

The Effect of Malachite Green on Photocatalytic Cracking of n-Pentadecane Using Zinc Oxide and Visible Light

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Abstract

Modified zinc oxide by different weight of malachite green dye (0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2)gm was prepared using a pyrex static reactor (250)cm³ irradiated with modified immersion halogenated lamp (400-700)nm. The photocracking of n-pentadecane were studied by using naked and sensitized ZnO in reaction vessel (20)cm³ with a quartz window .The photocracking products were light hydrocarbons (saturated alkanes) and light oxygenated alkanes which identify by gas chromatographic technique using FID and IR spectrophotometric technique . Naked and sensitized ZnO were studied by XR diffraction . Reaction mechanisms of photocracking processes by sensitized ZnO suggested according to the experimental results obtained .

الخلاصة

حضرت مجموعه من اكاسيد الخارصين المهوره بأوزان مختلفة من صبغه خضراء الملخايت (0.1 , 0.2 , 0.4 , 0.6 , 1.0 , 0.8 و 1.2) غرام باستخدام خليه تشعيع بسعة (250) سم³ من البايوركس بوجود مصباح هالوجيني محور غاطس (400-600) نانوميتر . استخدمت خلية تفاعل سعة (20) سم³ لدراسة الفاعليه الضوئيه للعامل المساعد المجهز و مقارنتها بفعاليتها بعد التحوير بصبغه خضراء الملخايت في تجزئه النورمال بنتاديكان باستخدام ضوء صادر من مصباح هالوجيني من خلال نافذه من الكوارتز قطرها (2) سم .

درست نواتج التفاعل الضوئي المحسس باستخدام تقنيه كروماتوغرافيا الغاز و تقنيه الأشعه تحت الحمراء و كانت الكانات مشبعه خفيفه و هيدروكربونات مقابله مؤكسده (الديهيدات). كذلك درست العوامل المساعده بعد انتهاء عملية التفسير الضوئي بواسطة حيود الاشعه السينيه . تم اقتراح ميكانيكية التجزئة الضوئيه للنورمال بنتاديكان بوجود العوامل المساعدة المحورة بضوء النتائج التي تم الحصول عليها .

Introduction

A number of researches were carry out on photocatalytic [oxidation of CO and SO₂ (Formenti *et al* in 1971), hydrolysis of ethanoic acid (Kraeutler and Bard in 1978) , dissociation of adipic acid (Izuml *et al* in 1981), oxidation of ammonia (Pichat *et al* in 1982) , bactericidal and detoxification (Srinivasan and Somasundaram in 2003) , cleavage of water (Zou *et al* in 2003)] using different semiconductor oxides with direct excitation by Ultra-Violet irradiation sources as figure (1).

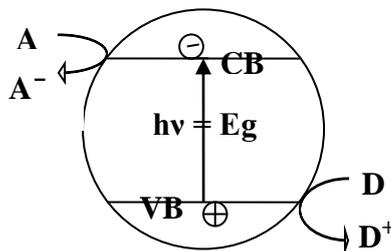
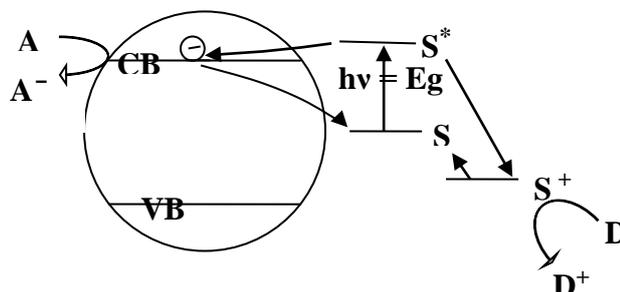


Figure (1) : Direct excitation of semiconductor oxide

Recently, many researchers were succeeded to improve in the photoelectrochemical processes using organic dyes (Al-Sayyed *et al* in 1991 , vinodgopal *et al* in 1994 and Nasr *et al* in 1995) , SnO₂ /TiO₂ coupled semiconductor thin films (Vinodgopal and Kamat in 1995) or Ag – modified TiO₂ (Arabatzis *et al* in 2003 , Sung- Suh *et al* in 2004 and Jeong *et al* in 2005) to sensitized semiconductor oxides with large band gap.

The adsorbed (dyes , Ag or SnO₂) on the surface of metal oxide absorbed visible light and promoted to excited state which leads to inject an photoelectrons into the conduction band of semiconductor oxides and become oxidized to cation radical as in figure (2).



