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Preparation and Characterization of Pure and Na_2O Doped Co_3O_4 Spinel Supported Catalyst for Photocatalytic Degradation of Reactive Yellow Dye 145

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Abstract : The co-catalysts Co_3O_4-MgO and Co_3O_4-CaO spinel supported catalyst were prepared by the co-precipitation method in different ratios. The Na_2O doped Co_3O_4-MgO catalyst was prepared using wet impregnation method by addition weight of sodium nitrate corresponding to the desired percentage (0.5,1.0 and 1.5 %) of Na_2O to bicarbonates catalyst. The pure and doped bicarbonates of catalysts were calcinated at 600 ^{0}C for 4 hrs. The pure and Na_2O doped catalysts were characterized by using Fourier transform infrared spectroscopy (FTIR), X-rays diffraction (XRD) and atomic force microscopy (AFM) techniques. In addition to that, band gap energy of these materials were estimated using the UV-visible spectrophotometer. Physical properties of these catalysts were investigated by wet impregnation method. The 0.5 %Na_2O-30Co_3O_4-70MgO catalyst has a best physical properties, therefore it showed high activity for photocatalytic degradation of reactive yellow dye 145. Different reaction conditions were performed such as pH of reaction mixture, weight of catalysts and the effect of temperature. Activation energy for the prepared catalysts was investigated and it was equal to 16 kJ. mol^{-1} and 22 kJ. mol^{-1}for Na_2O doped and pure 30Co_3O_4-70MgO catalysts respectively. The photocatalytic activity of these materials was investigated by following photocatalytic removal of reactive yellow dye from its aqueous solution using UV-visible spectrophotometer. The absorbance of supernatant liquid was recorded at 416 nm.

Key words: spinel catalyst, Na_2O doped spinel catalyst,Na_2O-Co_3O_4-MgO.

1. Introduction

In the last few decades, different transition metals oxides have been used to design heterogeneous catalysts[1] single or supported on different materials such as Al_2O_3,MgO and CaO to increase the dispersion of the metal oxides such as MnO and CoO on the surface of the supported materials[2]. This leads to increase the surface area and the catalytic activity of these materials[3]. The cobalt oxides can exist in different oxidation states such as CoO, Co_2O_3 and Co_3O_4. These oxides were prepared as a catalyst for different oxidation reactions. In this context, Co_3O_4 as a spinel oxide was more interested and considered as a p-type semiconductor with presence of substrate and depending on the preparation method. The Co_3O_4 spinel catalyst has the formula AB_2O_4 ,where A and B represent the cobalt in two different oxidation statesCo^{II} and Co^{III} respectively in the spinel crystal lattice structure ,that are occupy the tetrahedral and octahedral sites respectively in the spinel lattice[4,5].This spinal oxide used in many industrial applications as electrolytic capacitor [6,7]and partial oxidation and steam reforming of methane[8], oxidation of ethanol, volatile organic compounds[9],combustion of toluene, methanol and ammonia[10] Co_3O_4 spinel supported on CeO_2 was used for decomposition of N_2O[11],decomposition of H_2O_2[12]and used for the treatment of industrial wastewater ,especially the textile wastewater. The textile dyes which are used to coloring the textile fibers and cotton are classified into three types:basic, acidic and despise dyes which are released toxic and carcinogenic compounds in to the aqueous phase. These compounds are difficulty to be treated by biological and physic-chemical processes[13,14]. Furthermore ,best method to treat these wastewaters pollutants by using the heterogeneous photocatalytic methods, which are capable of removing color and toxic organic compounds from textile effluents[15].

The aim of this work is the preparation of pure Co_3O_4spinel supported on MgO and CaO, and Na_2O doped and study the effect of supporting materials and dopant process on the physic-chemical properties of the catalyst and study of its activity for the degradation of reactive yellow dye(RYD).

2.Experimental Part

2.1.Preparation of Catalyst:

The Co_3O_4-MgOcatalyst with different ratios (30:70 , 40:60) and Co_3O_4-CaO with (60:40) ratio were prepared by co-precipitation method of their mixed bicarbonates from their nitrates(purity 99% supplied from Merck and B.D.H.Companies) using a solution of 1M $NaHCO_3$(99% supplied from B.D.H Company) as a precipitating agent at pH =9under a range of reaction temperature between 60-70°C. The obtained precipitate was washed with deionized water until the content of sodium equal to 100 ppm or less and was dried at 120°C in oven(Oven Bs Size Two, Gallenkamp, England) for 24 hrs. The precursors carbonates were formulated as a tablets with diameter equal to 10 mm ,and then subjected to heating at 600°C for 4 hrs in muffle furnace (muffle furnace size two, Gallenkamp).

2.2.Preparation of Na_2O doped catalyst

The Na_2O doped catalysts were prepared by the wet impregnation method with different ratios(0.5,1.0,1.5 and 2%).The samples were dried at 110 ^{0}C for 24 hrs. and then calcinated at 600 ^{0}C for 4hrs.

2.3.Determination the average particle size of the catalyst:

The particle size of pure Co_3O_4-MgO , Co_3O_4-CaO and Na_2O doped catalysts were calculated from the line broadening profile analysis of the main diffraction lines of these phases using Scherrer equation[16]: $d = K\lambda / \beta_{1/2} \cos \theta$, d: the mean crystallite diameter, λ is X – ray wavelength = 0.1545 A^o, K the Scherrer constant (0.89), β1/2 is the full – width at half maximum (FWHM) of the diffraction peaks of crystalline phases and θ is the diffraction angle.

2.4.Physical Properties of Catalysts

The physical properties of both pure Co_3O_4-MgO, Co_3O_4-CaO and Na_2O doped catalysts were investigated in this work by wet impregnation method[17],these include apparent porosity (P_A%), total pore Volume(V_P),and particle density(D_P).

2.5.Characterization of catalyst:

The Co_3O_4 spinel pure and supported catalysts were investigated by Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD) and atomic force microscope(AFM) techniques.

