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Characteristic study of CoO-ZnO Catalyst

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Abstract:

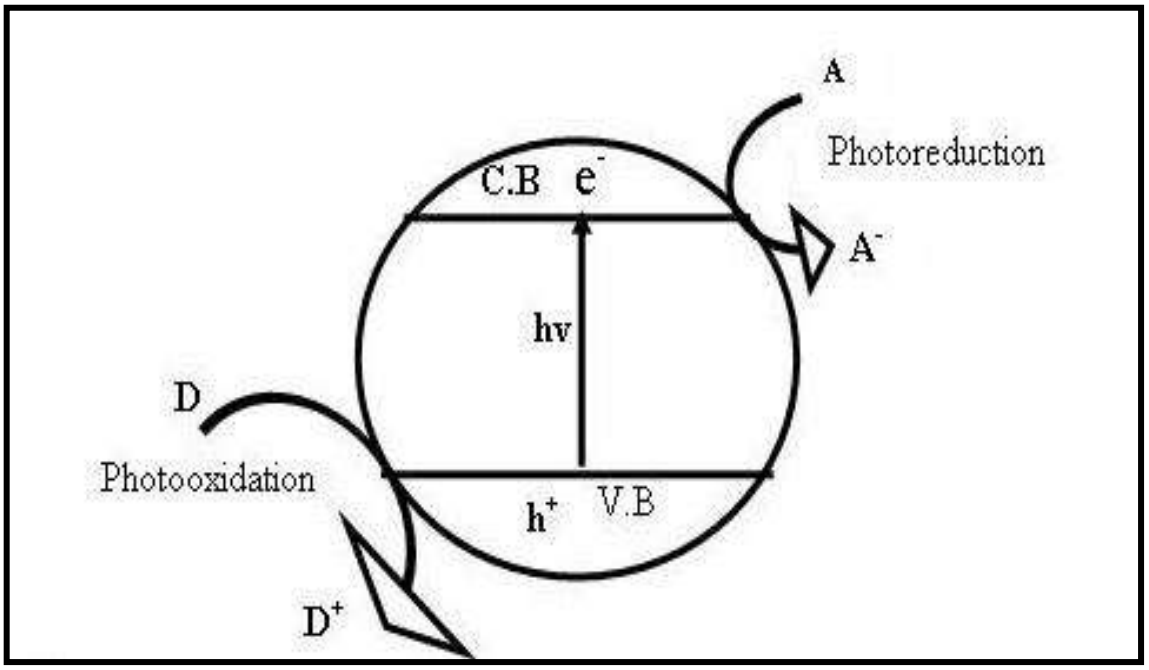
CoO-ZnO catalyst was prepared by using the coprecipitation method, by adding sodium bicarbonate to cobalt and zinc nitrates solution until pH equal to 8.The resulted cobalt and zinc bicarbonate was calcinated at 773 Kº for 4 hours. Then the catalyst was characterized by chemical analysis, and X-Ray Diffraction Teqnique(XRD).The activity of CoO-ZnO catalyst was examinated in the photocatalytic oxidation of benzyl alcohol, to the corresponding benzaldehyde,at different times, and temperatures. The results showed that the activation energy for CoO-ZnO catalyst equal 16 $kJmol^{-1}$, it is lower than that, for ZnO which equal to 21 $kJmol^{-1}$.

الخلاصة:

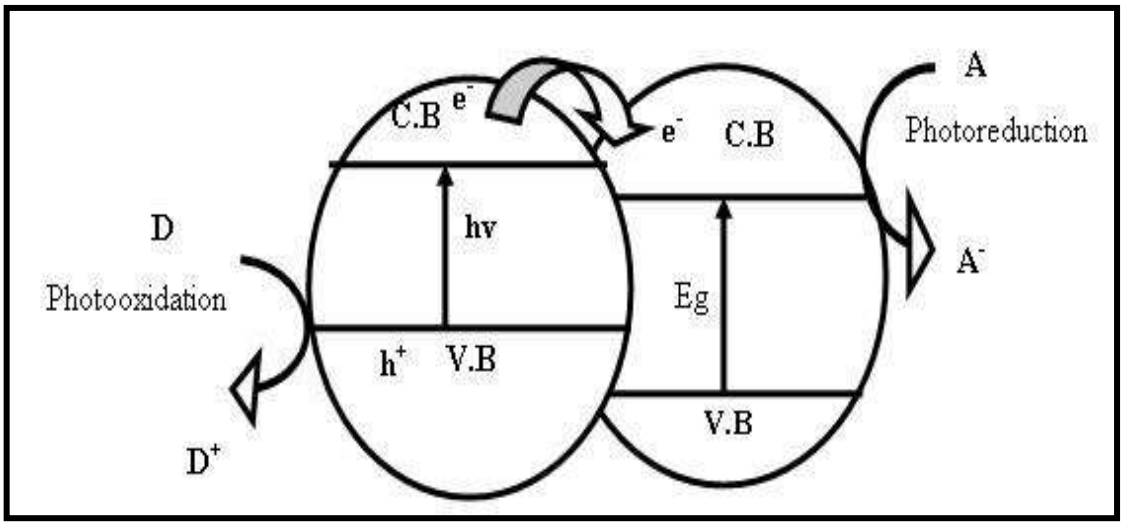
تم تحضير العامل المساعد CoO-ZnO ، باستعمال طريقة الترسيب المشارك بإضافة بيكاربونات الصوديوم إلى محلول نترات الكوبلت والخارصين الى أن تصبح الدالة الحامضية (pH) للمحلول تساوي 8 و تم تحميص كاربونات الكوبلت والخارصين الناتجة قي درجة حرارة 773 كلفن لمدة 4 ساعات. شخص العامل المساعد بواسطة التحاليل الكيميائية وحيود الاشعة السينية. تم اختبار فعالية العامل المساعد CoO-ZnO في الأكسدة الضوئية للكحول البنزيلي الى البنزالدهايد المناظر، في فترات زمنية ودرجات حرارة مختلفة. بينت النتائج بان طاقة التنشيط للعامل المساعد CoO-ZnO تساوي $16\ kJmol^{-1}$, وهي أوطأ من طاقة التنشيط لاوكسيد الخارصين ZnO والتي تساوي $21\ kJmol^{-1}$.

Introduction:

In recent years , the semiconductor metal oxides are widely used for the heterogeneous photocatalytic oxidation in the field of synthetic organic chemistry[1-2]. The oxidation of alcohol to the corresponding carbonyl compounds ,is one of the most important organic transformations[3],and chemical manufacturing[4].The photocatalytic oxidation is considered as an effective method[5] in the removal of the organic pollutants from the wastewater and air , because it has many advantages such as: high destruction efficiencies at room temperature , complete oxidation of organics to CO_2,and H_2O ,applicable to large number of organics, and works in humid conditions. The photocatalytic oxidation of organic compounds[6-9],is based on the combination of a semiconductor metal catalytic surface , with the ultraviolet radiations of the appropriate wave length, that is used in the photocatalytic reactions, and utilizes the UV-radiation to promote electrons from the valence band in to the conduction band of a semiconductor metal oxides, which produce an a positive hole(h^+) in the covalent band and an electron(e^-) in the conduction band, as shown in figure(1) .In the coupled semiconductors, the electrons in the conduction band of one with small band gap transfer to the conduction band of the other, leaving a positive hole in the first one ,while the electron remains in the conduction band of the other as shown in figure(2).



Figure(1):Photooxidation, and photoreduction reactions on the single semiconductor molecule



Figure(2):Photooxidation,and photoreduction reaction on the coupled semiconductor molecules

Boot ***et al*** [10] prepared the catalyst which consists of CoO, and MnO supported on ZrO_2 surface ,by using the wet impregnation method for the supported oxide. The CoO-MgO catalyst was prepared by Jang ***et al*** [11],by using the coprecipitation method with addition of $LiOH.H_2O$.The $CoO-Al_2O_3$ catalyst was also prepared by Nga and Chi [12] using the sol-gel method with citric acid with addition of aqueous ammonia, and calcinated the gel at different temperature(823-1073) K° for 4 hours. Abass[13] prepared the CuO-CoO catalyst by the coprecipitation method of copper and cobalt carbonates with sodium carbonate as a precipitated factor, and studied the activity of this catalyst in the photooxidation of 2-butanol to 2-butanone. The photocatalytic oxidation of benzyl alcohol to the corresponding benzaldehyde studied by , Rüther[14],Fattima Al-Zahra[15], Farhadi ***et al*** [16],and Ohkubo[17],by using the heteropolyoxometalate catalysts,TiO_2 and sensitized TiO_2, heteropolyoxotungstate(H4SiW12O40/SiO2),and 9-phenyl-10-methylacridinium as a

photocatalysts respectively. Plassimano ***et al*** [18] studied the photocatalytic oxidation of 4-methoxy benzyl alcohol to p-anisaldehyde by using TiO_2 catalyst. The aim of this work is preparation of CoO-ZnO catalyst, and study its activity in the photocatalytic oxidation of benzyl alcohol to the corresponding benzaldehyde .

