

SENSITIZED PHOTOCATALYTIC OXIDATION OF PROPAN -2-OL BY TITANIUM DIOXIDE

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Received : 10/10/1999 Accepted : 7/11/1999

الخلاصة

اجري تفاعل الاكسدة الضوئية المحفزة لكحول البروبان -2- اول باستخدام عالق مسحوق ثاني اوكسيد التيتانيوم المجرد عند درجة حرارة 298 كلفن بوجود بعض الاصباغ كمتحسسات ضوئية مثل السافرانين (SafraninO) والرودامين Rhodamine 6G والرايوفلافين (RF) والاريتروسين (ERB) واحمر كونجو (CR) والرودامين (RB)B وازرق الميثيلين (MB) والثايونين (TH) باستخدام مصباح زئبقي عالي الضغط من النوع الغاطس ومفاعل مزدوج الاسطوانة ، ودلت النتائج على ان فاعلية المتحسس تعتمد على ثباتته اتجاه الضوء وعلى حزمة امتصاصه للضوء المرئي .

وكانت فاعلية المتحسسات الثابتة تجاه الضوء واقعة في التسلسل الاتي :-

Riboflavin > Safranin O > Rhodamine 6G > Rhodamine B

اشتمل البحث كذلك على دراسة التداخل بين هذه الاصباغ مع سطح ثاني اوكسيد التيتانيوم ، حيث استخدمت اطيفاف فلورة وانحراف الاشعة السينية لتشخيص هذا التداخل .

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In a second process they can support the photocatalytic process by acting as mediators for the charge transfer between two adsorbed species. This process is called photosensitization which involves excitation of sensitive colored materials (organic or inorganic dyes and pigments), then the singlet or triplet excited state of sensitizer are quenched by semiconductor particles via accepting the electrons in conduction band of semiconductor and converting charge to another adsorbed substrate or generate photocurrent .

Many of the reported sensitizers such as eosin B, erythrosine B, rhodamine B, Thionine, rose bengal, ... are absorbed in visible region of solar spectrum whose extend the effective wavelength of large band gap semiconductors to this region .

The important requirement for performing an efficient charge transfer is to select a sensitizer whose oxidation potential is higher than the conduction band level of semiconductor^(1,2) . However, this process, generally, associated with low quantum yield which attributes to most of injected electrons will recombine with radical cations of sensitizer in exothermic process (back electron transfer), or lose of excitation energy in non-radiative process⁽³⁾ .

The photosensitization processes in the presence of TiO₂ or Pt/TiO₂ suspensions was widely used in photodegradation of pollutants such as phenolic compounds⁽⁴⁻¹⁰⁾, humic substances⁽¹¹⁾, and azo compounds⁽¹²⁾, photocracking of saturated hydrocarbons⁽¹³⁾, photocatalytic cleavage of water⁽¹⁴⁾ and photodehydrogenation of alcohols^(15,16).

In the present paper, the photocatalytic oxidation of propan-2-ol was investigated in presence of TiO₂ and eleven dyes at 298K using high pressure mercury lamp (immersion type) fitted with pyrex cylindrical reactor .

The work includes the study of interaction of these dyes on TiO₂ surface X-rays diffraction (XRD) and X-rays fluorescence spectra which have been used to identify this interact .

temperature , Pye Unicam 308 gas chromatograph supplied with gas control, readout and ionization ampelifier and dual pen recorder was used mainly to determination the concentration of converted propan – 2-ol to propanone at different times using PEG20 Column (1.5mx 0.4mm) at 353K , flow rate of carrier gas 20 cm³/min, injection temprature 383K, flame ionization detector temperature 398K, attinuation 64 x 10³ Hz, chart speed 300mm hr-1, volume of injected sample 0.2 μl.

The liquid samples for gas chromatography analysis were taken from reactor by syringe through the septum on the top, then centerfuged to remove the TiO₂ particles before analysis .

Suspension in all photocatalytic oxidation of propan –2-ol experiments were irradiated for 90 min and purging with air (15cm³min⁻¹).

