

# Physico-chemical studies on catalytic decomposition of hydrogen peroxide by promoted cobalt oxide catalysts

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**ABSTRACT** :Addition of certain amount of magnesium oxide to cobalt oxide catalyst was studied by thermal decomposition at the selected temperature of pure cobalt carbonate and that added to different percentage of magnesium nitrate ranged from 0.5-2.5 weight percentage of magnesium oxide. The specific surface area of pure and doped solids were determined by BET analysis of nitrogen adsorption isotherm, then the crystalline bulk structure investigated by X-ray diffractometer. The catalytic activity was determined by Gasometrical apparatus of the reaction kinetics at 20-40 °C. the results obtained exhibit that the doping cobalt with magnesium oxide for above calcinations temperature in air at 400-800 °C increase the specific surface area of cobalt oxide and also show gradual increase in catalytic activity in hydrogen peroxide decomposition. It is cleared that the activation energy of cobalt oxide is higher than of cobalt oxide doped with magnesium oxides which reflect the role of magnesium oxide treatment in modifying the concentration of catalytically active constituents, i.e. the doping increase the concentration of cobalt ion pairs and forming or initiating cobalt-Magnesium ion pairs which increase the number of active sites during the catalytic decomposition of hydrogen peroxide.

**Key words:** XRD,IR, Surface area and Specific catalytic activity.

## INTRODUCTION

Hydrogen peroxide and its solutions find use as antiseptic in medicine.(1,2) Hydrogen peroxide is environmentally being oxidant, is expected to play an increasingly important role in the chemical industry, other application of hydrogen peroxide such as bleach in the textile and paper pulp industry, in treatment of waste (3). The sterilization of packages food, beverages, drugs. The sterilization by hydrogen peroxide vapor offers one distinct advantage over other chemical methods (4).

The controlled decomposition of hydrogen peroxide on oxide and mixed oxides has been studied extensively by many researchers ( 5- 9 ).

Cobalt oxide is one of the most common transition metal oxide catalysts for oxidation-reduction reaction (10-12).

The specific catalytic activity and the selectivity of a catalyst are affected by several factors such as, method of preparation, (13-14) nature of promoter,(15-16) active phase initiated,(17-18) doping with foreign ions, (19-20) and atomic radii.

The surface feature can be influenced by the doping process, as the thermal stability and oxidation state of solid catalysts (21-23).

The thermal stability change due to the doping with certain amounts of oxides have been attributed to the dissolution of some of doped oxides added in the lattice oxide solid, forming solid solutions with subsequent change in the oxidation state of cobalt ions in cobalt oxides solid.

The mutual change of oxidation state of cobalt ions from divalent to trivalent or vice versa due to the doping process (24-26) increase the thermal stability and followed by changes in surface area and catalytic activity of cobalt oxide (CO<sub>3</sub>O<sub>4</sub>).

The present investigation was devoted to study the effect of MgO addition the specific surface area and catalytic activity of cobalt oxide catalyst calcined at different temperature, followed by XRD and surface area measurements, then the decomposition kinetics of H<sub>2</sub>O<sub>2</sub> solution of pure and doped catalysts was determined in through gasometrical technique.

## Experimental Preparation

The pure cobalt oxide and its promotion were prepared by thermal decomposition of pure basic cobalt carbonate with different concentrations of magnesium nitrate. The promoted catalyst were prepared by adding known amounts of finely powdered basic cobalt carbonate with different amounts of magnesium nitrate dissolved in the least amount of distilled water, then dried at 120°C, and heated in open sphere at the selected

calcinations temperature 400-800 °C for six hours. The concentration of promoter were 0.5, 1 and 2.5 weight percent of MgO.

### Catalyst characterization

X-ray spectroscopy represents one of the most powerful tool available for rapid determination of the feature of samples such as mixed oxide catalysts (27).

The X-ray diffract meter has the following specification:

X-ray generates or type pw 1120/00/60.

