



Photocatalytic oxidation of benzyl alcohol using pure and sensitized anatase

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Abstract

The photocatalytic oxidation of liquid benzyl alcohol by suspension of titanium dioxide (anatase) and sensitized anatase has been investigated under an oxygen atmosphere. Measurements were made over the temperature range 278–303 K, using low pressure mercury lamp. Spectrophotometer measurements have been used to determine the concentration of benzaldehyde by following the formation of 2,4-dinitrophenyl hydrazone derivatives at a wavelength 480 nm. Activation energies for benzaldehyde formation were effectively identical on naked and sensitized anatase ($21 \pm 1 \text{ kJ mol}^{-1}$), however, the activity of sensitized anatase was higher than that of naked anatase. The identical activation energy for the photoreaction of benzyl alcohol over sensitized and naked TiO_2 in the presence of oxygen is believed to be associated with the transport of photoelectrons through the catalyst to the adsorbed oxygen on the surface.

Keywords: Photocatalytic oxidation; Anatase; Benzyl alcohol

1. Introduction

In heterogeneous photocatalysis, when a suspension of a particular semiconductor is irradiated with a natural or artificial light, with an energy equals to or larger than the band gap, electrons will be promoted to the conduction band (C.B.), leaving positive holes in the valence band (V.B.). If the electrons and holes are in a reaction, a steady state will be reached

when the removal of electrons and holes equal the rate of generation by illumination.

Recombination and trapping processes are the de-excitation processes, which are responsible for the creation of the steady state if no reaction occurs. There are three important mechanisms for recombination, namely; direct recombination, recombination at recombination centers and surface recombination.

There are different types of semiconductors, where their band gaps ranged between between 1.4 and 3.9 eV, i.e., it could be excited with a

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Table 1
Band positions for some common semiconductors at pH = 1^a

Semiconductors	V.B. (V vs. NHE)	C.B. (V vs NHE)	Band gap (eV)	Band gap (nm)
TiO ₂	+3.1	-1.0	3.2	387
SnO ₂	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	387
ZnS	+1.4	-2.3	3.7	335
WO ₃	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	496
CdSe	+1.6	-0.1	1.7	729
GaAs	+1.0	-0.4	1.4	886
GaP	+1.3	-1.0	2.3	539

^aRef. [1]

light of 318–886 nm wavelength, which means that most of the known semiconductors could be excited by using a visible light. Table 1 shows different types of semiconductors [1].

However, not all these semiconductors could be used in the photocatalytic reactions, Pelizzetti et al. [2] reported that the most appropriate photocatalysts should be stable toward chemicals and illumination and devoid of any toxic constituents, especially for that used in environmental studies. The authors also explained that TiO₂ and ZnO are the most used in photocatalytic reactions, due to their efficient absorbing of long wavelength radiation, and their stability towards chemicals. Other semiconductors like WO₃, CdS, GaP, CdSe and GaAs absorb a wide range of the solar spectrum and can form chemically activated surface-bound intermediates, but unfortunately, these photocatalysts are degraded during the repeated catalytic cycles involved in heterogeneous photocatalysis. The disadvantage of using ZnO is its tendency to dissolve in acidic solutions, and as a result it is difficult to use it in technical properties [2].

Hussein et al. [3–9] investigated the photocatalytic oxidation of aliphatic and aromatic alcohols on different types of TiO₂ and metalized TiO₂. The products were the corresponding

aldehydes for primary alcohols and ketones for secondary alcohols. They suggested that these methods provide a clean and convenient procedure for the formation of aldehydes and ketones on preparative scale. The percents of conversion are equal to 72–82% in the case of using rutile and 86–93% in the case of anatase [3,8].

Dispersion of titanium dioxide particle in petroleum molecules showed an effective role in photocracking of heavy petroleum molecules in the existence of zeolite [10]. In another study [11], titanium dioxide was found to be an excellent catalyst for the treatment of water polluted with petroleum in aquatic environment under weathering condition. Photosensitization of anatase showed an increase in the activity of anatase for photo-oxidation of alcohols [12–15] and decolorization of industrial water [16].