Experimental:

1-Preparation of CoO-ZnO catalyst:

The coprecipitation method has been used to prepare CoO-ZnO mixed oxides, with the ratio (1:1), by using cobalt and zinc nitrates (purity 99.8% supplied from Merck company),and addition of sodium bicarbonate (purity 99.8 % supplied from BDH company),until a constant pH=8 is reached, at a reaction temperature (333) Kº for 30 minutes .The mixture of cobalt and zinc bicarbonates was dried at (393) Kº for(16) hours and calcinated at (773)Kº for (4) hours.

2-Characterization of CoO-ZnO catalyst:

2-1-Chemical analysis:

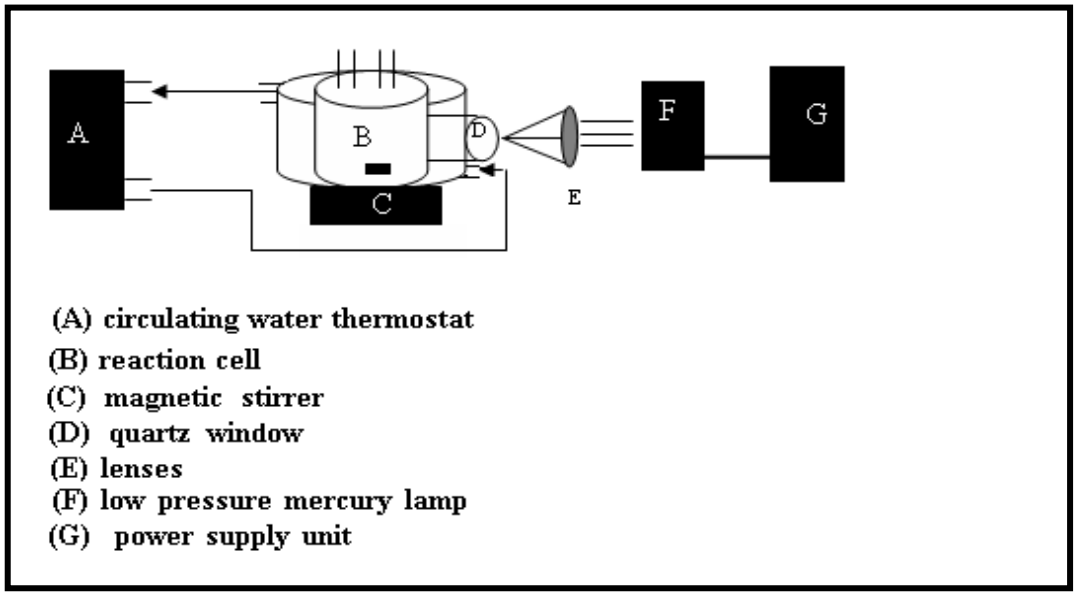
The quantity of cobalt ,and zinc in the mixture oxides was determined by flame atomic absorption (Pye unicam SP9 atomic absorption spectrophotometer, supplied from Phillips company).The absorbance of cobalt and zinc in mixed oxides was compared with the calibration curve of known concentrations of these elements.

2-2-X-Ray Diffraction technique:

The x-ray diffraction powder patterns were obtained with XRD-instrument(PW1410/20 supplied from Phillips company),and by using the Bragg's law ($n\lambda=2d \sin\theta$) ,and compared the results of space –d with the standard patterns[19].

3-photocatalytic oxidation of benzyl alcohol:

The activity of CoO-ZnO catalyst has been done in the photocatalytic oxidation of benzyl alcohol(purity 99 % supplied from BDH company),in all experiments, (150)mg of CoO-ZnO or ZnO is suspended in (30)cm^3 of benzyl alcohol(0.01 molar), which is placed in the photoreaction cell, the reaction mixture is kept homogeneous by stirring with magnetic stirrer. The UV-light is supplied to the reaction mixture through the quartz window in the reaction cell,which was desined by Hussein[20], by using mercury lamp(type TQ150 Z2 supplied by Karl Kolb company).The desired temperature of the reaction is adjusted by water circulation around the reaction cell, a schematic diagram of the reaction system is shown in figure (3) . 2cm^3 of irradiated sample are withdrawn periodically at different reaction times by microsyring,and centrifuged to separate the solid catalyst, and measured the absorbance of the supernatant liquid at (λ=240 nm) using UV-visible spectrophotometer(UV-1650 PC supplied from Shimadzu company) .The concentration of benzaldehyd yield is pursued by the comparison of the absorbance decrease of the supernatant at a given time with the absorbance of starting benzyl alcohol before the reaction .



