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Effect of electric field in liquid phase oxidation of benzhydrol by aqueous hydrogen peroxide

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ABSTRACT

Electric-field-induced oxidation of benzhydrol to benzophenone over conducting surface containing titanium dioxide has been carried out by using hydrogen peroxide as oxidant. The results suggest the occurrence of synergistic effect of electric field and titania in which the interphase area between the titania particles and conducting surface is the most active region for the reaction. The electrical field on the generation of surface charge to induce the adsorption of organic substrate has also been confirmed by dye adsorption experiments.

| Electric-field-induced catalytic oxidation; Benzohydrol; Titania|

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1. INTRODUCTION

In general, liquid phase reactions can be enhanced by manipulation of relevant local environmental conditions [1]. The rate of the reaction and selectivity might increase. Reactions may also be enhanced by increasing the temperature or pressure. The mechanism for this enhancement is usually expressed in terms of increasing the likelihood of overcoming the activation energy. It is an objective of the present study to enhance chemical reactions without requiring a high temperature of the reaction environment by applying the electric field. One considers that the electric field may affect the molecular processes of the catalytic reaction on the heterogeneous catalyst's surface [2-7]. When a substrate hits on a solid surface from a liquid phase, there are a number of possible outcomes [8]. The substrate molecule may simply either bounce back or be adsorbed. It is the latter case that carries the most interesting possibilities. The interaction with the substrate of the surface can be so strong that the molecule dissociates into constituent groups or atoms. The substrate molecule can also react directly with surface groups and change the chemical properties of the surface. A third possibility is that the adsorbed molecule encounters another previously adsorbed one and there is a binary chemical reaction on the surface.

Based on the above consideration, it is of interest to explore the effect of electric field on the liquid phase reaction over a heterogeneous catalyst's surface. Here, the

effect of electric field enhanced on catalytic oxidation of benzhydrol to benzophenone was investigated. The oxidation of benzhydrol to benzophenone was studied in the system containing titania (TiO_2) attached on the conducting carbon grease under electric field.

2. EXPERIMENTAL

2.1 The catalyst system

Fig. 1 shows the schematic representation of PPy-TiO₂ mixture attached to carbon grease which is supported by the bronze foil. The titania (TiO_2) powder with anatase structure was supplied by Merck. Polypyrrole (PPy) containing proprietary organic sulfonic acid dopant with electrical conductivity 10-40 S cm⁻¹ was supplied by Aldrich. Carbon conductive grease supplied by MG Chemicals was used to stick PPy titanium oxide powder on the bronze foil. A series of PPy-TiO₂ mixture in various proportions (0-100% TiO₂) was prepared by stirring manually the PPy-TiO₂ particles with a spatula until uniformly mixture was obtained. In this mixture, PPy act as conducting "solid" solvent to dilute TiO₂. The bronze foil coated with carbon grease was dipped into the specified PPy-TiO₂ mixture. Direct current voltage-stabilized power source was used in supplying electric field in catalyst system. A multi meter was used for measurement of the current and voltage in the system.

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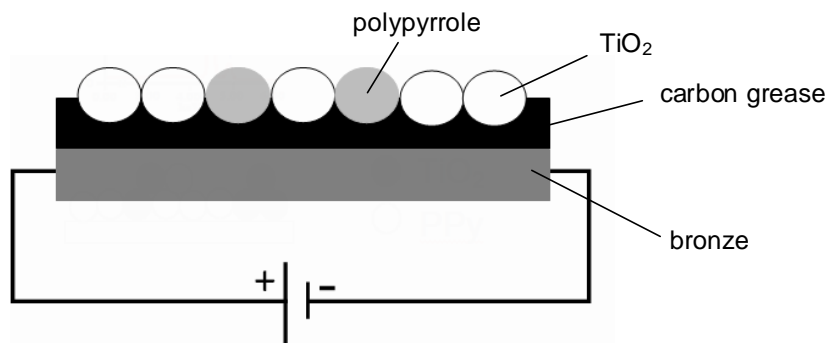


Fig. 1: The schematic representation of the catalyst system induced by electric field.