RESULTS AND DISCUSSION

XRF and XRD Spectra

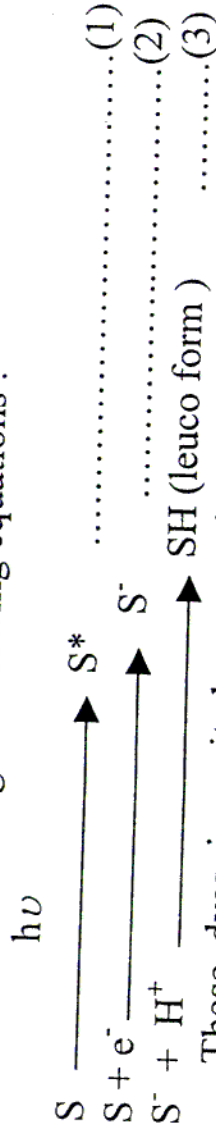
The modification of TiO₂ surface by loading of dyes was investigated using XRF spectra (Table 1) which determined the percentages of dyes on surface . The structure of dye can play an important role in the adsorption process, cationic dyes tends to bounding with surface of TiO₂ stronger than others⁽³⁾ , This process correlate with state of semiconductor in solution because the TiO₂ particles are similar to surfactants , i.e the neutral dyes are mobile between solution and micell .

XRD of adsorbed dyes are show in fig .1,2 and 3 which are compared with pure TiO₂ spectra (fig.4), It is clear that the peak of high intensity of TiO₂ (2θ = 25.3) is stable in all spectra but its intensity is decrease as a result of covering the TiO₂ surface with dye which causes the reduction of x-rays penetrating force. This meaning those dyes were adsorbed on the external faces of unit cells of surface

using naked TiO₂ with sensitizers. Fig.6,6 and 7 show the effect of those sensitizers on the activity of TiO₂ to produce of carbonyl compound .

Table(3) shows the concentration and rate production of propanone of irradiate the suspension for 90min, the different in the rates of oxidation due to different of components of heterogeneous photocatalysis system in this reaction , the modifying of TiO₂ surface with sensitizers can play an important role for increasing the activity of semiconductor which as turnover and converting the excitation energy to another adsorbed material .

It is clear that the activity of dyes is quite different due to spectroscopic behavior of dyes in the presence of light, using EB, ERB and MB dyes Fig.5 led which low production of propanone because of their instability towards to light which causes the photobleaching of those dyes according to following equations :



These dyes in excited states received an electron from medium and then abstract a propan to convert to colorless form (leuco). This phenomena also happen when the cation radical of dye combines with neighbouring anion to convert to leuco form ⁽²⁰⁾. This process correlates with temperature, PH and intensity of light ⁽²¹⁾.

The use of MR, CR and CV dyes Fig.6 also is deficient in the above system because these dyes are unstable toward light and thus they degrade after short time from irradiation . Also TH dye Fig.6 is considered as an inhibitor dye because of its far absorption band comparison with absorption of TiO₂.

The use of RB, RF, R6G and SO dyes Fig 7 is successful as a result of stability , activity and wide absorption band in effective region of spectrum of those dyes .

The main difference of this mechanism is the absence of hole which recombines with ecb when only TiO_2 is used. However the back electron transfer may occur between oxidized form of dye(S^+) and surface electrons or solution electrons which causes the reduce the efficiency of process, but when donor of electrons (EDTA, cystein, carboxylic acids, aldehydes, ...) are intered in system. This convert (S^+) to (S) which improve the efficiency of the meaning process⁽²⁶⁾.

Table (1) : Percentages of adsorbed dyes on TiO_2 surface determined by XRF spectra .

No.	Dye TiO_2	%
1	RF	0.031
2	EB	0.028
3	TH	0.042
4	RB	0.006
5	MR	0.068
6	CR	0.047
7	SO	0.042
8	R6G	0.002
9	CV	0.04
10	MR	0.018
11	ERB	0.039

ABSTRACT

The Sensitized photocatalytic oxidation of propan -2-ol using naked TiO_2 powder suspension at 298K has been investigated in the presence of some organic dyes as sensitizers such as: safranin O (SO), rhodamine 6G(R6G), crystal violet(CV),eosin B(EB), methyl red (MR), riboflavin (RF),Erythrosin B (ERB), congo red (CR), rhodamineB (RB) methylene blue (MB) and thionine (TH), using high pressure mercury lamp (immersion type) fitted with double layer pyrex cylindrical reactor .