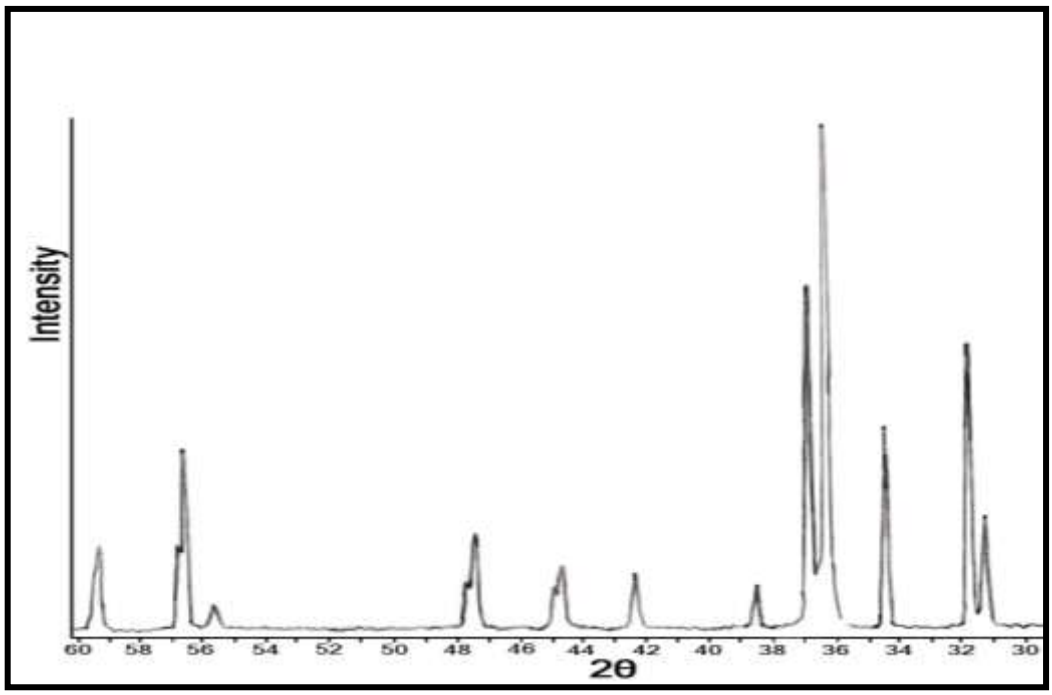
Figure(3):Schematic diagram of the experimental apparatus for photocatalytic oxidation reaction

Results and Discussion:

1- Characterization of CoO-ZnO Catalyst:

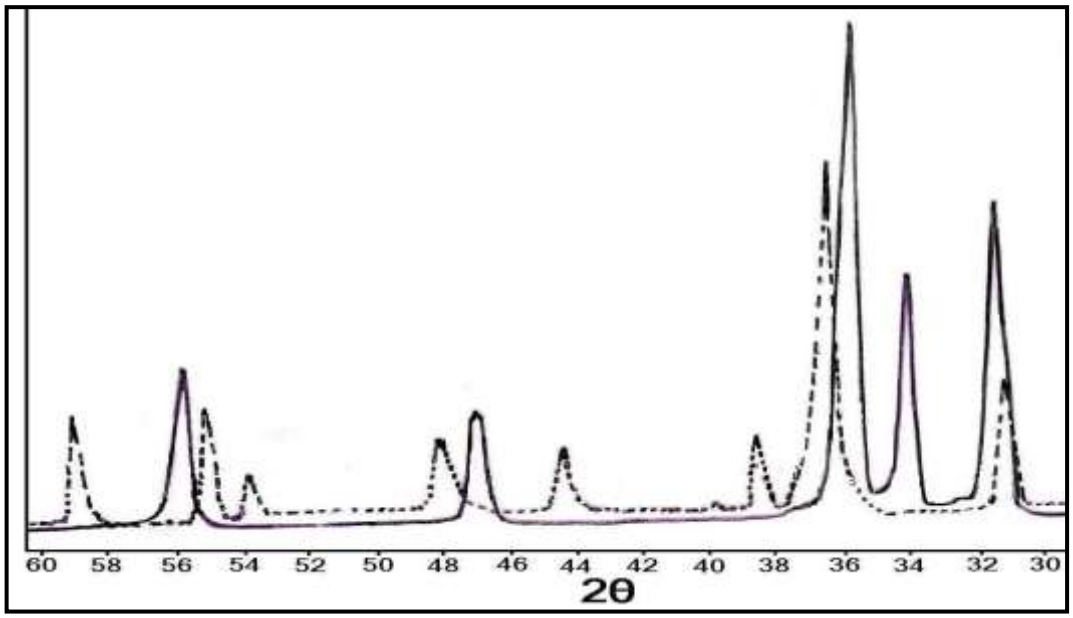
1-1- XRD results:

The XRD powder patterns of CoO-ZnO catalyst is shown in figure(4).



Figure(4):XRD powder patterns of CoO-ZnO catalyst

From the comparison of these peaks position, and d-space with the diffractograms of the reference cobalt and zinc oxides[19] that is shown in figure (5),and table(1),which indicates the obtaining of the required CoO-ZnO catalyst.



Figure(5):XRD powder patterns of standard CoO and ZnO single oxides

and d(Aº)values for CoO-ZnO oxide and standard oxide Θ2 Table(1):

values for Θ2 CoO-ZnO oxide	d (Aº) values for CoO-ZnO oxide	valuesΘ2 for standard oxide	Aº)values(d for standard oxide	metal oxide and relative ،I/I intensity
31.6	2.829	31.3	2.855	CoO 40%
31.7	2.820	31.7	2.816	ZnO 71%
34.2	2.620	34.4	2.602	ZnO 50%
36.5	2.506	36.3	2.476	ZnO 100%
36.9	2.473	36.8	2.438	CoO 100%
38.6	2.319	38.5	2.333	CoO 12%
44.9	2.019	44.8	2.021	CoO 20%
47.6	1.918	47.5	1.911	ZnO 25%
48.4	1.881	48.2	2.021	CoO 25%
55.6	1.661	55.7	1.651	CoO 12%
56.7	1.621	56.6	1.626	ZnO 40%
59.5	1.555	59.4	1.556	CoO 30%

1-2-Chemical analysis:

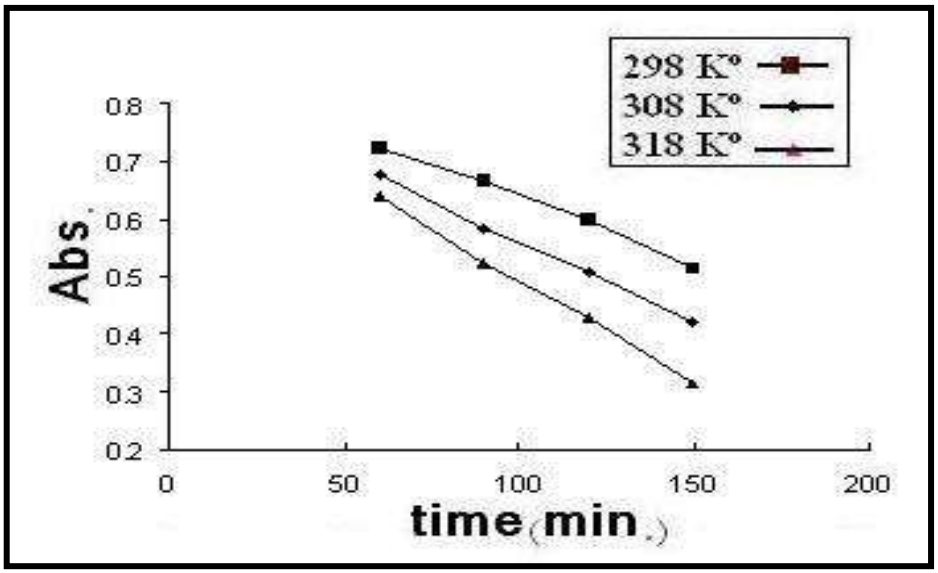
The weight percent(wt %) of cobalt and zinc in the combined oxides of zinc and cobalt, is obtained by flame atomic absorption spectrophotometer, and then the weight percent(w%) of CoO and ZnO in CoO-ZnO catalyst could be obtained , as shown in table (2).