The identical reactivity of photoconversion of different alcohols on riboflavin sensitized anatase was considered to be achieved from the common rate-controlling process which was the transport of photoelectrons through the catalyst to the adsorbed oxygen [15]. However, the activity of photo-oxidation of single alcohol on different sensitized catalysts was found falling in the sequence [14]:

Riboflavin > Safranin O > Rhodamin 6G > TiO₂ (alone)
 > Methyl red > Eosin B > Crystal violet > Congo red
 > Thionine > Methyl blue.

The present work reports an investigation of photocatalytic oxidation of benzyl alcohol on sensitized anatase with different sensitizers. The sensitization process was done by impregnation method.

Experimental chemicals: Benzyl alcohol was purchased from BDH (purity 99%) and used without further treatment. Titanium dioxide was Degussa P25 (mostly anatase BET 55 m² g⁻¹). Sensitized anatase was prepared by impregnation of riboflavin (purchased from BDH with a purity of 98%) or safranin O (purchased from BDH with a purity of 95%) with a concentration 5.0 × 10⁻⁶ mol dm⁻³.

2. Experimental techniques

The photolytic apparatus used is shown in Fig. 1. The measurement of the incident light intensity was carried out, as described before [17], by using a standard method of potassium ferrioxalate actinometry, utilizing the following equation:

$$I_0 = \frac{AV_1}{\Sigma \Phi_\lambda V_2 t} \quad (1)$$

where, I_0 is the intensity of the incident radiation, A is the absorption at 510 nm, V_1 is the final volume which equals to 25 cm³, ε is the extinction coefficient which equals to the slop of calibration curve, Φ_λ is the quantum yield which equals to 1.21 at 365 nm, V_2 is the volume taken from irradiated solution which equals to 1 cm³ and t is the time of irradiation of actinometer solution. I_0 was found to be equal to 4.33 × 10⁻⁶ einstein s⁻¹.

In all experiments, 25 cm³ of liquid benzyl alcohol was added to a known weight of naked or sensitized TiO₂ in the reaction cell and suspended by using a magnetic stirrer. Periodically,

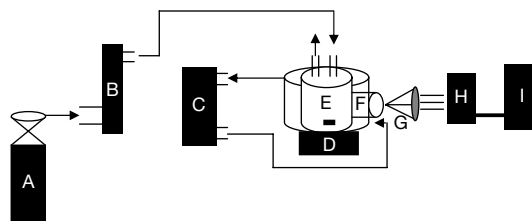


Fig. 1. Schematic diagram of the experimental apparatus for photocatalytic reaction: (A) gas container, (B) gas flowmeter, (C) circulating water thermostat, (D) magnetic stirrer, (E) quartz cell, (G) lenses, (H) low pressure mercury lamp, (I) power supply unit.

0.2 cm³ samples of irradiated mixture were withdrawn by using a syringe with a long pliable needle. These were centrifuged to separate the solid catalyst and the supernatant liquid analyzed for the reaction products. 0.1 cm³ of the supernatant was added to 5 cm³ of a mixed hexane/ethanol solvent (3:7). The mixture was reacted with 25 cm³ of 2,4-dinitrophenylhydrazine reagent for 30 minutes at 329 K to produce the 2,4-dinitrophenylhydrazone of the aldehyde. The product was cooled to room temperature and diluted to 25 cm³ in a volumetric flask with alcoholic potassium hydroxide solution. The solution was thoroughly mixed, and the absorbance was measured at 480 nm after appropriate dilutions, on a SP8-100 Pye Unicam Ultraviolet/Visible spectrophotometer using a 1 cm glass cell.

The absorbance was directly proportional to the amount of the reaction product, whose concentration was determined from a typical calibration plot. The calibrating plot was obtained by using a known concentration of a standard benzaldehyde solution instead of the reaction mixture. This method was adapted from that used before [4–6].