Vertical type diffractometer type pw 1050/70.

Proportional detector type pw 1965/50.

Vertical chromium lamp of wave length 2290.9 Å.

An infrared spectra of the selected pure and doped catalysts under investigation by KBr disc technique using perking-Elmer 1430 double beam spectrophotometer in the range 4000-200 cm<sup>-1</sup>.

The high selectivity of the method permitted an accurate determination of the catalyst components (28).

The sample disks were placed in the holder of double beam spectrophotometer.

The specific surface area was measured by applying the BET theory (29) of nitrogen adsorption isotherms at 77k for pure and doped catalyst solids in through using a conventional volumetric apparatus, the examined catalysts were out-gassed at 200°C and 10<sup>-5</sup> torr for three hours. The catalytic decomposition of hydrogen peroxide on the different catalyst samples was measured, since a weight quantity of the catalyst was added with 10 cm<sup>3</sup> H<sub>2</sub>O<sub>2</sub> in a closed vessel kept in a thermostatic water bath and the volume of oxygen evolved was measured by using gasometrical technique (30,31).

Experiment were carried out at three different temperature (T) in the range 20-40°C. the specific reaction rates (k) were calculated from the plot of log (a-x) verses time (t) where a and x are the volumes of oxygen evolved after completion of decomposition and at any time respectively.

The ln k values were plotted against 1/T (Arrhenius plot). The slope of straight line obtained is -E<sub>a</sub>/R, thus, the activation energy (E<sub>a</sub>) was calculated from slope.

The activation parameters, ΔH\*, ΔG\* and ΔS\*, were calculated by Eyring equation, H..Ali and Derene et. al (32, 33).

## RESULT AND DISCUSSION

X-ray diffractograms of thermal products of pure and promoted catalysts solid calcined at 400-800°C were determined. The obtained diffractograms in Fig (1) showed that these solids presented mainly of very crystallized phase, where by increasing the calcinations temperature, the intensity lines of pure cobalt oxide phase is relay increased.

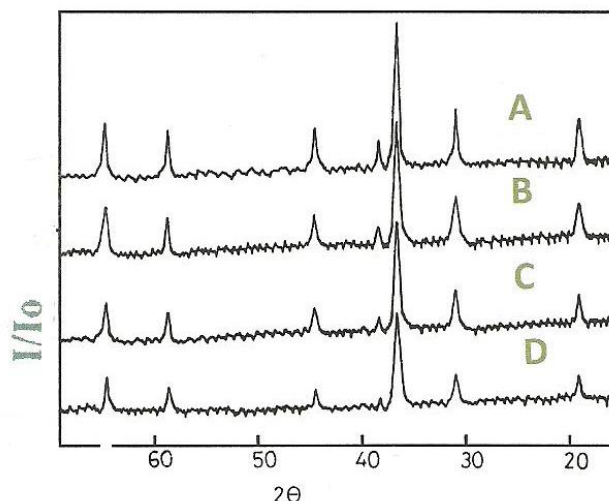


Figure 1 . X-ray diffraction of pure cobalt oxide calcined at different temperature.

The sharpness peak of pure cobalt oxide at 800 °C, denotes that the high crystallinity of cobalt oxide at this calcinations temperature rather than the former other calcinations degree.

As the result of studying the X-ray diffraction pattern of the pure cobalt oxide and doped cobalt oxide calcined at 800 °C as shown in Fig.2. It denote that the doping cobalt oxide with different percentage of magnesium oxide did not lead to any formation of new crystalline phase that permitting to dissolve the doping content in crystal lattice of cobalt oxide forming an solid solution (34).

Pure  $\text{CO}_3\text{O}_4$ .  
0.5wt% MgO.  
1.0wt% MgO.  
2.5Wt% MgO.