The results showed that the activity of sensitizer depending on its stability towards light and also depend on its absorption spectrum .

The activity of excellent and stable sensitizer fell in the following sequence. :

Riboflavin > Safranin O> Rhodamine 6G> Rhodamine B

The work also includes the study of interaction of eleven dyes with oxide surface. X-rays diffraction (XRD) and x-rays fluorescence (XRF) spectra have been used to detect this interaction .

INTRODUCTION

In recent years a considerable interest has been occur in improving the utilization of solar energy using colloidal semiconductors particles as photocatalysts .

The participation of semiconductor particles such TiO_2 , ZnO , SnO_2 , CdSe , ... or metallized TiO_2 in photocatalytic reactions can be direct or indirect ⁽¹⁾, in first, by irradiation of these particles with suitable energy ($\geq E_g$) generate abound electron-hole pair which can recombine in competition with separation to give a conduction band electron and valence band hole, in this process semiconductor particles act as short circuited photoelectrochemical cells and directly oxidize adsorb electron donors or reduce adsorb electron acceptors by electron and hole transfer at two positions on semiconductor surface .

EXPERIMENTAL

Materials : naked TiO_2 P-25 (anatase) of surface area $55\text{m}^2\text{gm}^{-1}$ and Cryatallite sizes 25-35nm was used as supplied by Degussa, propan-2-ol (99.5%), propanone (99.5%), ethanol (99.98%), safranine O, rhodamine B, and crystal violet were also used as supplied by B.D.H., eosin B, methyl red, riboflavin and erythrosin B were supplied by Aldrich, methylene blue, congo red, rhodamine B and thionine were supplied by Riedel De Haen , E Marck, Eastman and Fluka respectively .

The adsorbing of dyes on TiO_2 surface was performed using impregnation process adding TiO_2 (1%) to alcoholic dye solution ($1 \times 10^{-5}\text{M}$), then the suspension was purged with air ($100\text{cm}^3\text{min}^{-1}$) with continuous stirring for 120 min . at 298K, TiO_2 particles were separated using Janetzki T5 centrifuge and washed with ethanol for several times until the color of dye disappeared from washings and dried using Gallenkamp vaccum oven at 303K for four hours .

Philips X-rays diffractometer was used to detection of interact of dyes with oxide surface. The specimens for XRD analysis were prepared by mixing the powder of sensitized TiO_2 with boric acid 2:1, Then $\text{CuK}\alpha$ radiation ($\lambda = 1.541\text{\AA}$) and Ni filter were used to performance this analysis .

Philips X-rays imession spectrometer was used determination the percentages of adsorbed dyes on TiO_2 surface .

The photocatalytic oxidation of propan-2-ol was carried out using Kori-Kolb high pressure mercury lamp (TQ150Z₂ immersion lamp) jointed to Hareas power supply . The lamp was immersed inide pyrex double layer cylindrical reactor of 250cm^3 from DEMA and surrounded by water coling jacket and the reactor supplied with inlet and outlet paths for purging the suspension with air ($15\text{cm}^3/\text{min}$).

Gerhardt magnetic stirrer was used to stirring the suspension , HAAKEG8 thermostat was also used to maintain the reactor

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particles in thin layer from which causes the coloring of TiO_2 particles with dye color.

XRF and XRD spectra indicated of happening of desirable adsorption of dyes which may improve the catalysis by TiO_2 if those dyes will be stable towards light.

The ability of dye adsorption may be effected by its concentration and time of impregnation⁽¹³⁾, solubility⁽¹⁷⁾, pressure, temperature and pretreatment of surface⁽¹⁸⁾.

XRD spectra of pure TiO_2 was identified by turning to powder diffraction cards (PDC) supplied by American society for testing and materials (ASTM).