Figure(2): Charge transfer processes at semiconductor particle interface by charge injection from excited state of the adsorbed molecules into the condition band of the semiconductor oxides .

The aim of present work , to extend the range of photocatalysis to longer wavelength (400-600)nm by modification of zinc oxide surface by adsorption of malachite green on its surface .

Experimental

A-Chemicals:

- 1- Zinc Oxide: Band gap (3.4)ev. , purity (99%) , particle size(100) mesh , supplied by Fluka AG . Grinded to smaller particle size of (200 , 300 and 400)mesh.
- 2 - Malachite green: It is supplied by B.D.H . Chemical Ltd .Pool, England , with purity (99%) and used as supplied .
- 3 - Methane and Ethane were supplied by Varian , diluted to 1% with helium gas . Propane and butane gases were obtained from Petroleum Research and Development Center , Baghdad, with high purity in a liquid form and pressure , n-pentane to n – pentadecane were supplied by Fluka AG . A typical gas chromatogram has been done for standard hydrocarbons from C₁ to C₁₅ to identify photocatalytic products by its retention time of each hydrocarbons in mixture as shown in figure(3). Hydrogen gas was electrically generated by Pye Unicam Hydrogen Generated HG10.

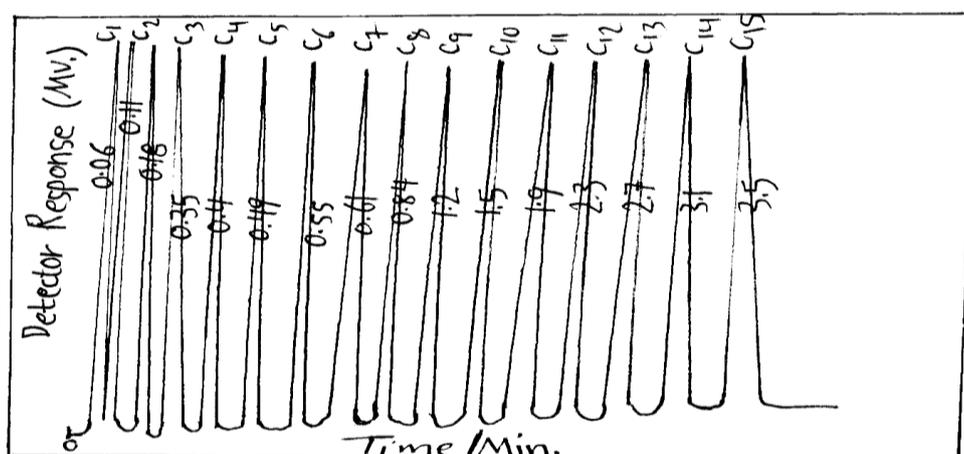


Figure (3): Gas chromatogram of methane to n-pentadecane separated on OV1 Column , detected by FID .

B-Preparation of Sensitized ZnO:

The sensitized ZnO by malachite green was prepared by suspending (1.2) gm. of ZnO in (250)ml. of H₂O containing different weight of malachite green(0.1 , 0.2 , 0.4 , 0.6 , 0.8 , 1.0, and 1.2) gm. Each mixture was flushed with air of (30)ml./min. at (298)K and irradiated for (2) hours in reaction vessel supplied with modified halogenated lamp (400-700)nm. as in Figure (4).

The irradiated products was separated by filtration and washed several times with distilled water until the colour of crystal violet disappeared from washings . It was dried overnight at(350)K. The sensitized ZnO was sieved to mesh size 100, 200, 300 and 400 mesh using Karl Kolb DW 4188 stainless steel sieves.

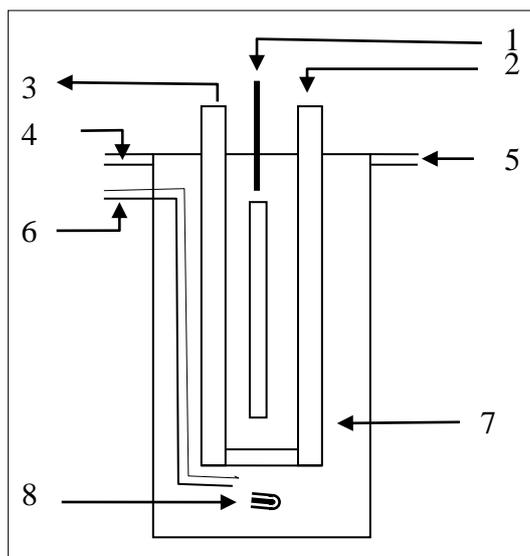


Figure (4) : Main parts of the photolytic cell used in photocatalytic degradation of saturated hydrocarbons .