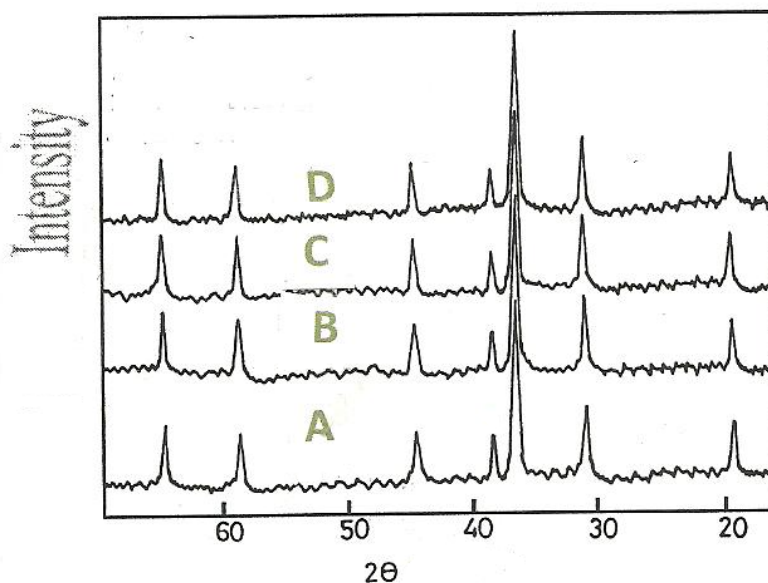


Fig.2. X-ray diffraction of pure and doped cobalt oxide calcined at 800 °C.

The infrared spectra were determined for pure and doped cobalt oxide calcined at different temperature from 400-800 °C.

The obtained transmission spectra were seemed to be similar to each other as shown in Fig. 3., which all bands are specially for cobalt oxide structure in the form of  $\text{CO}_3\text{O}_4$ .

Pure  $\text{CO}_3\text{O}_4$ .  
0.5wt% MgO.  
1.0wt% MgO.  
2.5wt% MgO.

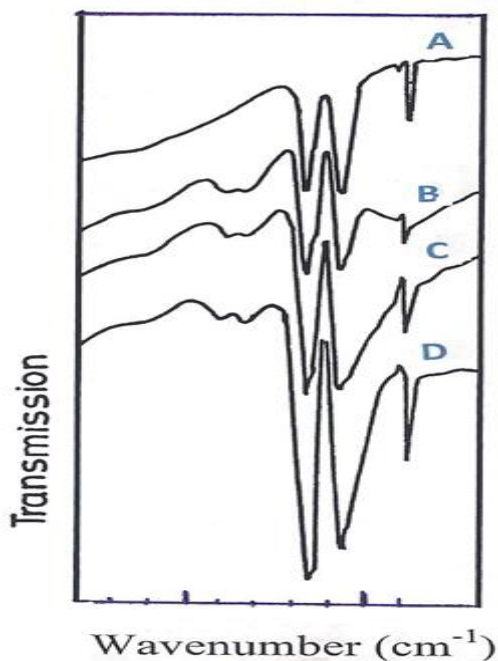


Figure 3. IR spectra of pure and doped catalysts calcined at 800°C.

The textural properties as specific surface area and pore volume distribution of the pure and doped catalysts were investigated by analyzing the nitrogen adsorption isotherms measured at 77 K. representative nitrogen adsorption-desorption isotherms and  $V_L$ - $t$  plots are shown in Figs.4,5.