ELECTRONIC SPECTRA OF DYES

The results concluded from absorption spectra of dyes are shown in table 2. It is clear that most of the spectra have a wide and effective range of visible region and there is λ_{max} interacting with lower absorption of TiO_2 (540nm)⁽¹⁹⁾; so the dyes which are expected to show considerable efficiency in heterogeneous photocatalysis using TiO_2 are eosin B, erythrosin B, Safranin O, rhodamine 6G, rhodamine B, congo red and riboflavin if they are stable towards light.

The molar absorption coefficients of dye solutions in the presence of TiO_2 are less than in the absence of or after TiO_2 separation. This indicates that the TiO_2 particles are characterized with reflecting and scattering of most of light which led to the decrease of absorption of dye as a result of the harvested visible light by dye molecules in however shielded by TiO_2 particles. The difference between E in absence or after separate of TiO_2 shows that the trace amount of dye is adsorbed on TiO_2 surface.

PHOTOCATALYTIC OXIDATION OF PROPAN-2-OL

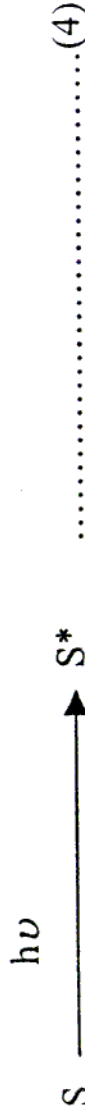
The important aim of the present work is to optimize the photocatalytic oxidation conditions of propan-2-ol to propanone

The difference of the activity of latter four dyes is due to ability of dye to harvesting the incident photons and injection the charge in conduction band of TiO₂, which may relate with chromophores in dye and adsorbed quantity of dye on TiO₂.

The excited molecules of sensitizer in solution are quenched by dissolved O₂ to produce desorbed O₂ species. This process depends on dye oxidation potential⁽²²⁾, so the presence of N₂ reduces it⁽²³⁾.

MECHANISM OF REACTION

The first step in photosensitization process is the excitation of sensitizer molecules (S).



The tripled or singlet excited state (S*) are quenched by TiO₂ particle :



Then adsorbed oxygen will capture the injected electron :



The O_{2(ads)} and [•]OH_(s) Radicals are contribute in proton abstraction process as suggested by Hussein and coworkers^(2,4) :



Bickley and Jayanty⁽²⁵⁾ are suggested :

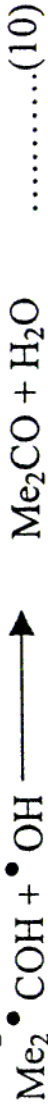


Table (2) : λ_{\max} and of dyes solutions in presence and absence of TiO_2 .

No.	Dye	Conc., M	λ_{\max} nm	Absorption Edges nm			Σ 1/mol. cm		
				High Edge	Row Edge	TiO_2 .	TiO_2 .	TiO_2 .	
1	RF	5×10^{-5}	545	490	580	33600	21000	29800	
2	EB	5×10^{-5}	535	460	560	36400	21600	26600	
3	TH	1×10^{-5}	595	500	640	135000	71000	110000	
4	RB	5×10^{-5}	530	400	580	38200	23000	28200	
5	MR	5×10^{-5}	660	550	700	27600	23500	21800	
6	CR	1×10^{-4}	525	450	570	18100	11800	15000	
7	SO	1×10^{-4}	410	350	520	14500	7500	9500	
8	R6G	1×10^{-4}	590	480	540	27800	14600	21800	
9	CV	1×10^{-4}	515	460	550	17600	11800	14800	
10	MR	1×10^{-4}	445	300	520	13900	7300	10900	
11	ERB	1×10^{-4}	500	380	290	16100	8300	12900	

Table (3): Conversion of propan-2-ol to propanone of 298K and saturation with air ($15 \text{ cm}^3 \text{ min}^{-1}$) in the presence of TiO_2 (1.2 gm/l) and $1 \times 10^{-5} \text{ M}$ of dye for 90 min .