- 1-lamp 2-water cooling inlet 3-water cooling outlet
 4-vent 5-in-out sampling 6-gas entry
 7-reaction chamber 8-magnetic stirrer

C-Methods and Apparatus:

Photocatalytic cracking of n-pentadecane was carried out in pyrex static reactor with quartz window to received the irradiation generated from modified halogenated lamp (400-700) nm . In all experiments (20)cm³ of n-pentadecane was used with (0.1) gm. of semiconductors oxides required. The solution was suspended by a magnetic stirrer, and air was saturated with n- pentadecane before being passed through the photolysis cell with rate (2.5) cm³ /min. as in figure (5) .

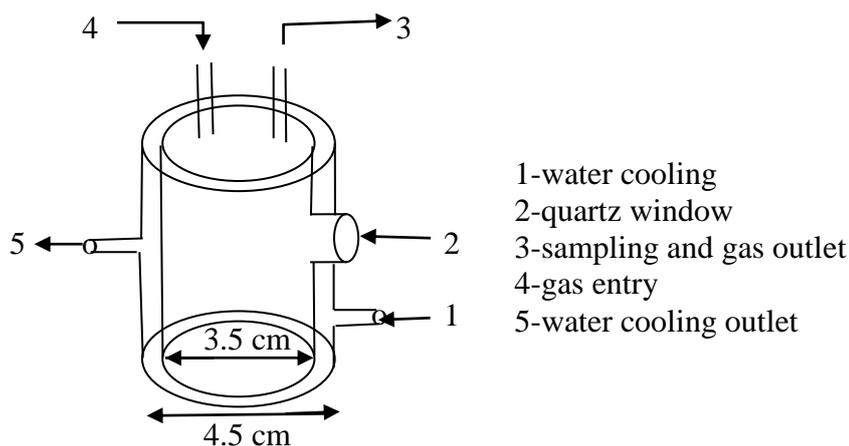


Figure (5): Photolysis cell.

Periodically (0.25) cm³ samples of reaction mixture were with drawn by microsyringe and centrifuged to separate solid catalyst . The supernatant liquid analyzed for reaction products using gas chromatographic technique which supplied by the Pye Unicam Series 304 with FID and Computing Integrator type PU 4811 Phillips for data analysis. Also IR spectra were recorded for samples using Perkin-Elmer 1330 KBr disc was used as measuring technique. X-Ray Diffraction type D5000 with Cu K α radiation supplied by Siemens , Germany was used to studied the naked and sensitized ZnO.

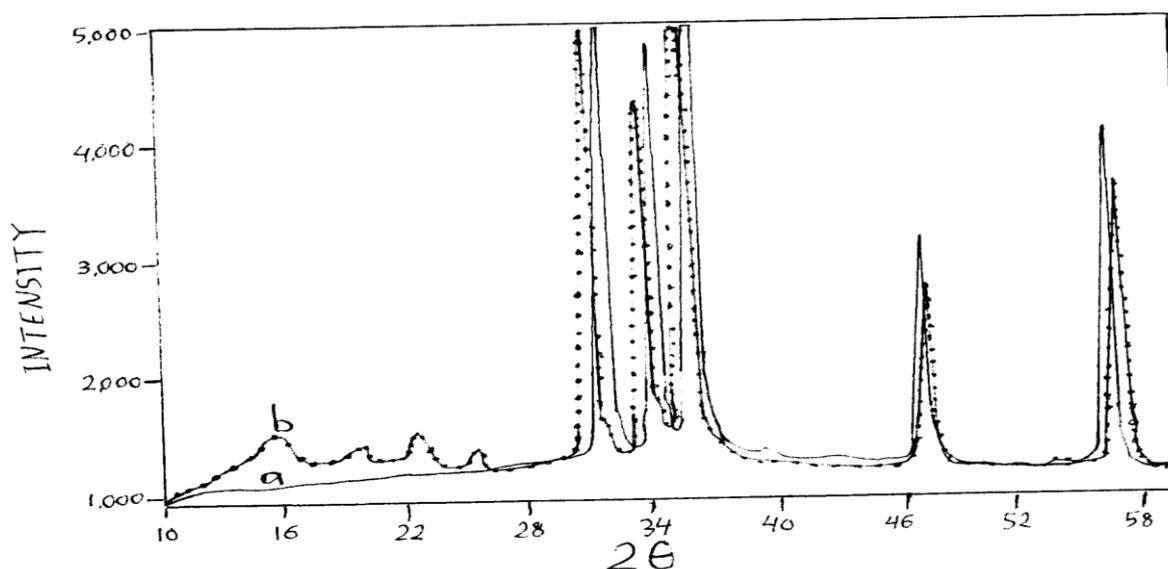
Results and Discussion

1-Structural Characterization:

The naked and prepared sensitized ZnO were characterized by:

A- XRD Spectrum :

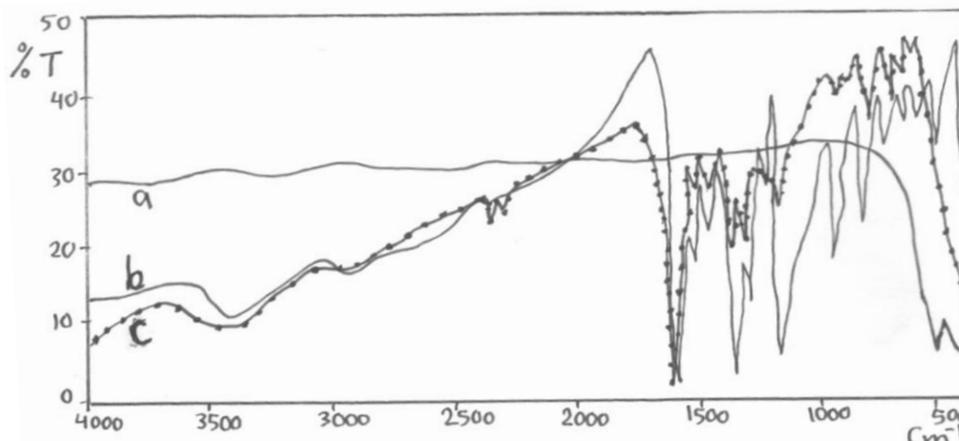
Figure (6 - a)show the zinc oxide spectrum with specific two theta (2θ) and intensity, while the deposition of malachite green on the surface of ZnO give new spectrum figure (6-b) which indicates a shift in (2θ) and reduce its intensity . Also the adsorption of malachite green on the ZnO surface leads to appear of new peak (2θ) in spectrum not exist in the original spectrum , this may due to the distortion of the crystal lattice of ZnO.



Figure(6): XRD spectrum of : (a) Zinc oxide (b) Modified zinc oxide.

B- IR Spectrum:

Figure (7-a and b) show IR spectra of naked zinc oxide and malachite green, while Figure (7-c) for modified (sensitized) ZnO. From the latter spectrum can see clearly the presence of malachite green on the surface of ZnO by appearance of specific peaks in (1000-1500) cm^{-1} which return to malachite green , not present in the spectrum of naked ZnO.



**Figure(7): IR spectrum for: (a)Zinc oxide
(b)Malachite green
(c)Modified zinc oxide**

2-Preliminary Experiments :

These experiments were made to determine the conditions necessary for photocatalytic activity before and after adsorption of sensitizer . The experiments results of the photocracking of n-pentadecane at (298)K at different conditions are given in table (1).

Table (1): The effect of different condition on photocracking of n- pentadecane at (298)K and (5) hours irradiation.

Exp no.	Hydro-carbons	Retenti-on time	Conc.(mol./lit.)		Experiments conditions	Reaction products
			(0)hr.s	(5)hr.s		
1	n-C ₁₅	3.5	3.720	3.720	n-C ₁₅ + air	No products
2	n-C ₁₅	3.5	3.720	3.720	n-C ₁₅ + air + ZnO	No products
3	n-C ₁₅	3.5	3.720	3.720	n-C ₁₅ + air + light	No products
4	n-C ₁₅	3.5	3.720	3.720	n-C ₁₅ + air + malachite green	No products
5	n-C ₁₅	3.5	3.720	3.660	n-C ₁₅ +air + malachite green+ light	See products
	n-C ₇	0.61	0.000	0.022		
	n-C ₈	0.84	0.000	0.033		
6	n-C ₁₅	3.5	3.720	3.400	n-C ₁₅ +air + sensitized ZnO + light	Detectable change see conc. of light hydrocarbons
	n-C ₆	0.55	0.000	0.044		
	n-C ₇	0.61	0.000	0.089		
	n-C ₈	0.84	0.000	0.130		
	n-C ₉	1.2	0.000	0.040		

The experiment (6) of photocracking of n-pentadecane using sensitized ZnO and visible light are detected by appearance of new peak of light hydrocarbons (n-hexane ,

n-heptane , n-octane and n-nonane). While the presence of traces light hydrocarbons in experiment (5) were due to slow and seased photoactivity of malachite green and the table show no dark reaction in all others experiments .