Table(2):the weight % of Cobalt and zinc and their oxides in CuO-ZnO mixed

Catalyst	Weight(gm)	Conc.(ppm)		Wt%		Wt %		Wt%
CoO-ZnO	0.2163	Co	Zn	Co	Zn	CoO	ZnO	(CoO+ZnO)
		8.2	10.6	37.91	39.366	48.2	49.0	97.2

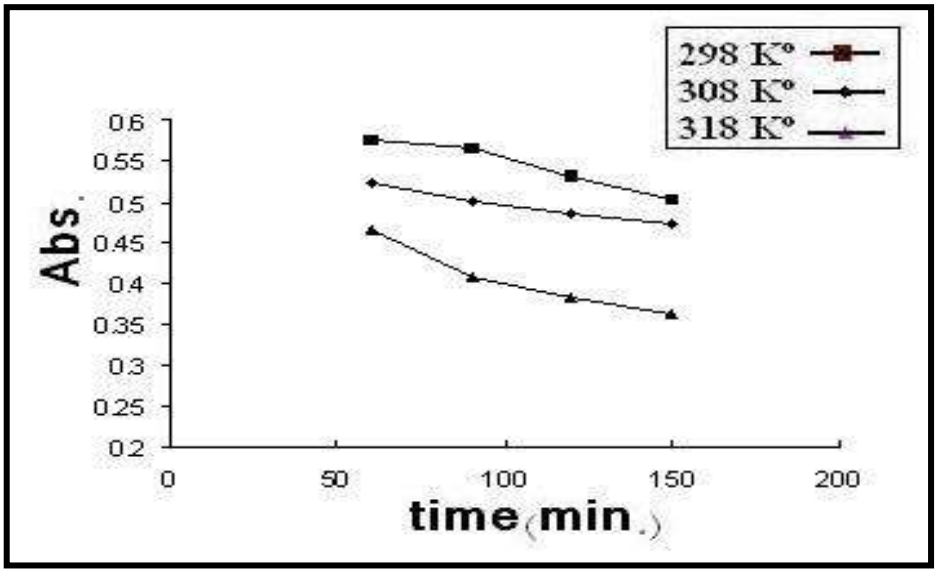
2-Photocatalytic oxidation of benzyl alcohol:

The examination of photocatalytic activity of CoO-ZnO catalyst, is carried out by the oxidation of benzyl alcohol , at three different temperatures under irradiation with UV-light . The results of the photooxidation are shown in figures (6)



Figure(6):Effect of irradiation time on the benzyl alcohol conc. at different temperatures by using CoO-ZnO catalyst

From figure(6),shows that the absorbance of reactant benzyl alcohol decrease with the increase of reaction time at different temperatures as an indication for the decreasing of benzyl alcohol concentration. Acomparative study it has been carried out, to compare the activation energy of CoO-ZnO catalyst and ZnO,as shown in figure(7).



Figure(7):Effect of irradiation time on the benzyl alcohol conc. at different temperatures by using zinc oxide

The effect of temperature on the rate of the photocatalytic oxidation can be used in the calculation of activation energy for the reaction by using Arrhenius equation as follow:

$k = Ae^{\Delta E/RT}$ (1)