3. Results and discussions

3.1. The effect of the catalyst concentration

Fig. 2, shows that the rate of benzaldehyde formation increases with the increasing of TiO₂

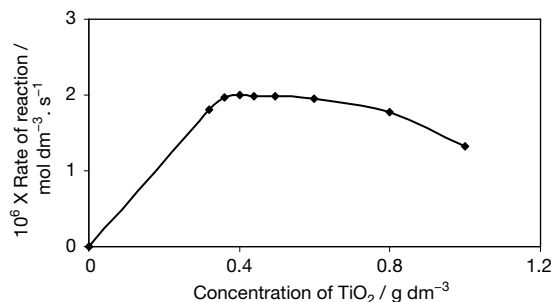


Fig. 2. The reaction rate for photocatalytic oxidation of benzyl alcohol in the presence of different concentrations of TiO₂

loading. However, above 0.6 g dm⁻³ it showed a negative deviation as the titania loading increases. It follows that the increases in activity with increasing the catalyst loading below the plateau region is associated with an increase in the efficiency of utilizing incident radiation, whilst the plateau itself represents the most efficient utilization of the incident radiation, that can be achieved within the system used. The negative deviation could be explained due to the fact that the suspension became more opaque to the incident radiation and only the photons absorbed by the catalyst particles, onto which a benzyl alcohol molecule is pre-adsorbed, may be effective in carrying out the redox chemistry [18]. The residue photons were wasted.

4. Effect of benzyl alcohol concentration

4.1. Selection of the appropriate solvent

The selection of the appropriate solvent for benzyl alcohol in the photoreaction depends upon the capability of the alcohol to dissolve completely in different concentrations, and the absence of the solvent photo-oxidation, which results in the formation of carbonyl groups that lead to the interference with the carbonyl group of the benzaldehyde obtained from the catalytic photo-oxidation of the benzyl alcohol.

After accomplishing many tests for the solvents; such as diethyl ether, benzene, heptane, toluene and *p*-xylene; it was observed that *p*-xylene is quite miscible with the alcohol with a spectrum of concentrations.

Irradiation of 25 cm³ of *p*-xylene has been done in the presence of TiO₂ with a concentration of 0.4 g dm⁻³, and the passage of oxygen gas with a speed of 15 cm³ min⁻¹. The mixture was thoroughly stirred at 293 K. After irradiation for 90 min, spectroscopic investigations showed the absence of the carbonyl group, indicating that *p*-xylene was not photo-oxidized. Hence, it is chosen to be the appropriate solvent for benzyl alcohol.

4.2. Photocatalytic oxidation using titanium dioxide with different concentrations of benzyl alcohol

A series of experiments has been accomplished including irradiation of different concentrations for benzyl alcohol, prepared by taking different volumes of the alcohol from 0 to 12.5 cm³ and diluted to 25 cm³ with *p*-xylene. In all cases, 0.4 g dm⁻³ of TiO₂ was added. Oxygen was passed with continuous stirring for 90 min at 293 K. The concentration of benzaldehyde was, spectroscopically, determined.

The rates of photoconversion of different molar concentrations of benzyl alcohol are shown in Fig. 3. Adsorption constant was found to be equal to 0.386 s⁻¹ as shown in Fig. 4. The rate constant was calculated from the relation between the relation log (C_∞-C_t) against time as shown in Fig. 5. The rate constant was observed to be 4 × 10⁻⁴ s⁻¹.

The high value of adsorption constant refers to the high electronic density of aromatic ring (electron donating group), which leads to strong adsorption on Ti⁴⁺ positions (electron withdrawing group).

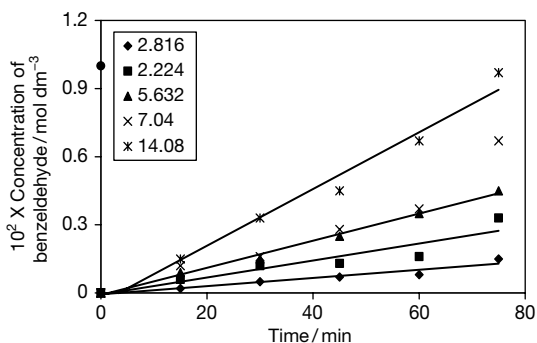


Fig. 3. Photocatalytic oxidation of different concentration of benzyl alcohol on TiO_2 at 293 K.