No.	Dye	Propanon Conc. $\times 10^2 \text{ mol/l}$	Rate $\times 10^6 \text{ mol /l.sec}$
1	---	0.78	1.44
2	EB	0.55	0.99
3	ERB	0.21	0.38
4	MB	0.30	0.55
5	MR	0.67	1.22
6	CR	0.39	0.72
7	CV	0.56	1.03
8	RB	1.04	1.91
9	RF	2.81	5.2
10	R6G	1.33	2.46
11	TH	0.35	0.46
12	SO	1.36	2.51

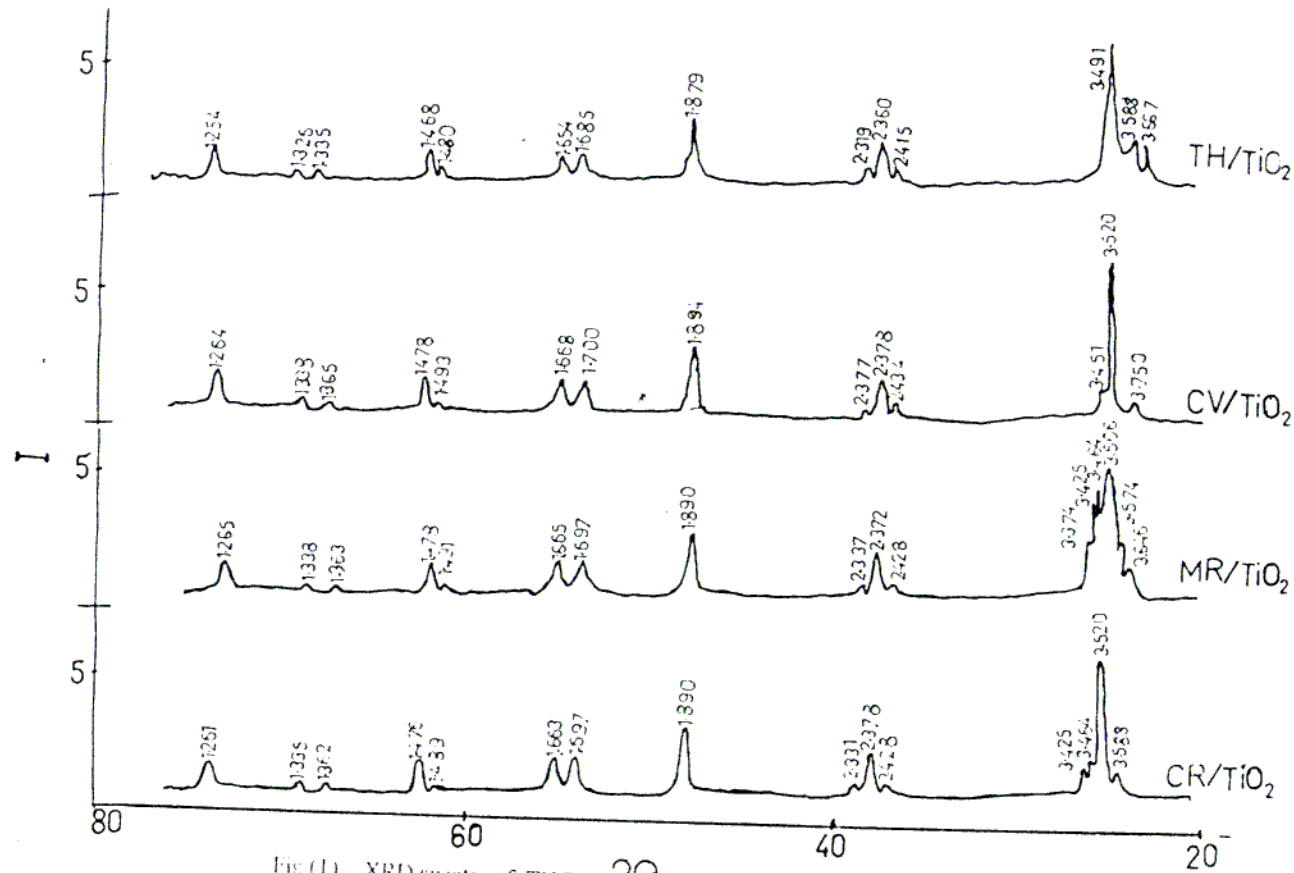