2.5.1.Fourier Transform Infrared (FTIR)

The Infrared Spectra for the prepared catalysts were studied by using Fourier Transform Infrared (FTIR) (supplied from Perkin Elminer company –England). The spectra were recorded in the range of wavenumbers from 400-4000 cm^{-1}

2.5.2.X-rays Diffraction (XRD)

The patterns of catalyst were investigated by X – ray powder diffractograms by using a Bruker diffractometer (XRD 6000, Shimadzu,Japan). The patterns were run with CuKα1 with secondly monochromator (λ = 0.1545 nm) at 40 kV and 40 mA.

2.5.3. Atomic force microscopy (AFM)

Surface morphology of both pure and doped catalysts were investigated using atomic force microscopy (AFM) type SPM-AA3000 Atomic Force Microscope Contact Mode Angstrom Advanced INC., 2005, USA,to investigate the surface morphology and particle size .

2.5.3.Determination of Band Gap Energy

The Bandgap energy(Eg) of the prepared catalysts were estimated by measuring the reflectance against the wavelength in the range 200-800 nm of these samples using the UV-visible spectrophotometer(26000 shimadzu, Japan),and then use the wave length to determine Eg from thePlank's equation , $E=hc/\lambda$,h plank's constant,c is the velocity of the light and λ is the wave length[18].

2.6.Catalytic activity of pure and Na_2O doped catalyst

In order to investigate the photocatalytic activity of the prepared catalysts, a series experiments were carried out to follow removal of RDY over a suspension of each of Co_3O_4, pure Co_3O_4-MgO ,Co_3O_4-CaO and Na_2O doped catalysts in the degradation of the reactive yellow dye 145(supplied from Al-Hilla textile Factory (scheme 1)). Reactions were performed at different periods of reaction time (10,20,30,40,50 and 60) min.at room temperature. In all experiments,25mg of pure and doped catalyst were suspended in 30 cm^3 of the reactive yellow textile dye(50 and 100 ppm) , in the photocell (fig.1) .The mixture of textile dye and catalyst was kept homogeneously by stirring with magnetic stirrer(supplied from Gallenkamp factory, England). The pH of the dye solution (100 ppm) was neutral without catalyst .The reaction cell was connected to circulating water thermostat through side arm in the cell andfor passing water around the cellto cooling the reaction mixture in order to keep temperature at a desired value.

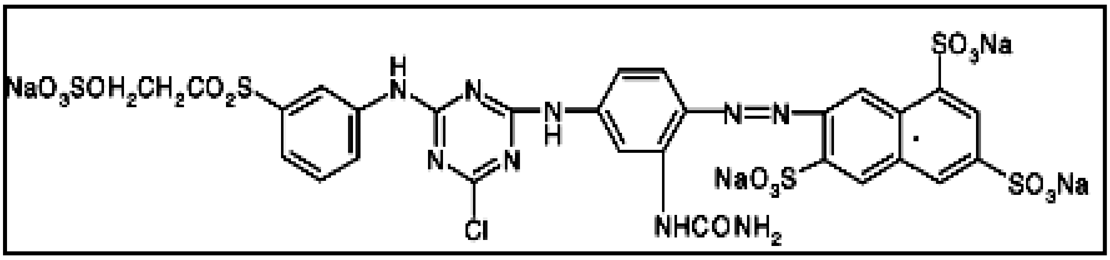


Figure1.The Molecular Structure of Reactive Yellow Dye 145 (RYD)

The low pressure mercury lamp, type TQ150Z2 (supplied from Karl Kolb Company) was used as a source of ultraviolet radiation. The scheme of the reaction system is shown in Figure 2, whichwas designed and used in our previous works[19].

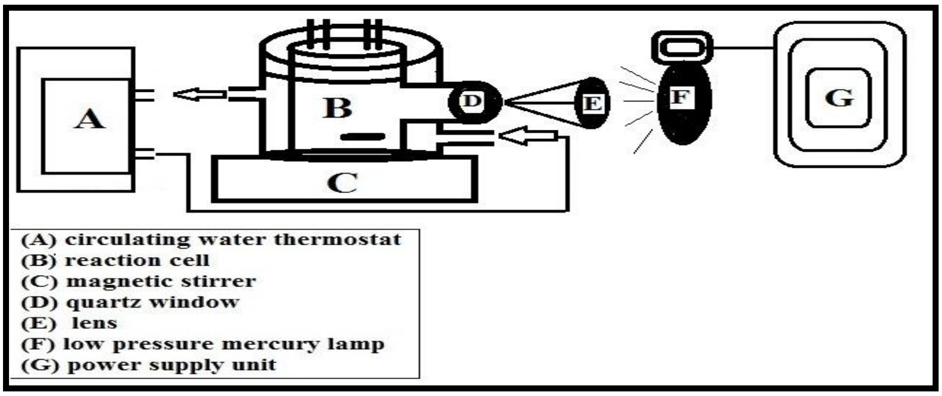


Figure 2.Schematic Diagramfor the photocatalytic Reaction System

The degradation reactions followed spectrophotometrically by using UV-Visible Spectrophotometer (UV-1650 PC supplied by shimadzu company),at λ =416 nm.

2.7. Other experiments were carried out to study the effect of variation of the used weight of catalyst on the degradation of RYD (100ppm). The used mass dosages in this study were as follows: 0.015,0.025,0.05 and 0.075 g. at the same reaction period and same reaction temperature as well as fixing of all other reaction conditions.

2.8. Study the effect of the amount of Na_2O dopant on the activity for the degradation of reactive yellow dye (100 ppm) of catalyst by using 0.025 g. of 0.5,1.0,1.5 and 2 % of Na_2O.

2.9. Study the effect of variation in reaction temperature on the catalytic activity of the used catalysts on dye removal under the same reaction conditions. These temperatures were as follows20,25,30 and 35°C.

3.Results and Discussion

3.1.Characterization of Catalysts

3.1.1. FT-IR Spectra for the prepared catalysts

FTIR spectra for the prepared catalysts are shown in Figures 2 ,3 and 4, from these spectra it can be seen appearance of a peak that can be assigned for Co-O bond which refer to present of two strong vibration bands ,the first band at 663 cm^{-1}, this band is due to Co^{II}-O bond in the tetrahedral hole. The second at 556-570 cm^{-1}can be assigned to Co^{III}-O bond in the octahedral hole for the spinal lattice structure of Co_3O_4 in the prepared catalysts[12,20]. These two strong vibration bands confirm formation of Co_3O_4 spinel structure. For Mg-O bond in the position of 423-449 cm^{-1} and for Ca-O bond at437 cm^{-1}. The stretching bond OH-Mg and OH-Ca of the surface of magnesium and calcium oxides in the frequencies 3421-3433 and 3404 cm^{-1} due to the adsorption of water from the atmosphere[21].The bands 1423-1492 and 1417cm^{-1} for the bending vibration for the surface hydroxyl group (–OH)[22].