2.2 Morphological properties and Ti mapping

The morphology of the catalyst system was examined using a scanning electron microscope. The distributions of Ti atoms on the surface of the catalyst system were obtained by SEM EDX mapping (JEOL JSM 840A).

2.3 The oxidation of benzohydrol

The oxidation of benzohydrol was carried out using the above catalyst system with and without electric field. Benzohydrol (1 mmol in 10 ml water), 30% aqueous H_2O_2 (5 mmol) were placed in reaction tube and the reaction was performed in oil bath with stirring at 70 °C for 20 min. After the reaction, the solution was transferred into a separatory funnel and extracted with diethyl ether. GC (Agilent 19091N-133) equipped with a flame ionization detector (FID) was used to identify the reaction product. The voltage and current of electric field measured during the reaction were 5 V and 2 A, respectively.

2.4 The adsorption of dye

The dye used was methylene blue from Sigma. Adsorption was carried out by stirring 20 ml of 2 ppm methylene blue in presence of the above catalyst system with and without electric field. The voltage and current of electric field applied during the adsorption were 5 V and 2 A, respectively. The methylene blue solutions were contacted for 1 h and analyzed spectrophotometrically at λ_{max} of 665 nm. Adsorption experiments were immediately conducted with 1.0 cm light path quartz cells using Perkin-Elmer Lambda 900.

3. RESULTS AND DISCUSSION

3.1 Oxidation of benzohydrol with aqueous hydrogen peroxide under electric field

Fig. 2 shows the results for oxidation of benzohydrol to benzophenone over electrically conducting surface containing titanium dioxide by using hydrogen peroxide under and without electrical field. The catalyst system without electric field showed a low performance for benzophenone production, whereas it exhibits reasonably good performance for this reaction under electric field. The best performance appears to be the catalyst system containing 30% TiO_2 under electric field (see Fig. 2). Note that although the catalyst system containing 30% TiO_2 appears to be best when comparing different loadings, if we replot Fig. 2 in terms of turnover number (TON) (Fig. 3), then 10% TiO_2 appears to be a better than the other TiO_2 loading, suggesting that amount of TiO_2 at 10% loading exhibited definite activity. This probably relates to the dispersibility of TiO_2 particles on the conducting surface of the catalyst system as shown in Fig. 1. EDX mapping of Ti (Fig. 2b) shows that TiO_2 particles agglomerate into big particles when TiO_2 loading is 60%.

Although the adsorption study of benzohydrol on the catalyst system is important to clarify the effect of electric field on catalytic activity, the experimental procedures to demonstrate it seem difficult. The only credible, tough complex, in the present study, we employed the feasible process of adsorption of methylene blue on the catalyst system as a model compound to evaluate the effect of electric field on the adsorption of organic substrates. The effect of the adsorption of the methylene blue on the surface of catalyst system under and without electric field is shown in Fig. 4. It was shown that the electric field induced the adsorption of methylene blue on the catalyst system. The amount of TiO_2 led to a considerable decrease of the adsorption of dye because the conducting surface was covered by non-conducting TiO_2 particles. Since the electric current flow only in conducting region, a suggestion that can be made is that the dye molecules preferentially adsorb on PPy and carbon grease surfaces.