3.The Effect of Malachite Green Concentration Deposited on ZnO :

For this purpose several sensitized ZnO samples using malachite green dye concentration ranged from (0.1 - 1.2) gm./lit. These sensitized ZnO have been used to monitor the rate of photocracking processes of n-pentadecane . The results were shown in figure (8):

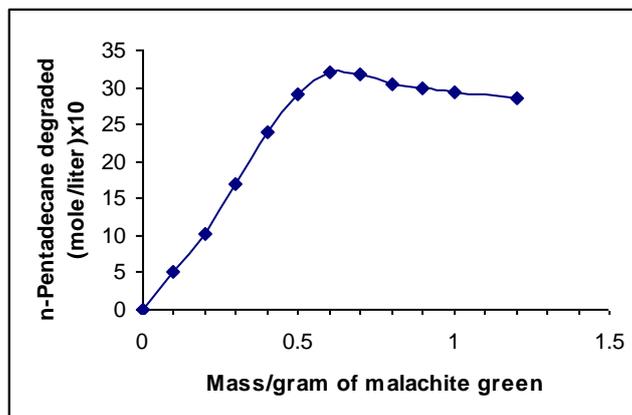


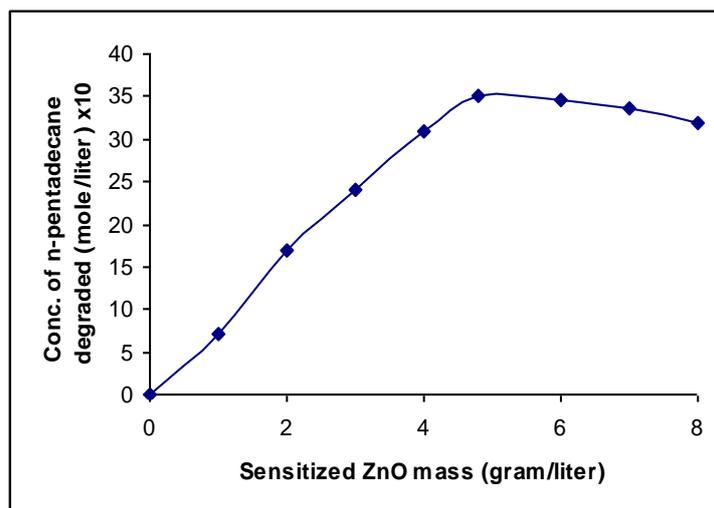
Figure (8): The effect of malachite green concentration fixed on (1.2)gm. ZnO on photocracking of n-pentadecane .

The rate of photocracking processes increases as the concentration of malachite green deposited (adsorbed)on the ZnO [fixed weight(1.2)gm.] increases until the concentration become (0.6)gm., then gradually decreases . This behavior could be explained by the idea that the concentration of (0.6)gm. malachite green on (1.2) gm. of ZnO was the optimum concentration to cover the largest area of the ZnO particles, therefore absorbed maximum exciting photons to generate higher concentration of the activated sensitized ZnO semiconductor. Another reason for this behavior is the strong absorption of light by the malachite green , in the sample which contain high concentration than (0.6)mg. of malachite green on (1.2)gm. ZnO. The excess of dye prevent the penetration of light through the successive layers of dye on the ZnO surface is weak to generate the required excited state of the malachite green adsorbed on ZnO.

Jeong *et al* were prepared silver- doped ZnO films and studied the structural and optical properties of sputtered films.

4. The Effect of Sensitized ZnO Mass on Photodegradation of n-Pentadecane:

The rate of photodegradation processes of n-pentadecane increases as the concentration of sensitized ZnO increases as a function of (5) hours irradiation of each experiment until the concentration become (4.8) gram/liter then gradually decreases as in figure (9):



Figure(9): The effect of sensitized ZnO concentration (gram/liter) on photocatalytic degradation of n-pentadecane.

This behavior could be explained by the idea that the concentration of (4.8)gram/liter of sensitized ZnO provides the highest absorption of light by sensitized ZnO and assures a homogeneous absorption of light through the layers of reaction vessel. The decrease in the efficiency of photodegradation process at the concentration of sensitized ZnO higher than (4.8)gm/lit. might be explained by the strong absorption of light through the first successive layers of solution and prevent light from passing through all other layers in the reaction vessel.