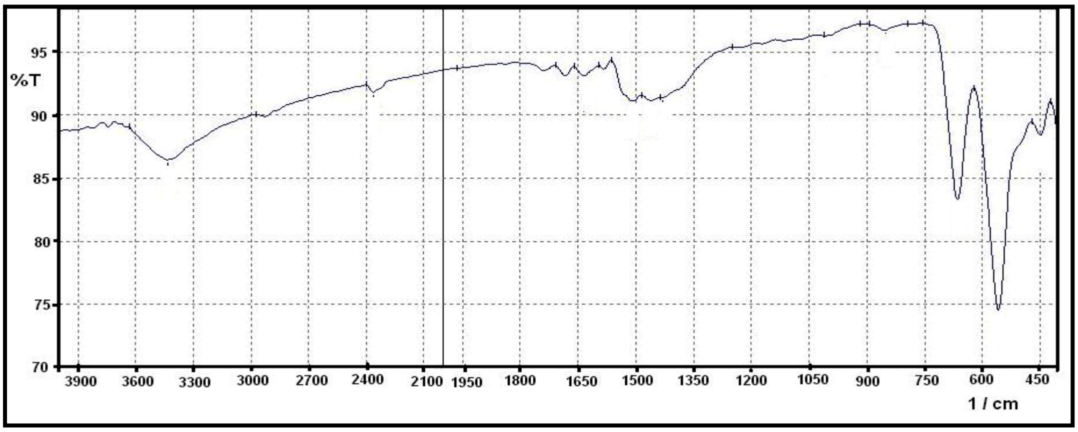


Figure 2.FT-IR spectrum for pur Co_3O_4-MgO catalyst

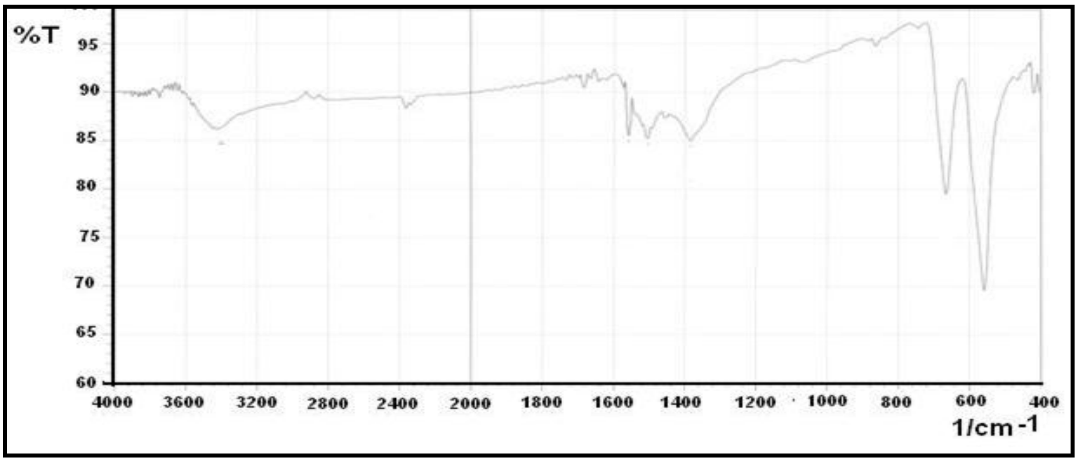


Figure 3. FT-IR spectrum for Na_2O doped Co_3O_4-MgO catalyst

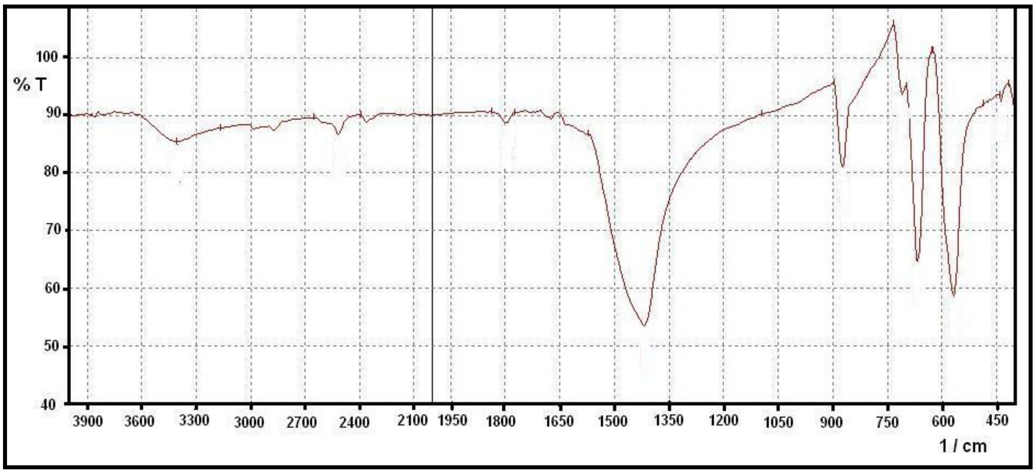


Figure 4.FT-IR spectrum for Co_3O_4-CaO catalyst

3.2.XRD Investigation of pure and Na_2O doped Co_3O_4-MgO and Co_3O_4-CaO catalysts: X-rays diffraction patterns of pure and Na_2O doped Co_3O_4- MgO and Co_3O_4-CaO catalysts are shown in Figures 5,6 and 7.