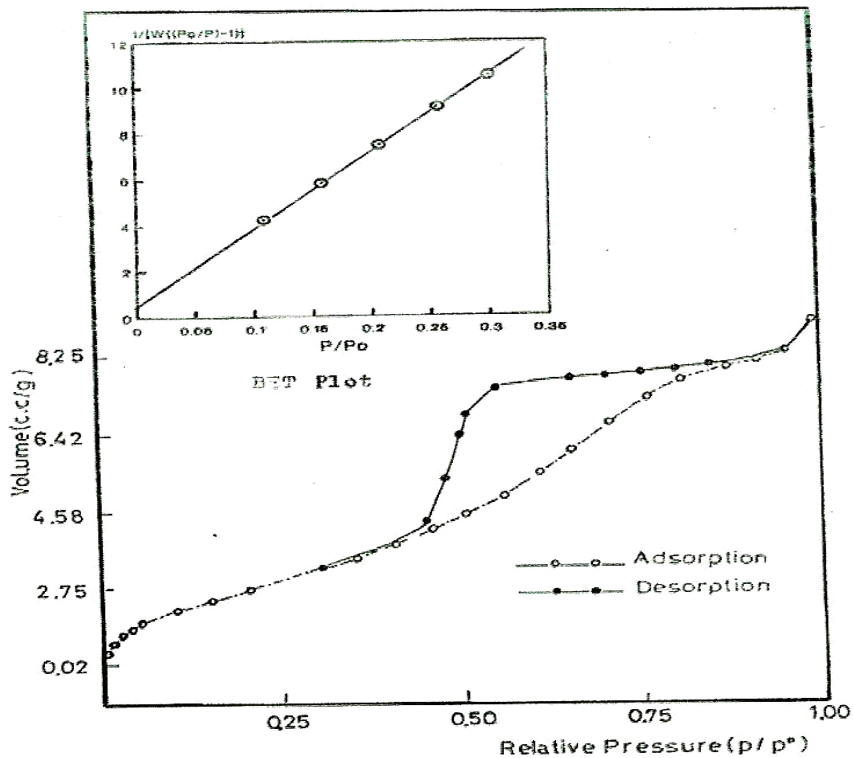


Figure 4. Adsorption-desorption isotherm of  $N_2$  at 77K on cobalt oxide doped with 2.5 wt% MgO at 600°C

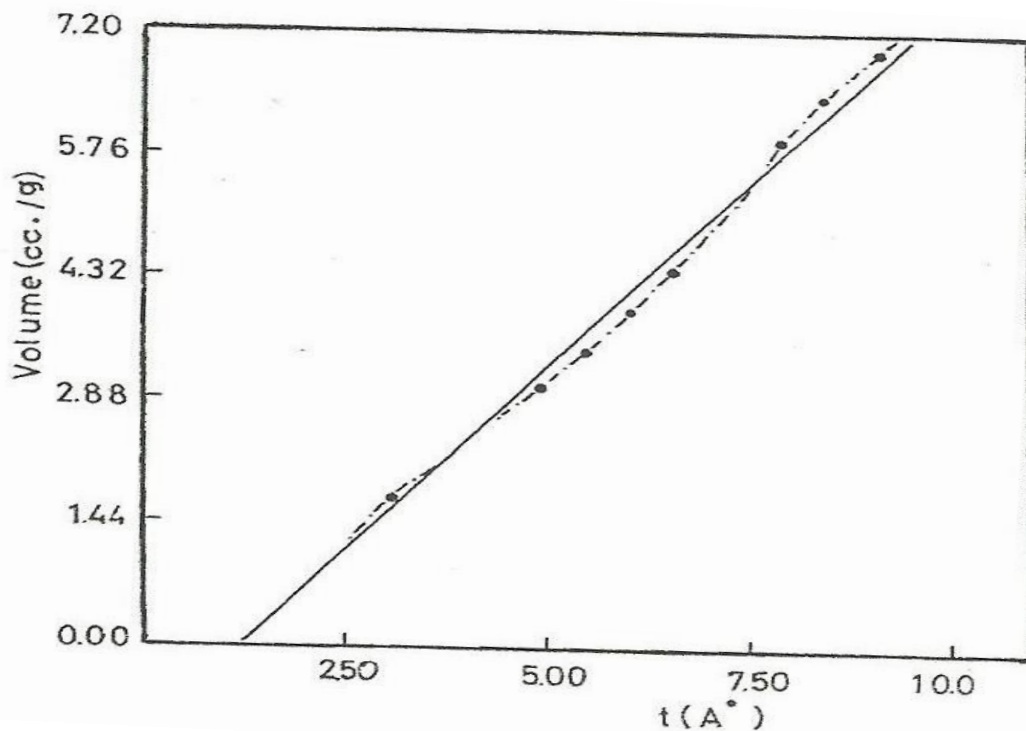


Figure 5.  $V_L$ - $t$  plots of  $N_2$  adsorption on cobalt oxide doped with 2.5 wt % MgO at 600°C.