5. The Effect of Air Flow Rate and Time Irradiation

The flow rate of air in the photolysis cell on photocracking of n-pentadecane using sensitized ZnO and visible light were studied. The flow rate of air was varied from (0.7, 1.4, 1.9, 2.7, 3.1 and 3.5) ml./min. for (5) hours irradiation to each experiment. The results were in figure (10) shows that the optimum flow rate of air passing through the photolysis cell was (2.5) ml./min. this might give the highest concentration of oxygen adsorbed on the surface of the sensitized ZnO under the employed condition.

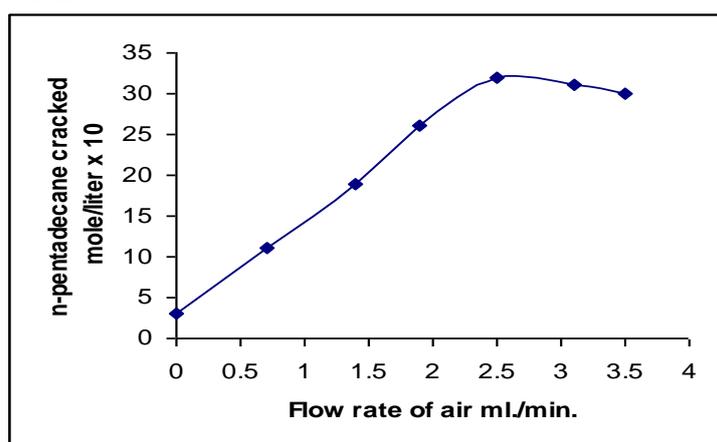


Figure (10) : The effect of flow rate of air on photocracking of n-pentadecane using sensitized ZnO and visible light at (298)K for (5) hours .

6- The Effect of The Sensitized ZnO Particle Size :

The effect of the particle size of the malachite green sensitized ZnO on the rate of photocracking of n-pentadecane has been studied for four different sample. For this

purpose (0.6) gm. of malachite green deposited on ZnO with mesh size (100, 200, 300 and 400) were used as in figure (11):

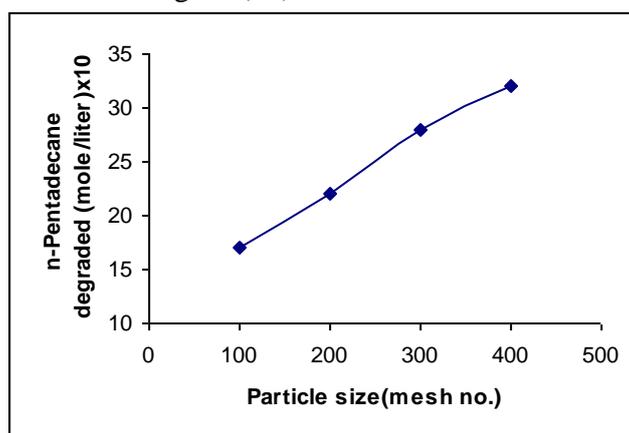


Figure (11) : The effect of the particle size of sensitized ZnO on photocracking of n-pentadecane at (298) K .

The results in figure (11) show that the rate of photocracking of n-pentadecane increases with particle size decreases (mesh size increases) . Thus in expected in term of the surface area available for the absorption of light by malachite green and therefore to generate more active site for photocatalytic processes. Formenti *et al* were noticed that the porosity of TiO₂ catalyst on photooxidation of isobutene dose not show any effect on the rate of phoyocatalytic process.

6. The Effect of Malachite Green Sensitizer :

From figure (12), it is clear the effect of the malachite green sensitization in the present photocatalytic system, so the variation of the concentration of n-pentadecane compound with time in the presences or absence of sensitizer .