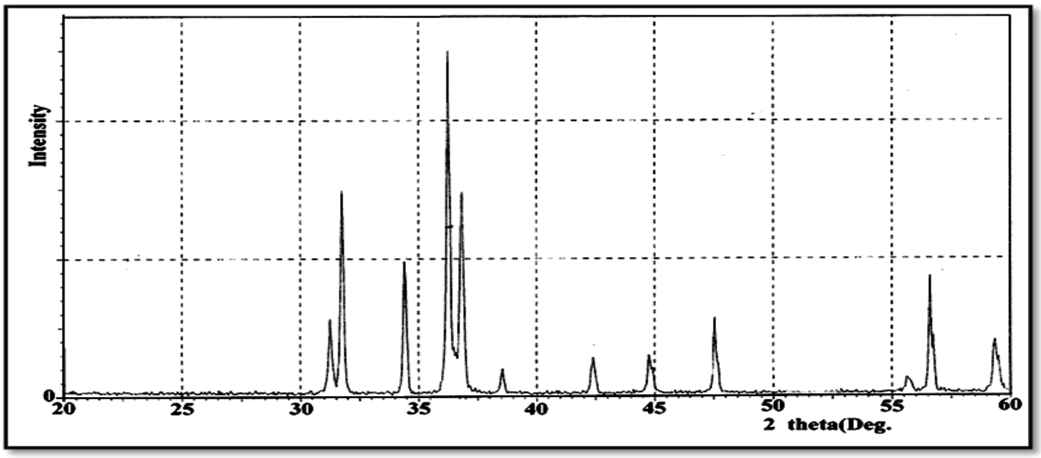


Figure 5. XRD patterns of $30Co_3O_4$-70MgO catalyst

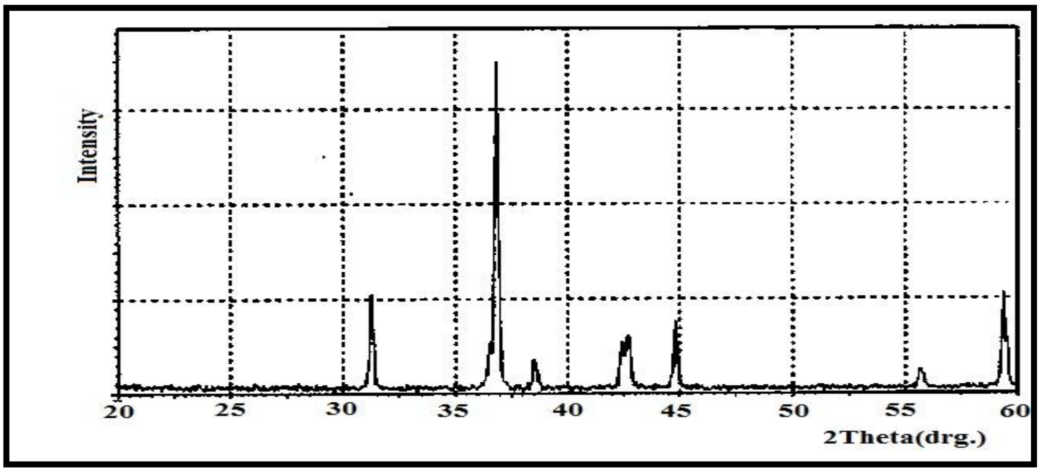


Figure6.XRD patterns of $30Co_3O_4$-70CaO catalyst

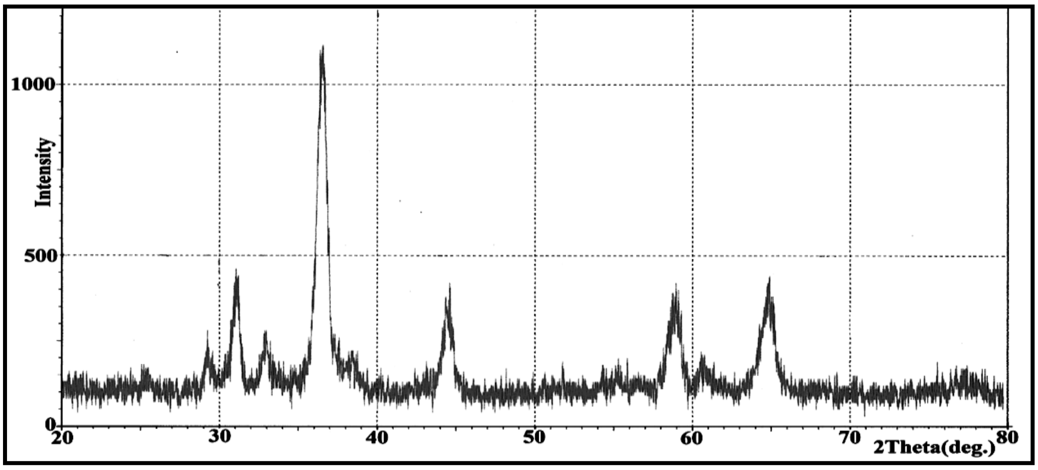


Figure7.XRD patterns of Na_2O doped $30Co_3O_4$-70MgO catalyst

From Comparison of X-rays diffraction patterns of pureCo_3O_4-MgO and Co_3O_4-CaO with those of standard single oxide[23]. It can be seen that there is a small deviation in the position of diffraction angles and change in the relative intensities of the main absorption peaks ,this due to the interaction between the mixed oxides in the catalyst[16].The best crystalline phases of the patterns of prepared catalyst and obtained a complete crystal size of the particles occurs in Co_3O_4-MgO catalyst. The main relative intensities of the diffraction lines of two catalysts with their 2 theta diffraction angles and the particle size of the two catalysts are shown in table1.The physical properties represented the apparent porosity (P_A%), total pore volume(V_P),and particle density(D_P) of pure Co_3O_4-MgO, Co_3O_4-CaO and Na_2O doped catalysts are summarized in table 2.

Table 1. The main diffraction line pattern with their relative intensitiesand diffraction angles.

Co_3O_4-MgO			**Co_3O_4-CaO**			**Na_2O-$30Co_3O_4$-70MgO**		
2 theta (deg.)	**Oxide**	**Relative intensities %**	**2 theta (deg.)**	**Oxide**	**Relative intensities %**	**2theta (deg.)**	**Oxide**	**Relative Intensity %**
31.3	Co_3O_4	33	28.8	CaO	28	28.2	Na_2O	20
36.9	Co_3O_4	100	31.0	Co_3O_4	33	31.2	Co_3O_4	36
37.2	MgO	65	32.4	CaO	37	32.8	Na_2O	19
38.5	Co_3O_4	08	36.8	Co_3O_4	100	36.6	Co_3O_4	100
42.5	MgO	12	36.9	CaO	100	38.4	MgO	10
43	MgO	20	44.8	Co_3O_4	20	44.4	MgO	28
44.8	Co_3O_4	20	59.3	Co_3O_4	32	44.8	Co_3O_4	30
59.5	Co_3O_4	32	64.1	CaO	19	59.0	MgO	25
			65.2	Co_3O_4	38	59.2	Co_3O_4	32
						64.5,65.2	MgO,Co_3O_4	33,27

Table 2. Physical properties of the prepared catalysts.