The isotherms show the characteristics of both type II and IV of Brunauer's classification and obey the conventional BET equation. The application of this equation allowed the determination of the monolayer capacities and consequently the surface areas of the cobalt oxide catalyst doped with 2.5 wt% MgO calcined at 600°C.

The data of surface area of pure and doped promoter are given in table 1. It's found that the  $S_{BET}$  increased, since the maximum increase in  $S_{BET}$  of cobalt oxide catalyst when doped by 2.5wt% MgO. However, the increase in calcinations temperature of pure and doped catalysts from 400-800°C induced a decrease in their surface areas, specially for calcinations at 800°C.

Table 1. BET surface areas of pure and doped catalysts calcined at different temperatures.

Calcinations temp. (°C)	Pure and doped percentage of CuO(wt% MgO)	Specific surface area $S_{BET}$ (m <sup>2</sup> /g)
400	0.00	80
	0.50	84
	1.00	95
	2.50	105
500	0.00	64
	0.50	71
	1.00	81
	2.50	94
600	0.00	60
	0.50	67
	1.00	80
	2.50	85
800	0.00	53
	0.50	59
	1.00	64
	2.50	81

The observed increase in the specific surface area of cobalt oxide doped with MgO could be attributed to the initiation of new pores resulting from the liberation of an gaseous during the dissociation of magnesium nitrate as nitrogen oxide during the thermal treatment.

But, the observed decrease in  $S_{BET}$  of pure and doped catalysts during thermal treatment from 400-800 °C. might be attributed to grain growth of the particles of cobalt oxide.

The kinetics of catalytic decomposition of H<sub>2</sub>O<sub>2</sub> in the presence of pure and doped catalysts calcined at different temperature from 400-800 °C were monitored by measuring the volume of oxygen liberated at different time intervals until equilibrium was attained. The catalytic reaction was carried out at 20, 30 and 40 °C, respectively. The obtained results showed that the reaction follows first-order kinetics in all cases as shown in Fig. 6. The slopes of first-order plots allow ready determination of the reaction rate constant, k which measured at a given temperature over a given catalyst sample.