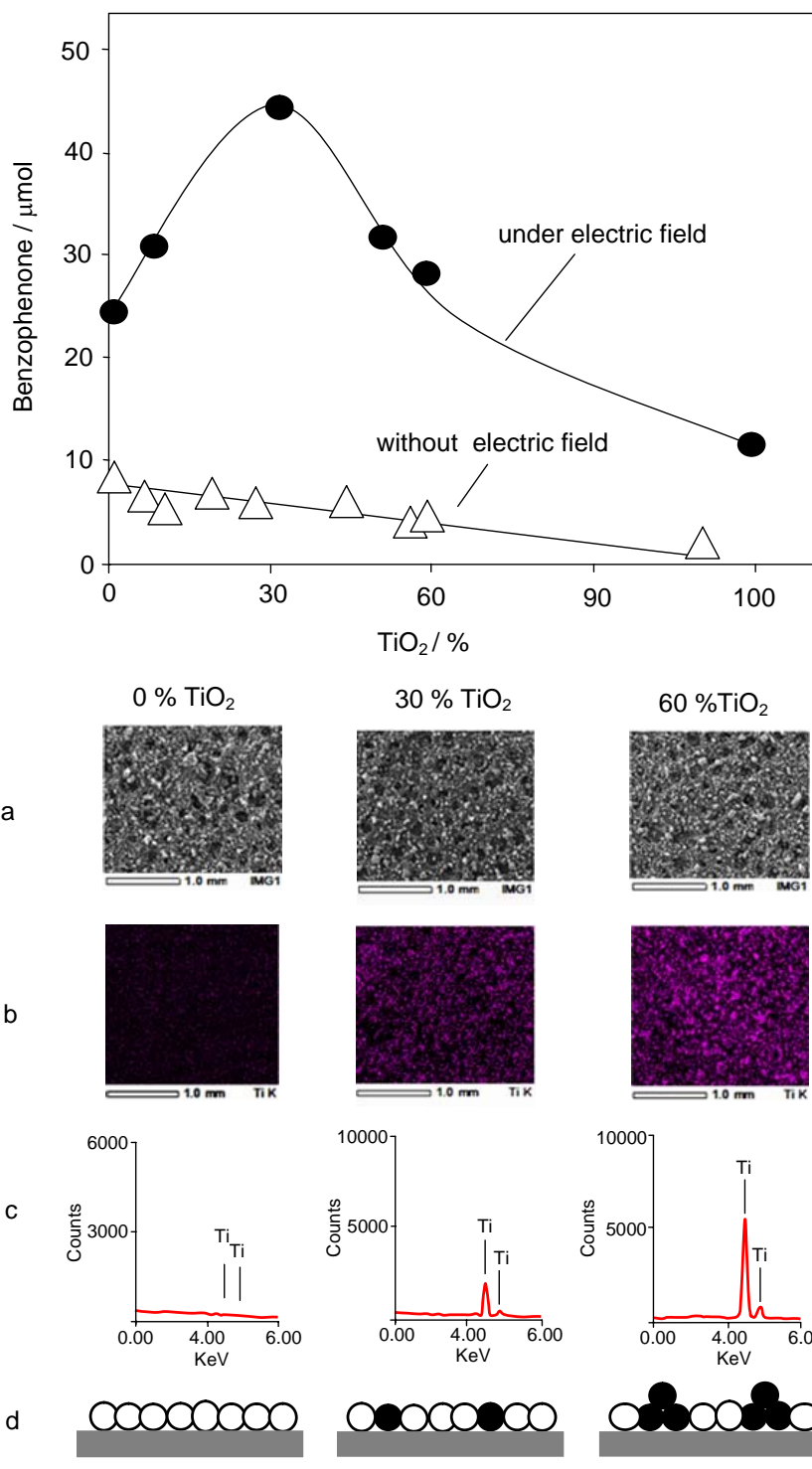


Fig. 2: The yield of benzophenone on the the oxidation of benzohydrol by aqueous hydrogen peroxide. All reactions were carried out at 70 °C for 20 min. The voltage and current of electric field measured during the reaction are 5 V and 2 A, respectively. (a) The SEM photographs, (b) EDX mapping, (c) elemental Ti count image and (d) arrangement of TiO₂ on the surface of catalyst system. The violet points in the Fig. 2(b) denote Ti atoms.