Catalyst	**Porosity %**	**Pore Volume(V_p) cm^3/gm**	**Particle Density(D_P) gm/cm^3**	**Average Particle Size of Catalyst (nm)**
$0.5Na_2O$-$30Co_3O_4$:70MgO	71.20	0.76	0.928	1.51
$40Co_3O_4$:60MgO	58.01	0.589	0.984	2.62
$30Co_3O_4$:70MgO	69.03	0.711	0.942	2.48
$30Co_3O_4$: 70CaO	49.00	0.50	1.00	2.73
CaO	34.40	0.17	2.40	-
Co_3O_4	38.59	0.22	1.77	-

3.3.Atomic force microscopy (AFM):

The images of the atomic force microscopy of Na_2O doped Co_3O_4-MgO ,Co_3O_4-MgO and Co_3O_4-CaO spinel catalysts show ,that the average particle size increase in the same orders of the catalysts ,these equal to 82.5,88.6 and 98.6 nm for the catalyst respectively as in Figure (8a,b,c),The variation of the particle size between pure and Na_2O doped Co_3O_4-MgO due to the effect of the doping, on the other hand the different between the particle size of Co_3O_4-MgO and Co_3O_4-CaO attributed to the effect of support materials[24,25].

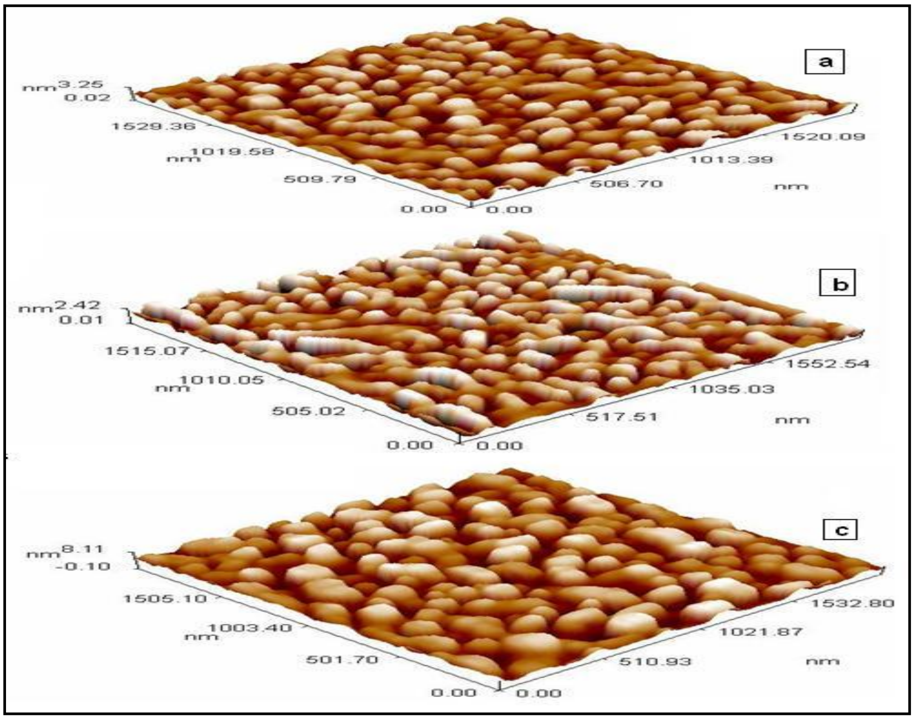
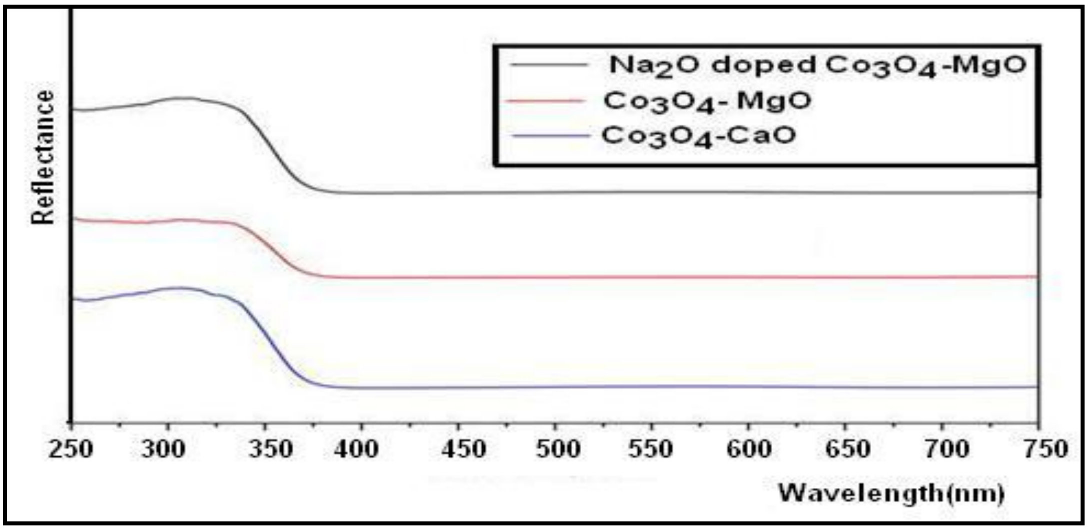


Figure 8.AFM imagesof : a-Na_2O doped Co_3O_4-MgO,b-Co_3O_4-MgO and c-Co_3O_4-CaO catalyst

3.4.Determination of band gap energy for the prepared catalysts

Figure 9 shows the reflectance diagram of the prepared catalysts,from this figure we determined the band gap energy for pure Co_3O_4-CaO,Co_3O_4-MgO and Na_2O doped Co_3O_4-MgO catalysts ,that are equal to 3.19,2.6 and 2.4 eV.For these catalysts respectively.However, decreasein the values of band gap energy for the doped catalysts can be attributed to the effectof doping process on these materials[24].