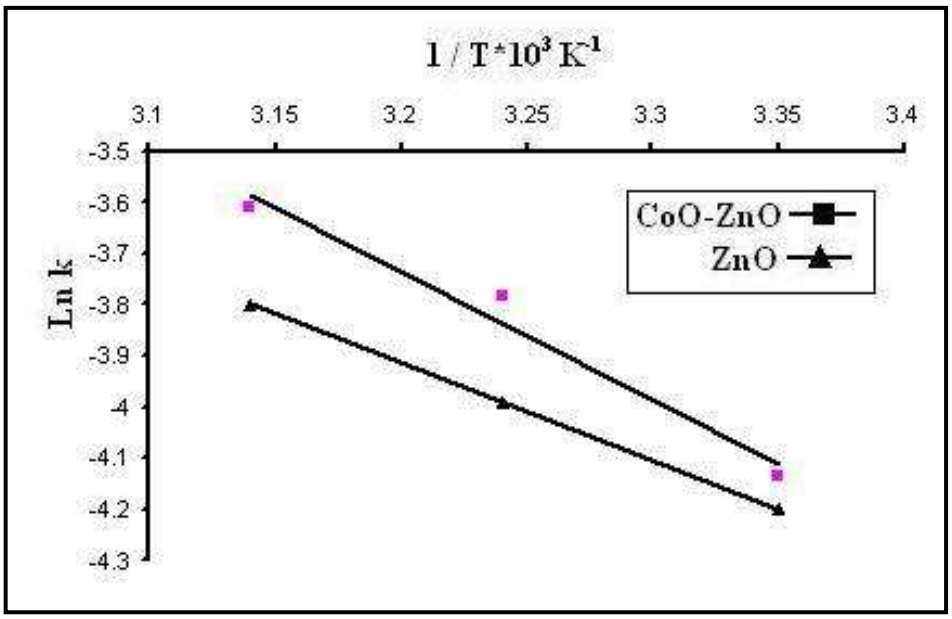
Where k is the rate constant ,ΔE is the activation energy ,R is the gas constant ,A is the Arrhenius constant ,and T is the absolute temperature of the reaction . Rate constant (k) for each temperature of reaction can be calculated by equation (2) :

$Ln(At - A\alpha) = Ln(Ao - A\alpha) - kt$ (2)

A_o is the absorbance before irradiation , At is the absorbance at a given time ,and Aα is the absorbance at final time of reaction .

Figure(8) shows that Arrhenius plot of the reaction rate constant versus reciprocal absolute temperature gives a straight line. The slope of the resulted line gives an activation energy for CoO-ZnO catalyst, which is (16) $kJ.mol^{-1}$.

The comparative study which has been carried out, to compare the activation energy of CoO-ZnO catalyst and ZnO,demonstrated that the activation energy for ZnO equal to (21) $kJmol^{-1}$ for the photooxidation of benzyl alcohol to the corresponding benzaldehyde as shown in figure (8), these energies are believed to be associated with transferring of photoelectron in the lattice of the used semiconductors, and does not depend on the type of reaction[21].From the results of activation energies ,we can be observed that the activation energy for CoO-ZnO catalyst is smaller than that of ZnO,this may be attributed to the large surface area of CoO-ZnO[22].



Figure(8):Temperature dependence for the photocatalytic oxidation of benzyl alcohol on CoO-ZnO ,and ZnO

The proposed mechanism of the photocatalytic oxidation of benzyl alcohol:

Absorption of light by semiconductor particles produces (e^-,h^+) as follow[23]:

$$CoO\text{-}ZnO \xrightarrow{h\nu} CoO\text{-}ZnO\ (e^-/\ h^+) \longrightarrow e^-_{CB} + h^+_{VB} \quad (3)$$

Photogenerated electrons are trapped by molecular adsorbed oxygen on the surface $(O_{2(ads.)})$,while photoholes are trapped by surface hydroxyl group $(OH^-_{(sur.)})$ as follow[24]:

$$O_{2(ads.)} + e^- \rightarrow {}^{\bullet}O^-_{2(ads.)} \quad (4)$$

$$OH^-_{(sur).} + h^+ \rightarrow OH^{\bullet}_{(sur.)} \quad (5)$$

Hydroxyl radical produces in equation (5) plays a main role in the reactions which are occurred on the surface of the photocatalyst as follow[25-27]:

$$OH^{\bullet}_{(sur.)} + C_6H_5\text{-}CH_2OH \rightarrow C_6H_5\text{-}{}^{\bullet}CHOH + H_2O \quad (6)$$

$^{\bullet}O^{-}_{2(ads.)} + H_2O \rightarrow HO^{\bullet}_2 + OH^{-}$ (7)

$C_6H_5\text{-}^{\bullet}CHOH + HO^{\bullet}_2 \rightarrow C_6H_5\text{-}COH + H_2O_2$ (8)

$C_6H_5\text{-}^{\bullet}CHOH + OH^{\bullet}_{(sur.)} \rightarrow C_6H_5\text{-}COH + H_2O$ (9)

$2HO^{\bullet}_2 + \rightarrow H_2O_2 + O_2$ (10)

Conclusions:

1-The concentration of benzyl alcohol decreases with the increasing of reaction times,and temperature.

2- The activation energy for the photocatalytic oxidation of benzyl alcohol reduced to lower value by using CoO-ZnO as a catalyst, the reason may be due to the increasing of the surface area for the combined oxide.

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