplies the effective atomic concentration of different substrates of investigated solids which are present on their top surface layers. Inspection of results given in Table 1 revealed the following: (i) The values of atomic abundance of elements present are near from those calculated and found experimentally. (ii) The complete disappearance of manganese species in top surface layer of the treated cordierite. This finding indicates clearly that the amount of Mn₂O₃ added dissolved completely in the matrix of the cordierite sample forming solid solution. The same conclusion has been reported by El-Shobaky and Fahmy [12]. (iii) The value of atomic abundance of nickel ions

found by EDX is about 4.6 % of that added to the cordierite sample calcined at 500°C. This finding might indicate that about one half of the amount of nickel dissolved effectively in the cordierite lattice forming solid solution and other portions remained as a separate phase. These results are in good agreement of those XRD previously given in the present work.

Surface Characteristics of Cordierite and Cordierite Treated Cobalt and Manganese Oxides:

The different surface characteristics namely S_{BET} , V_p and r of cordierite support material and nickel, manganese oxides treated-cordierite subjected to heating at 500°C were determined from nitrogen adsorption isotherms measured at -196°C. The isotherms not given belong to type ii [13] of Brunauer classification having hysteresis loop of small area closing at p/p_0 of about 0.2. The pore volume distribution curves of various adsorbents were also determined and illustrated in Fig. 2. The calculated values of S_{BET} , V_p and r measured 2.8 m², 0.036 cc/gm. 32 Å for untreated cordierite sample and that impregnated with 10 wt% NiO and 10 wt% Mn₂O₃. The pore volume distribution curve of untreated and transition metal oxides-treated cordierite are almost the same showing unimodal distribution with most probable hydraulic Pore radius found at 32 Å.

CONCLUSIONS

The results obtained permitted to draw the following main conclusions:

- The formula of commercial cordierite sample has been identified by EDX technique permitting the determination of relative atomic abundance of different species constituting the cordierite. The surfaces and bulk are almost the same and having the formula $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$
- The employed cordierite sample exists as very well crystalline phase and its degree of crystallinity was found to decrease slightly with a mixture of NiO and Mn_2O_3 .
- The surface composition of treated cordierite did not contain any trace amount of Mn_2O_3 added indicating its complete dissolution in the cordierite matrix forming solid solution. So, the cordierite dissolved 10.0 wt% Mn_2O_3 . While the employed cordierite sample dissolved only 4.6 wt% NiO
- All surface characteristics of untreated and treated cordierite are almost identical

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