Figure(9):UV-visible Reflectance for Co_3O_4-CaO, Co_3O_4-MgO and Na_2O doped Co_3O_4-MgO Catalysts

3.5. Evaluation of the Catalytic Activity of the prepared catalysts

The photocatalytic activity of Co_3O_4, $30Co_3O_4$-70MgO,$40Co_3O_4$-60MgO and $30Co_3O_4$-70CaO catalysts was investigated by following the photocatalytic degradation of RYD using an aqueous solution of this dye (50ppm) and the pH of solution equal to 7.5 at different time(min.). The obtained results are shown in Figure10.

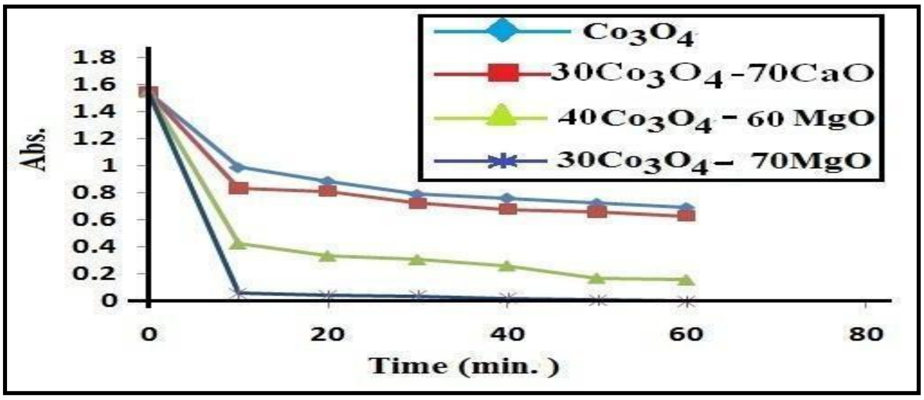


Figure10.Photodegradation of Reactive Yellow Dye(50ppm) Over Co_3O_4 , Co_3O_4- MgOand Co_3O_4-CaO

Figure (10), illustrated that the decrease in the absorbance of RYD in case of using the catalyst $30Co_3O_4$-70MgOis shown the best efficiency for dye removal. This result may be attributed to enhancement of physical properties of this catalyst such as increase of surface area, porosity and pore volume[26]as shown in Table 2.

3.6.Effect of weight of catalyst on the catalytic activity of photodegradation of reactive yellow dye (100ppm):

Because of completely released of reactive yellow dye 145 at a concentration of 50 ppm by using $30Co_3O_4$-70MgO Catalyst. Then higher dye concentration was used (100ppm). In order to study the effect of weight of the used catalyst (0.015, 0.025 , 0.05 and 0.075) g. on its activity in the photodegradation of the dye as shown in figure (11). The increasing of weight of catalyst caused to increasing of photodegradation of reactive yellow dye until to the completely released of the dye and the absorbance become equal to zero at the weight 0.075 gm,this attribute to increase of active site on the surface of catalyst[27].

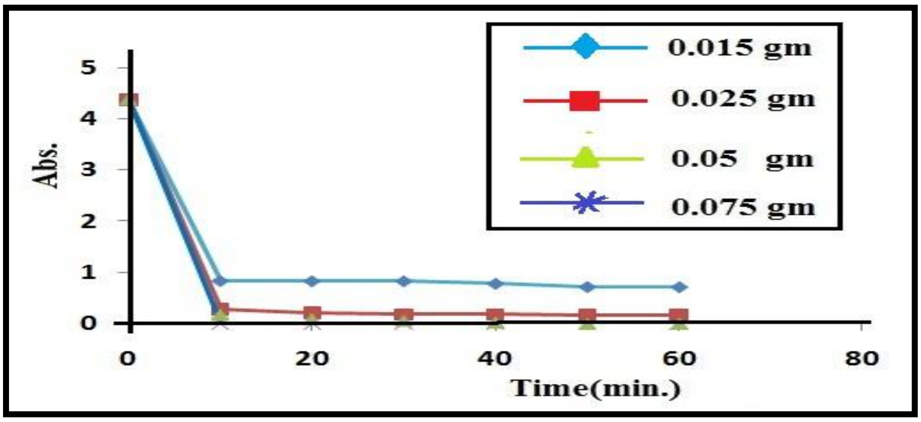


Figure11. Photodegradation of RYD (100ppm) over different weight of $30Co_3O_4$-70MgO catalyst

3.7. Effect of Na_2O doping on the catalytic activity of catalysts in the photodegradation of reactive yellow dye (100ppm)

Different percentages of Na_2Odopant in the prepared catalysts $30Co_3O_4$-70MgO,$40Co_3O_4$-60MgO and $30Co_3O_4$-70CaO improve this catalytic activity for degradation of reactive yellow dye as showing in figure 12which indicates that 0.5%Na_2O is the best dopant ratio to obtain best photodegradation of reactive yellow dye over this catalyst. The increasing of catalytic activity due to the dopant process, which decreasing the particle size and lowering the band gap energy [24,25].

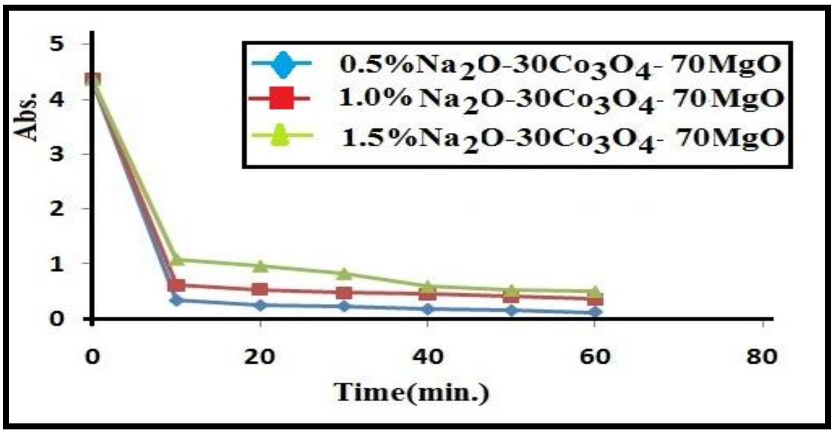


Figure12.Photodegradation of RYD(100ppm) over(0.025)gof Na_2O doped 70Co_3O_4-30MgO catalyst