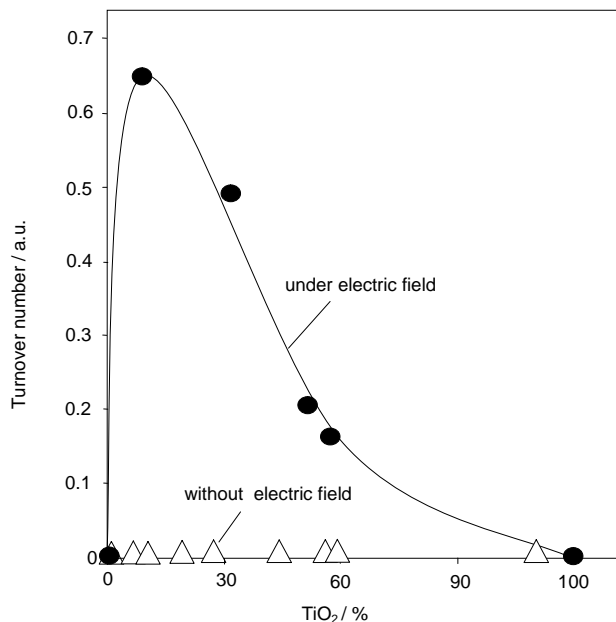


Fig. 3: The turnover number per Ti in the oxidation of benzohydrol by aqueous hydrogen peroxide. Reaction conditions are the same as given in Fig. 2.

3.2 The location of the most active oxidation site

As described above, the catalyst system containing $c10-30\%$ TiO_2 , effectively catalyzed benzohydrol oxidation by using H_2O_2 . The simple explanation for the decrease of the catalytic activity of the catalyst systems containing TiO_2 above 30% is that, as the TiO_2 loading increases, so does the effective interphase area between the TiO_2 particles. This is due to above a certain loading, the TiO_2 particles begin to agglomerate and overlap. One suggests that the catalyst system must satisfy the following requirements in order to achieve high catalytic activity: (i) existence of Ti

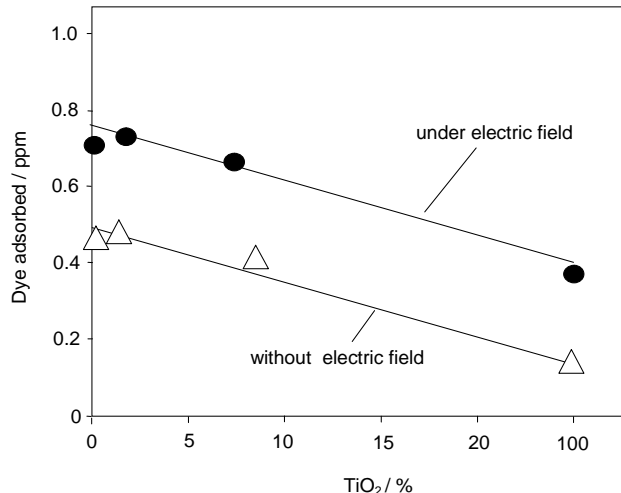


Fig. 4: Concentration of adsorbed methylene blue on the surface of catalyst system containing TiO_2

active sites, and (ii) the presence electric field. Therefore, if the catalyst particles exist in the agglomerate form, the number of Ti active sites which are in contact with conducting surface are limited and efficient oxidation reaction cannot be expected. The use of a certain amount of TiO_2 is necessary in order to increase the effective interphase area between the TiO_2 particles and conducting surface. On the basis of these results, a model of the catalyst system induced by electric field is proposed (see Fig.5).

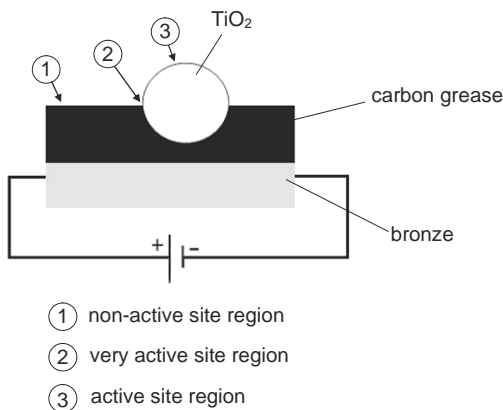


Fig. 5: Proposed model of an effective region for catalytic oxidation reaction induced by electric field.

All the results mentioned above seem consistent with the proposal that claimed the reaction takes place at the effective interphase area between the TiO_2 particles and

conducting surface. However, the apparent rate of oxidation of benzohydrol was much lower than previously reported [9]. One of the reasons for the low activity in our catalyst is

the presence of few four-coordinate Ti species which are considered to be the most active species in the oxidation reaction with H₂O₂ [10, 11]. It should be noted that we used the TiO₂ as an easily available material and the catalyst and the reaction conditions have not been optimized. Thus, we have shown that the oxidation reaction could be enhanced by electric field.

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