5. The effect of dye concentration on the photocatalytic reaction

Fig. 6 shows the effects of the variation of the concentrations of riboflavin and safranin O on the activity of photocatalytic conversion of benzyl alcohol to benzaldehyde. The results show that the rate of photoconversion increases with increasing the concentration of riboflavin or safranin O. However, it was observed that above 5.0×10^{-6} mol dm^{-3} show a negative deviation. The reason for this effect is that at high concentrations of the dye, the molecules of it form inner filters and absorb high portions of the incident radiation and prevents it to pass to other parts of the reaction vessel which reduced the amounts of photons reaching other parts of the reaction vessel.

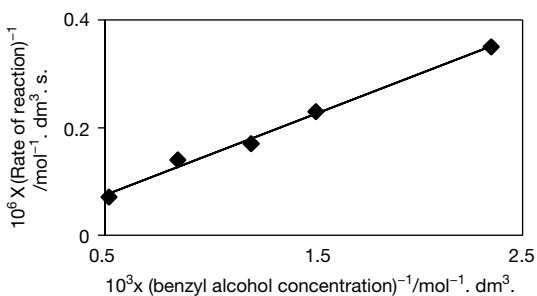


Fig. 4. The relation between the inverse of the rate of the reaction and the inverse of benzyl alcohol concentration at 293 K.

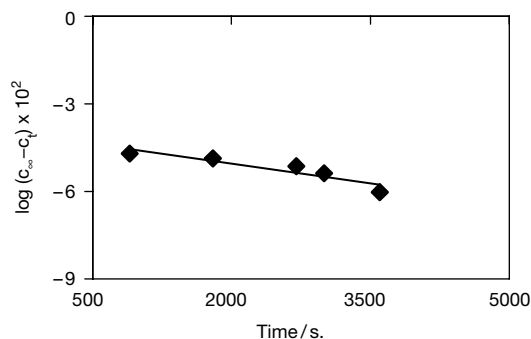


Fig. 5. The relation between $\log(c_\infty - c_t)$ and time of the reaction.

6. Photocatalytic oxidation on naked and sensitized anatase

Fig. 7 shows the effect of sensitizers on the activity of TiO_2 . The activity of photoconversion of benzyl alcohol to benzaldehyde fell in the sequence:

Riboflavin > Safranin > Naked TiO_2

The different activities of dyes reflect the ability of dye to absorb light and inject electrons to the conduction band of TiO_2 [14]. Riboflavin and safranin O have good overlapping of its spectrum with low absorption of TiO_2 . It was

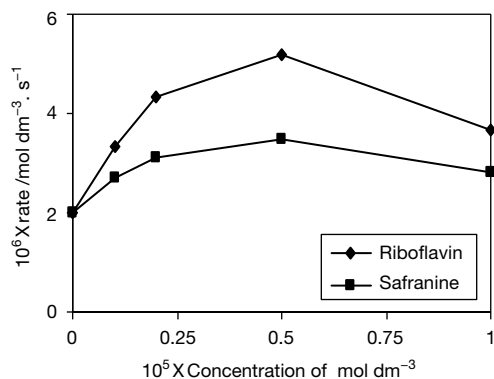


Fig. 6. The effect of dye concentration on the photocatalytic reaction.

found that λ_{\max} for riboflavin is 545 nm and 525 nm for safranin O [14], where the minimum absorption of TiO_2 is 520–540 nm [14].

The heterogeneous photocatalytic reactions depend upon the band gap energy of the semiconductor particle and the frequency of the incident radiation. It is well known that some semiconductors, especially TiO_2 , have a high stability besides the great surface area. However, they require high radiation energy for excitation. This energy could be decreased by utilizing the dyes as photosensitizers [12].