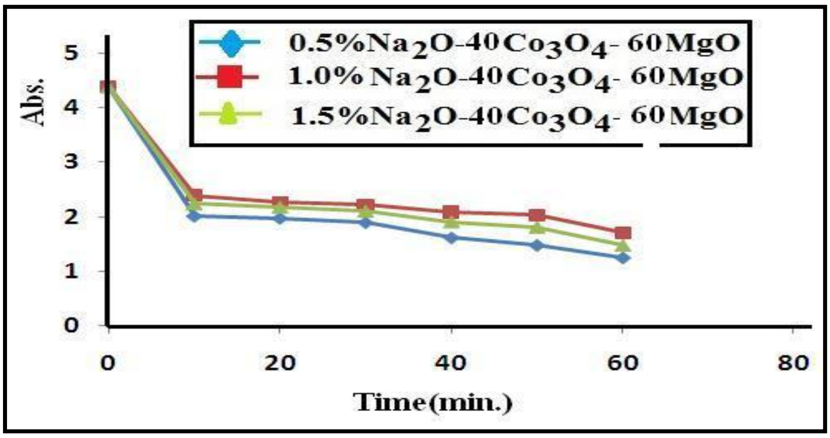


Figure13.Photodegradation of RYD(100ppm) over (0.025)g of Na_2O dopped 40Co_3O_4 -60MgO Catalyst

Figures 13 and 14 show that the best percentage of Na_2O dopant are 0.5 for each40Co_3O_4-60MgO and 30Co_3O_4-70CaO respectively ,and 1% for 30Co_3O_4-70CaOwhich are gave a high photodegradation of reactive yellow dye.

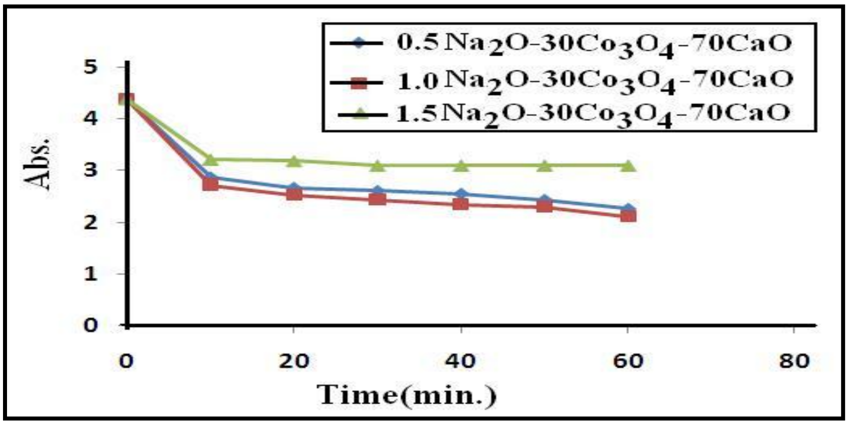


Figure14.Photocatalytic degradation of RYD(100ppm) over (0.025)g of Na_2O doped 30Co_3O_4-70CaO catalyst

The alkali metals increase the catalytic activity by acting as electronic promoters and forms of new ion pairs $Na^+(Co^{3+})$ in the lattice ,that is lead to the lowering of its Fermi -level, and improve the oxidation-reduction ability of the active site of doped catalyst[28-30].

3.8. Effect of temperature on the photocatalytic activity of the prepared catalyst in the removal of Reactive Yellow Dye(100 ppm)

Figures 15 and 16 show the increasing of degradation of the dye(100ppm) with increasing of reaction temperature from 20 to 35 °C over (0.025)g of 0.5%Na2O-30Co_3O_4-70MgO and pure 30Co_3O_4-70MgO catalyst respectively, this attribute to liberation of occupied site on the surface of catalyst and led to more adsorbed species of the reactant and give high activity[31].

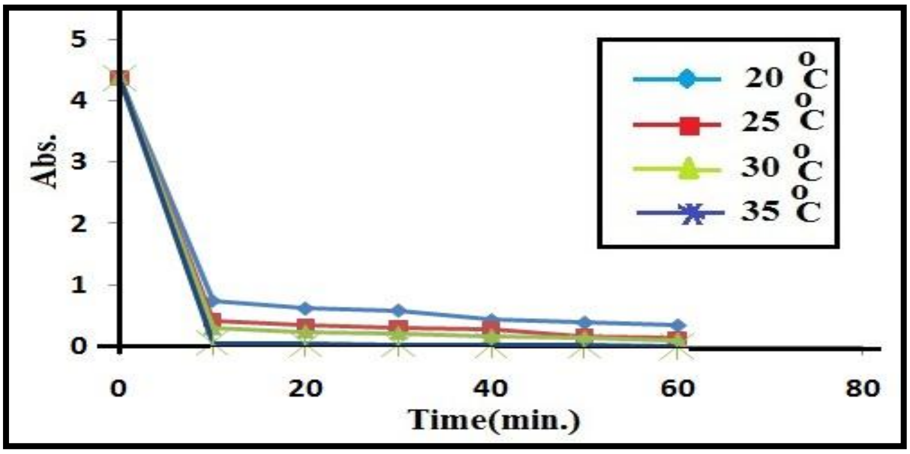


Figure15. Photocatalytic degradation of RYD(100ppm) over (0.025)g of 0.5%Na_2Odoped30Co_3O_4-70MgO catalyst atdifferent temperatures