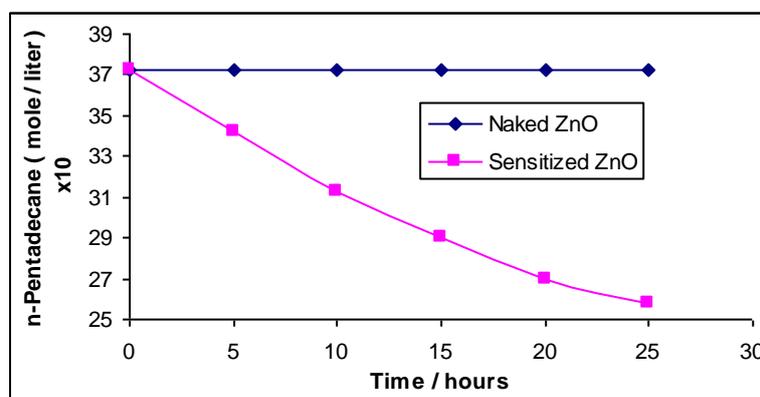
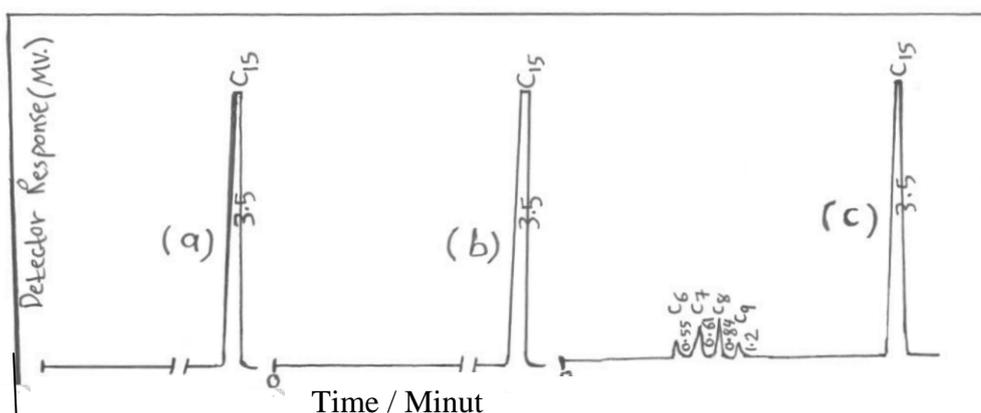


Figure (12) : The variation of concentration of n -pentadecane at (298)K for (25) hours irradiation.

The irradiated n-pentadecane with sensitized ZnO for (25) hours was analyzed by gas chromatographic technique as in Figure (13) .



Figure(13) : Gas chromatographic of n-pentadecane and generated light hydrocarbons at (298)K for (25)hours irradiation
a-n-pentadecane before irradiation.
b-n-pentadecane with naked ZnO .
c-n-pentadecane with sensitized ZnO.

The above figure(13-c) shows the generation of new light hydrocarbons compounds such as: C₆, C₇, C₈ and C₉, which not appear by using irradiation n-pentadecane with naked ZnO as in figure(13-b). From the initial concentration of n-pentadecane (C_i = 3.72 mole/liter) and the its initial peak area[(p.a.)_i = 100].The concentration (C_t) of residual (undegraded) n-C₁₅H₃₂ after (25) hours irradiation in the mixture can be calculated from the corresponding its peak area percentage (p.a.%)_t as in simple relation:

$$C_0 / (p.a.\%)_0 = C_t / (p.a.\%)_t$$

$$\text{Then } C_t = C_0 \times (p.a.\%)_t / (p.a.\%)_0$$

Then from the peaks area percentage (p.a.%)_t after (25) hours irradiation of light hydrocarbons generated,and initial concentration of n-pentadecane(C_i = 3.72 mole/ liter) and its initial peak area percentage [(p.a.%)₀ = 100], can be determine the concentration (C_t = mole/liter) of these generated light hydrocarbons as in table (2).

Table (2):Peak area% of n-hydrocarbons degraded (n-C₁₅H₃₂) and formed (C₆H₁₄- C₉H₂₀) with corresponding concentration(mole/liter) before and after (25) hours irradiation using sensitized ZnO .

n-hydro-carbon	Peak area% of n-hydrocarbon before and after irradiation		Concentration hydrocarbon(mole/ liter) before and after irradiation	
	(0) hours	(25) hours	(0) hours	(25) hours
C ₁₅ H ₃₂	100	68.6	3.72	2.552
C ₆ H ₁₄	0.0	3.2	0.0	0.119
C ₇ H ₁₆	0.0	11.3	0.0	0.416
C ₈ H ₁₈	0.0	14.5	0.0	0.544
C ₉ H ₂₀	0.0	2.4	0.0	0.089

Also IR spectrophotometric technique was used to identify the photosensitized catalytic products (function group) created during the photocracking of n-pentadecane after (25)hours irradiation as in figure (14):