Fig. (1). XRD spectra of TH/TiO₂, CV/TiO₂, MR/TiO₂ and CR/TiO₂ specimens

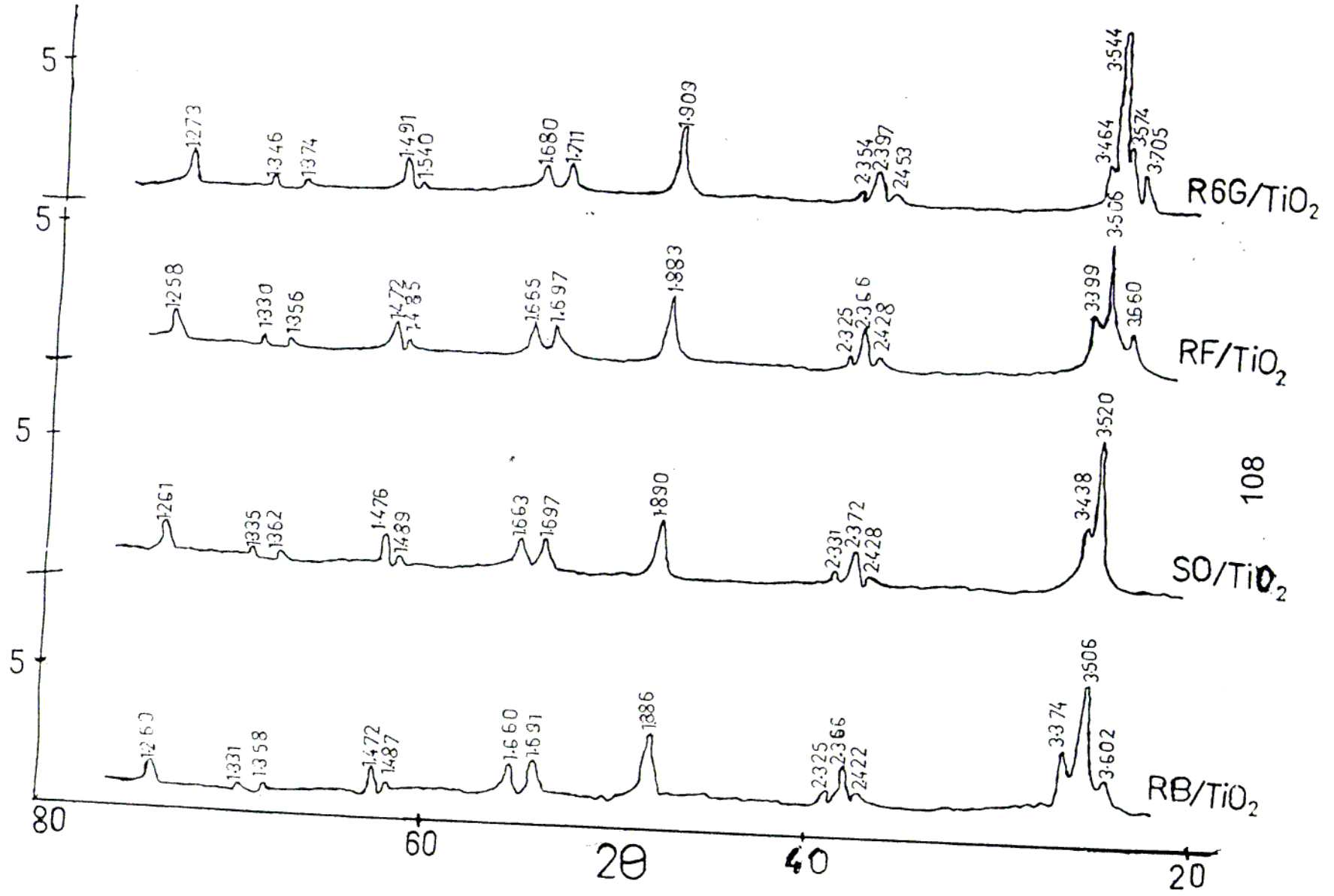
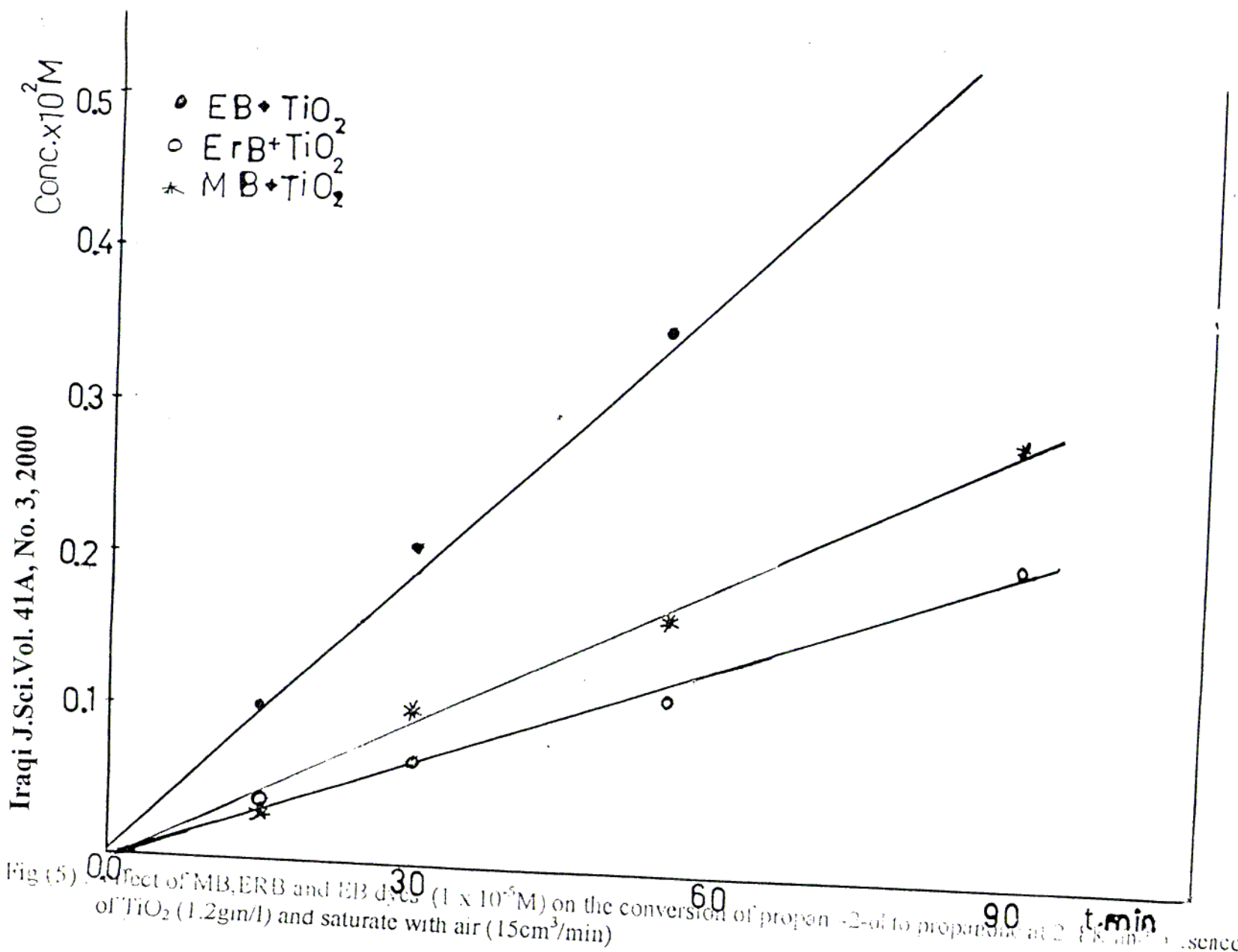