The dyes, whose absorption of radiation interferes with the lowest energy of the absorption spectrum for the catalyst, inject their excited electrons into the conduction band of the semiconductors, whereas the photo-holes are generated through the direct photo-oxidation of the reducing dye by the diffusion through the double-layer of the inter-surface to generate the electrons and the photo-holes by an indirect way using sunlight due to the existence of dyes as sensitizers.

7. Temperature dependence of reaction rate

Reaction was followed at six different temperatures, in the range 278–308 K. The activation energy of $21 \pm 1 \text{ kJ mol}^{-1}$ for benzaldehyde formation was calculated from Fig. 7, where ($10^6 \log$ rate of the reaction/mol $\text{dm}^{-3} \text{ s}^{-1}$) was plotted against $10^3 T^{-1}/\text{K}$, for naked and sensitized anatase.

The identical activation energies for the photocatalytic oxidation of benzyl alcohol on naked and sensitized anatase is similar to the findings of Hussein and Rudham [4–5] for photocatalytic oxidation of different types of alcohols on anatase and metallized anatase.

This phenomenon could be explained that the calculated activation energy for the photoreaction of benzyl alcohol over sensitized and naked anatase in the presence of oxygen is associated with the transport of photoelectron through the

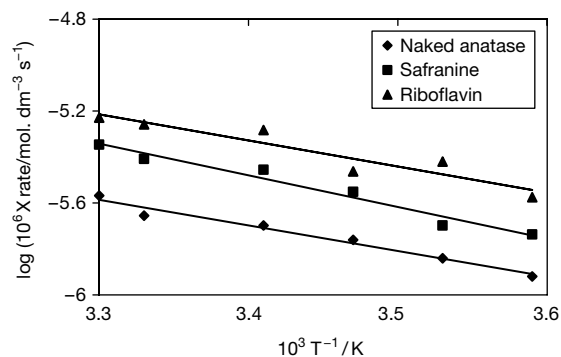


Fig. 7. Temperature dependence for the photocatalytic oxidation of benzyl alcohol on naked and sensitized anatase.

catalyst to the adsorbed oxygen on the surface. This could be explained by the identical activation energies for the photocatalytic oxidation of different alcohols on anatase [5], while different values of activation energies were obtained for anatase and rutile for the same reactions [9]. In this case, the rate controlling process is associated with surface steps and accordingly, a different type of sensitization gives a different reaction rate.

8. The mechanism for photocatalytic reaction on naked and sensitized anatase

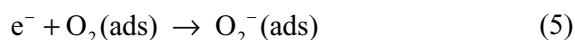
8.1. Naked TiO_2

When the suspension of titanium dioxide irradiated with light of energy 3.2 eV an electron will be promoted from valance band leaving a positive hole in the conduction band:

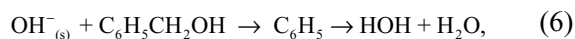


It was explained before [2], that the surface of TiO_2 with high surface area retains subsets of surface hydroxyls, where the net surface density is 4–5 hydroxyls per $(\text{nm})^2$. In addition, suspensions

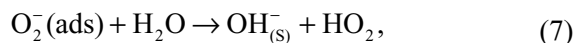
of TiO₂ in benzyl alcohol give a surface hydroxide ion as locations for primary photo-oxidation processes. Photoholes are trapped by surface hydroxide groups, whereas electrons are trapped by adsorbed oxygen:



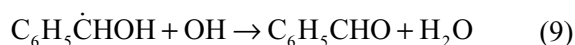
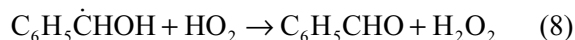
The formed radicals are reacted with adsorbed molecules of benzyl alcohol:



O₂⁻, which adsorbed on the surface, is reacted with the formed water to regenerate hydroxyl group on the surface of the catalyst:



Benzaldehyde could be formed according to following steps:

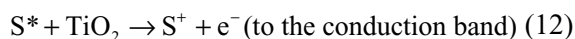


8.2. Sensitized TiO

Sensitized titanium dioxide excited to S* after absorption of light as follows:



The excited Sensitizer injects an electron into the conduction band of anatase:



The formed S⁺ and e⁻ in Eq. 12 will be used in the oxidation of benzyl alcohol as in the previous steps (Eqs. 4–10).