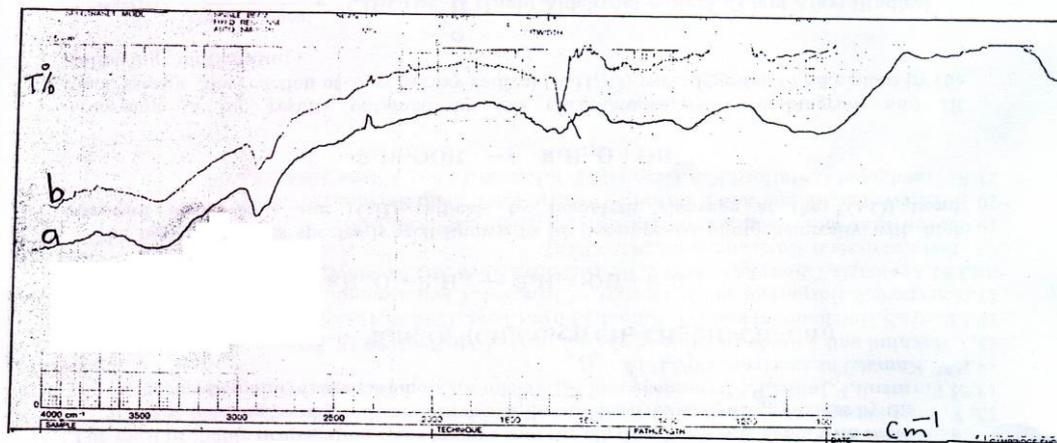
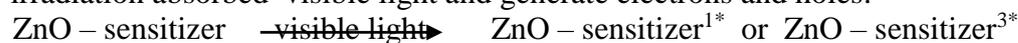


Figure (14) : IR spectrum for :
a- n-pentadecane before irradiation .
b- n-pentadecane after(25) hours irradiation.

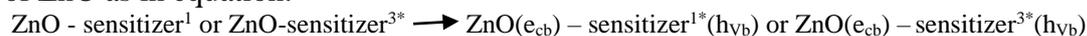
The above figure indicate ($\begin{matrix} \text{O} \\ \diagup \\ -\text{C}- \\ \diagdown \end{matrix}$) stretching vibration of aliphatic carbonyl group at 1720 cm^{-1} ,which not present in the original substrate (n-pentadecane)spectrum .

Proposed Reaction Mechanism

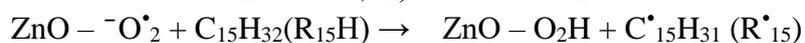
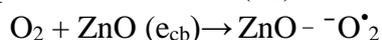
Figure (2) shows , sensitizer (malachite green) adsorbed on ZnO surface , upon irradiation absorbed visible light and generate electrons and holes.



Exited sensitizer singlet or triplet are injected photoelectron in conduction band of ZnO as in equation:



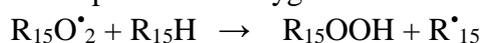
The valence band photogenerated holes are free to react with (OH^-) adsorbed on the ZnO surface to create hydroxyl radical (OH^\bullet). The ZnO conduction band electrons react with electron acceptors are oxygen creating oxygen radicals (O_2^\bullet , O^\bullet). These radicals (O_2^\bullet , O^\bullet and OH^\bullet) present extremely strong oxidizing properties are able to abstract in initial step a hydrogen atom from any carbon in the chain (n-pentadecane) except from carbon one(C_1) .



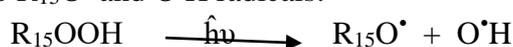
According to the results obtain by Gas Chromatography chromatogram and IR spectroscopy, the more suggested propagation steps are:

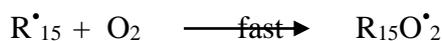
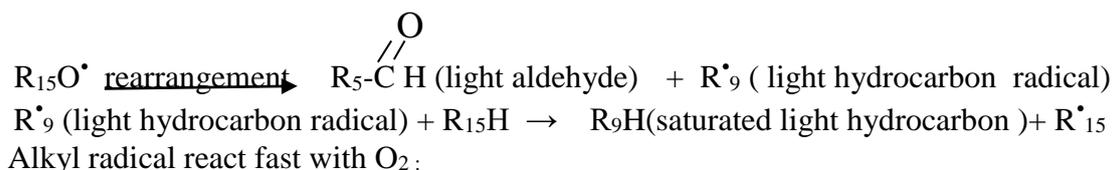


The peroxy radicals followed by hydrogen abstraction form the backbone of other $\text{C}_{15}\text{H}_{32}$ molecules and repeated fast oxygen addition :



The hydroperoxide species is well-known to decompose photochemically with high quantum yield to $\text{R}_{15}\text{O}^\bullet$ and OH^\bullet radicals:





Peroxyradical terminate to form light alkanes and light carbonyl compounds.

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