Fig (3): XRD spectra of R6G/TiO₂, RF/TiO₂, SO/TiO₂ and RB/TiO₂



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Fig (5) Effect of MB, ERB and EB dyes ($1 \times 10^{-5} M$) on the conversion of propene-2-ol to propandiol at 25°C in presence of TiO_2 (1.2gm/l) and saturate with air (15cm³/min)

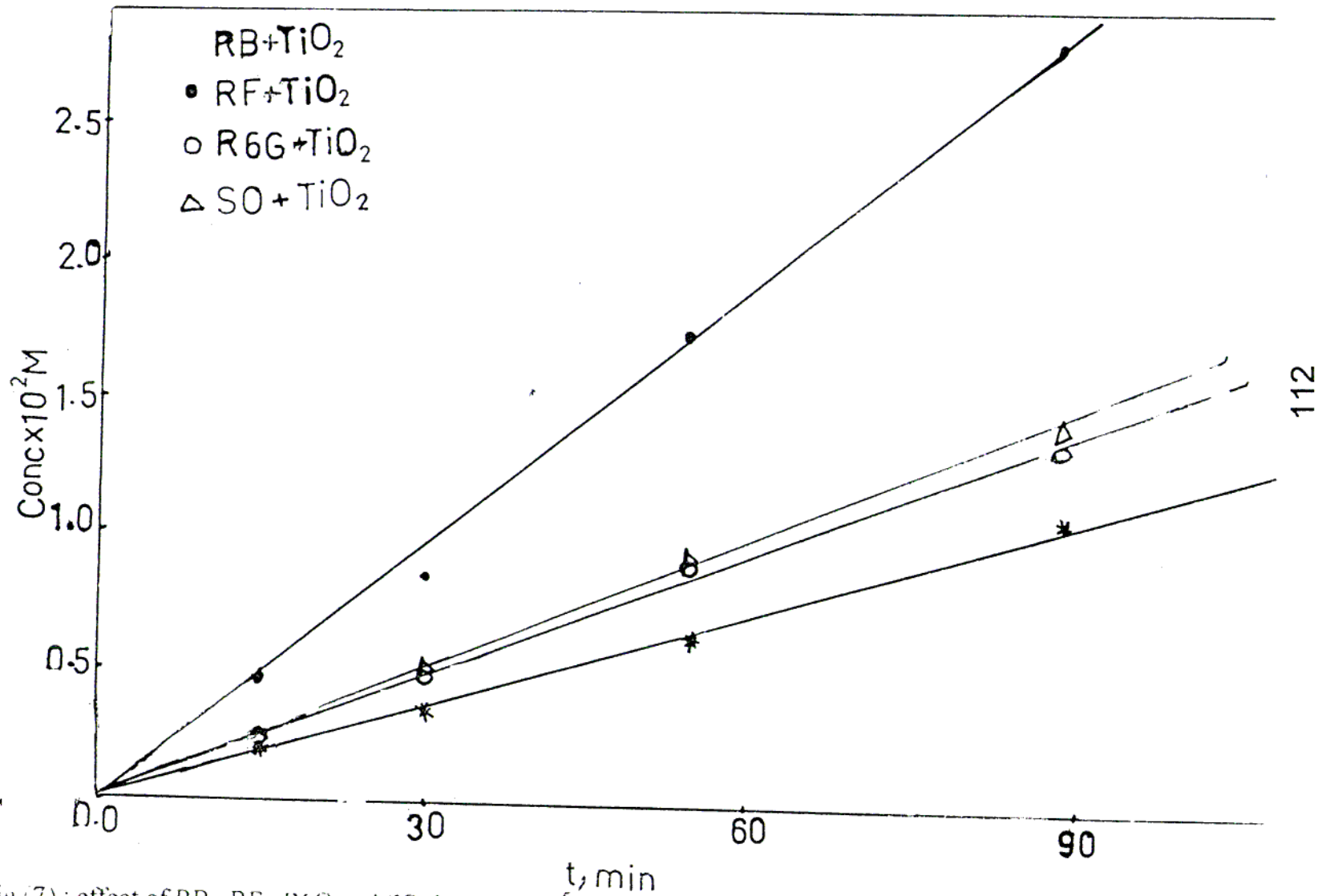


Fig (7) : effect of RB , RF,, R6G and SO dyes ($1 \times 10^{-5}M$) on the conversion of propan -2-ol to propanone at 298K and presence of TiO₂ 1.2gm/l and saturate with air ($15cm^3/min$)