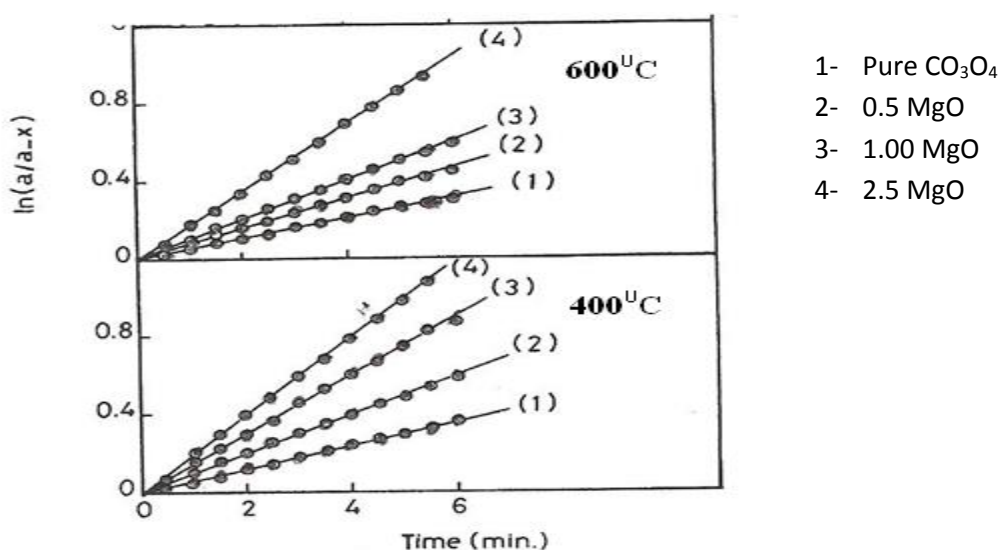
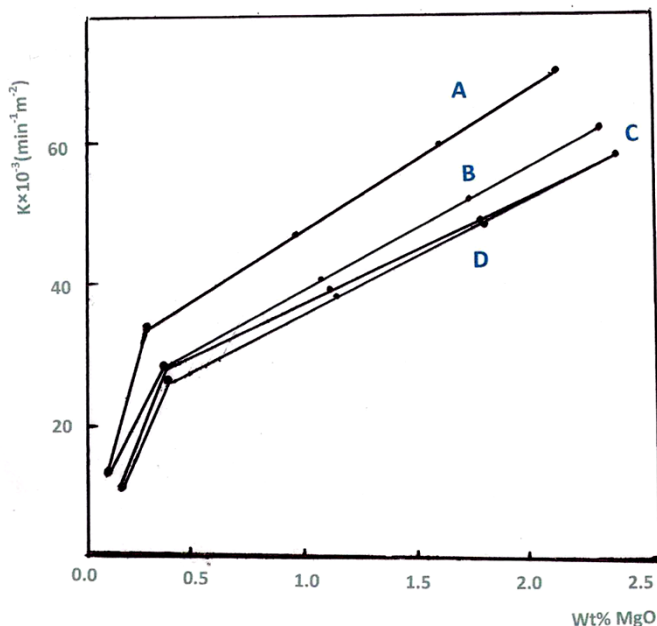


Figure 6. first-order plots of H<sub>2</sub>O<sub>2</sub> decomposition conducted at 20 °C over pure and doped calcined catalyst at 400 and 600°C. The specific catalytic activity (k) of cobalt oxide are investigated by comparing the values of k determined at the selected calcinations temperature of various catalyst solids as shown in Fig. 7.

Which Shows the variation of  $k$  as a function of dopent weight percent at 30 °C, it is cleared also that the values of  $k$  at 30°C increases as the amount of MgO added to the catalyst sample of cobalt oxide. The maximum increase is due to doping or promoting of cobalt oxide with 2.5 wt% MgO followed by calcinations at 400-800 °C



- A) 400°C.  
 B) 500°C.  
 C) 600°C.  
 D) 800°C.

Fig. 7. Variation of reaction rate constant per unit surface area for  $\text{H}_2\text{O}_2$  decomposition treated at 30°C as a function of MgO concentration for the catalyst calcined at 400 -800°C.

The maximum decrease in specific catalytic activity at 30°C due to increasing the calcinations temperature of 800°C and 2.5 wt% MgO doped catalysts; it could be attributed to an effective increase in the concentration of trivalent cobalt ions with increasing of active sites of  $\text{H}_2\text{O}_2$  decomposition ( $\text{Co}^{3+}$ - $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ - $\text{Mg}^{2+}$ ).

The dissolution process of MgO doped in  $\text{Co}_3\text{O}_4$  at convenient temperature is due to the similarity of the ionic radii of  $\text{Mg}^{2+}$  and  $\text{Co}^{2+}$  ions.

i.e. Any metal oxide doped over cobalt oxide to increase the catalytic decomposition of hydrogen peroxide, it will increase the trivalent cobalt ions (35).

The activation energy of catalytic decomposition of hydrogen peroxide performed at pure and doped catalysts solids at selected temperature, the value of reaction rate constant measured at 20-40°C enable us to calculate  $\Delta E$  (KJ / mol) by applying Arrhenius equation.