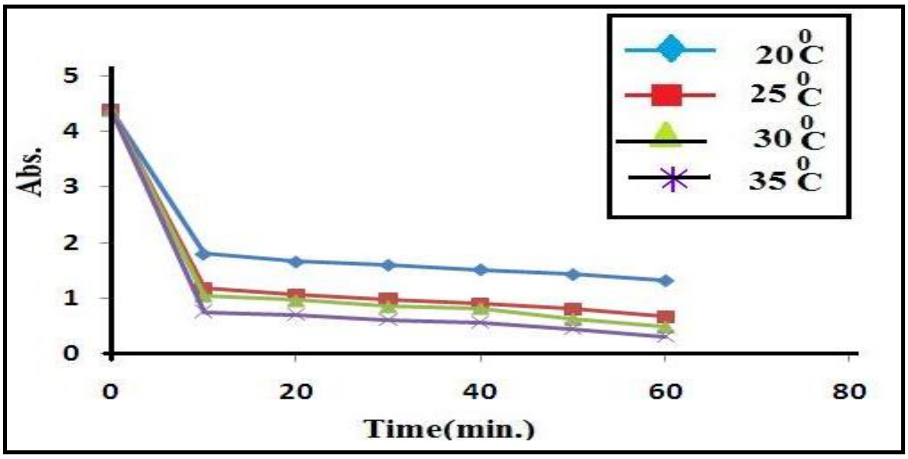


Figure16. Photocatalytic degradation of RYD(100ppm) over (0.025)g of pure 30Co_3O_4.70MgOcatalyst at different temperatures

Depending on the results of the absorbance of degradation of the dye in Figures 15 and 16, the rate constants can be calculated by plotting the Lnk versus 1/T °K as shown in Table (3) and Figure 17to calculate the activation energy (E_a) for the catalytic reaction.

Table 3.The constants of the rate of reactions at different temperature for pure and doped Co_3O_4-MgO catalyst

Temperature (K^0)	1000/ T (K^0)	Constants of rate of reactions(k sec^{-1}) For Na_2O Doped Catalyst	LnK (Sec^{-1})	Constants of rate of reactions(k sec^{-1}) For Pure Catalyst	LnK (Sec^{-1})
293	3.41	0.11	-2.2	0.085	-2.465
298	3.35	0.122	-2.1	0.104	-2.263
303	3.3	0.138	-1.977	0.114	-2.171
308	3.24	0.152	-1.88	0.135	-2.002

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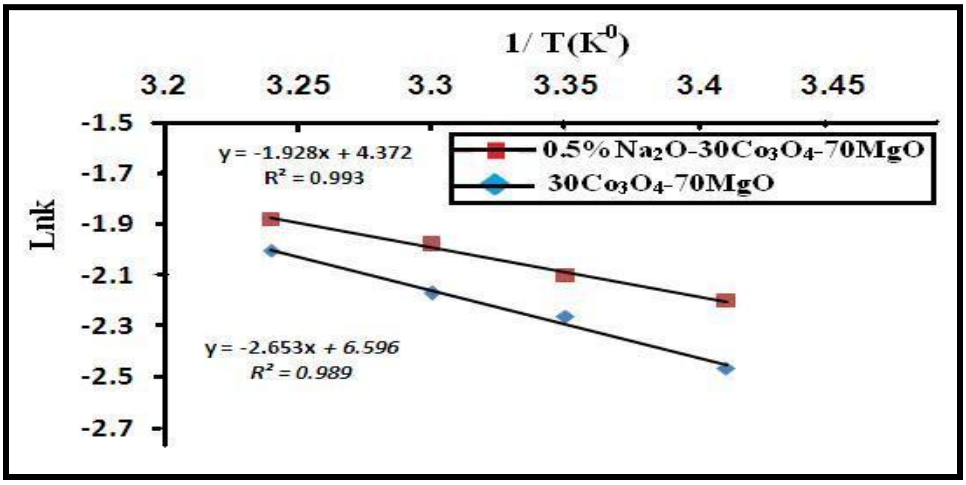

Figure 17. Temperature dependence for the photocatalytic degradation of Reactive Yellow Dye 145(100ppm) over (0.025)g of Na_2O doped $30Co_3O_4$-70CaO catalyst

From the recorded results those are shown inTable 3 and Figure 17, it can be see that, the activation energy of 0.5% Na_2O-$30Co_3O_4$-70MgO equal to(16 $kJmol^{-1}$) was less than that for $30Co_3O_4$-70MgO which equal to (22 $kJmol^{-1}$). Therefore it can be concluded that the activity of the catalyst 0.5% Na_2O-$30Co_3O_4$-70MgO is higher than that for Co_3O_4,$30Co_3O_4$-70MgO,$60Co_3O_4$-40MgO and $30Co_3O_4$-70CaO,this may be attributed to increasing of the surface area and porosity (active sites) of supported catalyst[26].About of 80-90% of reactive yellow dye is released by adsorption process only ,and another released completely by the photocatalytic degradation process .The removal of Reactive Yellow Dye by using 0.5%Na_2O-$30Co_3O_4$-70MgO is the best from the comparison of this results withthese that have beenobtained fromthe previous study[32],which used the materials:(SO_4^{2-},Cl^-,NO_3^-,CH_3COO^-,HCO_3^- and HPO_4^{2-}) to improvement of the catalytic properties of TiO_2 coated non-woven fibers as photocatalyst to treated the dye in the acidic medium at pH3,these materials considered itself contaminated to water and addition another pollutants ions. in additional to the unfavorable the acidic medium of the water.

4.Conclusions

From the obtained results in the current study, it can be concluded the followings points:

1. The doped Na_2O catalyst exhibited high porosity, pore volume and lower density, and these properties are very preferable in the action of catalyst,
2. Photocatalytic efficiency of dye removal over the used catalysts was full the order : 0.5% Na_2O-$30Co_3O_4$-70MgO > $30Co_3O_4$-70MgO>$60Co_3O_4$40MgO > $30Co_3O_4$-70CaO>Co_3O_4. Increase of the catalytic activity of the doping catalyst can be due to the decrease of the particle size which affecting on the decrease of band gap and lead to the increase of the activity,
3. It is possible to reduce the mass of $30Co_3O_4$-70MgO catalyst from 0.075 to 0.025 gm to obtained a completely removal of reactive yellow dye 145 by using 0.5 % Na_2O dopant at 35 ^{0}C,

4. Activation energy of 0.5 % Na_2O -30Co_3O_4-70MgO was less than that for the pure30Co_3O_4-70MgO catalyst,
5. Using 0.5 % Na_2O -30Co_3O_4-70MgO catalyst was efficient to reduce waste hazardous types and quantities that are resulted from the treated process as in the previous studies,
6. The applied treatment method in this study is good for removal of textile dye in the moderate pH without any further effect for the medium to living the aquatic organisms.

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