References

- [1] S. Para, Coupling of Photocatalytic and Biological Processes as a Contribution to the Detoxification of Water, Catalysis and Tecnological Aspects, Ph.D. Thesis, Lausanne, France, 2001.
- [2] D. Bahnemann, J. Cunningham, M. Fox, E. Pelizzetti, P. Pichat and N. Serpone, Photocatalytic treatment of water, in: Aquatic and surface photochemistry, G. Heiz, R. Zepp and D. Crosby. eds, Lewis Publishers, U.S.A., 261–316, 1994.
- [3] F. Hussein, G. Pattenden, R. Rudham and J. Russel Photo-Oxidation of Alcohols Catalyzed by Platinized Titanium Dioxide, Tetrahedron Lett., 25 (1984) 3336–3364.
- [4] F. Hussein and R. Rudham, Photocatalytic dehydrogenation of liquid propan-2-ol by platinized anatase and other catalysts, J. Chem. Soc. Farad. Trans. I, 25 (1984) 2817–2825.
- [5] F. Hussein and R. Rudham, Photocatalytic dehydrogenation of liquid alcohols by platinized anatase, J. Chem. Soc. Farad. Trans. I, 83 (1987) 1631–1639.
- [6] F. Hussein, A. Ibrahim and S. Shakir, Photo-oxidation of aromatic alcohols catalyzed by platinized titanium dioxide (Part I), Zanco, 2 (1988) 82–91.
- [7] F. Hussein, A. Ibrahim and S. Shakir, Photo-oxidation of aromatic alcohols catalyzed by platinized titanium dioxide (Part II), Zanco, 4 (1989) 73–81.
- [8] F. Hussein, A. Ibrahim and R. Jameel, Photo-oxidation of Some Substituted benzoin by titanium dioxide, Iraqi J. Chem., 15 (1990) 133–135.
- [9] F. Hussein, Photocatalytic oxidation of liquid alcohols by titanium dioxide, abhath alyarmouk J., 11 (2002) 327–335.
- [10] F. Hussein, A. Abdulsahab and S. Naman, Cracking of heavy petroleum molecules by visible light irradiation of TiO₂ dispersion in the presence of zeolites, J. Coll. Edu. For Women, Univ. Bag., 5(1) (1994) 69–75.
- [11] F. Hussein and F. Amara, The effect of TiO₂ catalyst upon the treatment of oil in aquatic environment under weathering condition, Basra J. Science, 18(2) (2000) 29–34.

- [12] H. Habeeb and F. Hussein, Sensitized photocatalytic oxidation of propan-2-ol by titanium dioxide, *Iraqi J. Science*, 41(3) (2000) 94–113.
- [13] F. Hussein and H. Habeeb, Photo sensitized dehydrogenation of propan-2-ol by titanium dioxide suspension, *J. Al-Qadisiya*, 6 (2001) 176–181.
- [14] A. Attia and F. Hussein, Sensitized photocatalytic oxidation of butan-2-ol, *national J. Chem.*, 2 (2001) 229–244.
- [15] A. Attia and F. Hussein Sensitized Photocatalytic Oxidation of Aliphatic Alcohols by Naked and Riboflavin Sensitized Anatase, *National J. Chem.*, 3 (2001) 404–415.
- [16] F. Hussein, H. Mashkoo and A. Al-Sharafy, Effect of TiO₂ and ZnO catalysts upon the treatment of industrial water under weathering condition, *National J. Chem.* 9 (2003) 94–100.
- [17] S. Naman, A. Jassim, and M. Alias, Photodecomposition of molybdenum (II) and tungsten (II) carbonyl complexes with Triazole, Benzimidazole and oxadiazol acetylinic derivatives, *J. Photochem. and Photobiol. A: Chemistry*, 150 (2002) 4–8.
- [18] N. Serpone, Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis, *European Photochemistry Association Newsletter*, No. 59, 54–81, 1997.