The data which correlate the relation between dopent concentration, calcinations temperature, and the activation energy are shown in table.2.

Table 2. The calculated activation energy, for catalytic decomposition of  $\text{H}_2\text{O}_2$  on pure and doped catalysts calcined at selected temperature.

Calcinations temp. (°C)	Weight percent of pure and doped solids	Activation energy $\Delta E$ (KJ / mol)
400	0.00	40
	0.50	37
	1.00	34
	2.50	30
500	0.00	49
	0.50	46
	1.00	44
	2.50	42
600	0.00	58
	0.50	54
	1.00	51
	2.50	45
800	0.00	69
	0.50	63
	1.00	57
	2.50	53

From the above results of table 2, it is obviously that the values of activation energy are increased which the MgO doped cobalt oxide catalyst are more active than the pure ones at different temperature.

Finally, the increase in values of  $\Delta E$  of pure and doped catalysts calcined at 400-800°C, indicating the decrease in their catalytic activity.

Another aspect used to study the catalytic activity for decomposition of hydrogen peroxide over the mixed oxide as cobalt oxide doped with different wt% of magnesium oxide thermally treated at different calcinations temperature, which graphically represented on Fig.8.

It can be seen that all samples calcined at 400°C were active in hydrogen peroxide decomposition. The activity increased as the magnesium oxide content increased from 0.5-2.5 wt%.

The calcinations of all sample at 500°C produced highly active catalyst. Since at calcinations temperature reached to 800°C, it produced very low catalyst activity for hydrogen peroxide decomposition, which it may be attributed to sintering or formation of spaniel solids.

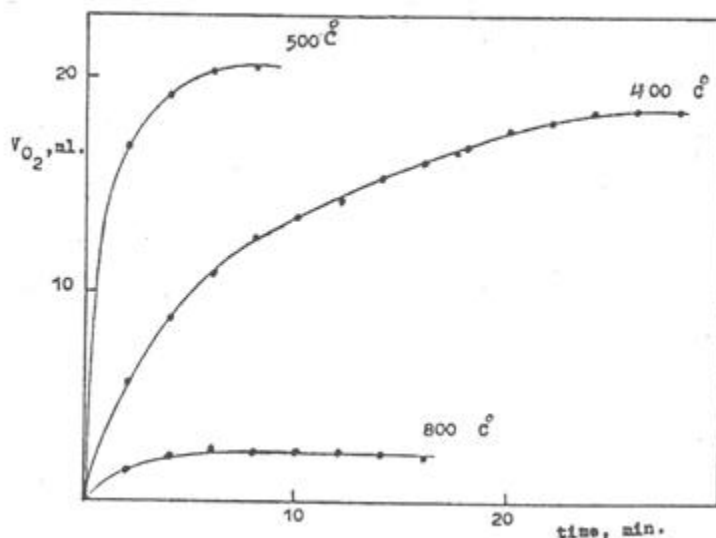


Figure 8. The activity of cobalt oxide catalyst promoted with one wt % of MgO calcined at different temperature.

## CONCLUSIONS

The doping of cobalt oxide with magnesium oxide of (0.5-2.5 wt %) followed by calcinations at 400-800°C, increases of  $S_{BET}$  and decrease of catalytic activity at 800°C.

The hydrogen peroxide decomposition activity is promoted by doping with wt% of MgO due to generation of the optimal electron-mobile environment at the surface, which used to enhance the oxidation-reduction pathway of the reaction.

The decreasing values of calculated MgO doped catalysts calcined at different temperatures are indicator of increasing their catalytic activity.

The difference in atomic radius does not exceed 15% of the small radius to form solid solution at room temperature.

It was previously thought that the support only provides a physical base for the metal oxide crystallites and also provide some stability against sintering.

Metal oxide supports have two function, structural promotion and electronic promotion.

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