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Photooxidation of Ethylbenzene with TiO_2 and Metal Coated TiO_2 and its Kinetics

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Summary. Photooxidation of ethylbenzene with oxygen to give ethylbenzene hydroperoxide has been achieved in a stirred photochemical reactor that was cooled by a water system by irradiation with a 400 W high-pressure mercury lamp and using TiO_2 powder and metal coated TiO_2. The effects of the amount of copper or silver coated on TiO_2 and of the temperature on the rate of oxidation have been investigated. It is suggested that thermal cleavage of the O–O bond and photochemically generated singlet oxygen should be considered as the initiating step in a radical chain mechanism. An optimum loading of 6% Ag or 4–5% Cu was observed for photooxidation of ethylbenzene.

Keywords. Photooxidation; Ethylbenzene; TiO_2; Metal coated; Kinetics.

Introduction

Over the past several years, a large number of examinations on the application, production, and testing of TiO_2 as photocatalyst have been performed [1–7]. Coating of some metals on the TiO_2 surface has been known for the improvement of photocatalytic oxidation of organic compounds [8–12]. It has been reported that palladium, gold, and silver are effective for improvement of photocatalytic activity of TiO_2 [13–15]. Propylene oxide is produced by epoxidation of propylene with ethylbenzene hydroperoxide (*EBHP*). The latter is produced by oxidation of ethylbenzene (*EB*) with oxygen. The by-product of the above reaction is dehydrated to yield the monomer styrene (Scheme 1). In this work, we investigated the effect of loaded Cu or Ag on TiO_2 for the photocatalytic oxidation of *EB* to *EBHP* with oxygen.

It is expected that loaded Cu or Ag may improve photocatalytic activity of TiO_2, since the work function of Cu is quite similar to the TiO_2 conduction band and to the standard reduction potential of oxygen, which is considered to be a

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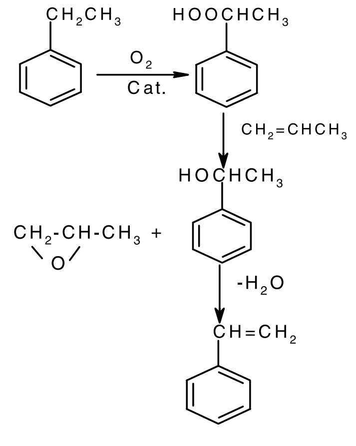

Scheme 1

probable electron acceptor in TiO_2 [16]. The oxidation of *EB* to *EBHP* is a liquid-phase radical reaction, carried out at industrial level (Scheme 1). The oxidation of a C–H bond to a C–O–O–H group (hydroperoxide) occurs with oxygen and is catalyzed by light [17, 18]. The active oxygen species is an excited singlet state oxygen and the function of the photosensitizer is to promote the oxygen triplet to singlet state. Excited singlet oxygen is the reactive intermediate in the photooxygenation of organic compounds [19–21], non-photochemical reaction between H_2O_2 and NaOCl, or between ozone and triphenylphosphite [22]. The singlet oxygen generated by either non-photochemical or photochemical methods is also the reacting species in the oxidation reaction [23–30].

Results and Discussion

The *EB* that we used as raw material in our photooxidation experiments was a Merck product that contained about $0.4\%w/w$ of *EBHP*. Moreover, any *EB* without radical inhibitor added would always contain trace amounts of *EBHP* due to autooxidation. Thus, a thermal cleavage of the –O–O– bond of *EBHP* should be taken into account while working at 120°C, and the radicals formed can act as radical chain initiators abstracting hydrogen from *EB*.

This was an important concern at the beginning of our experiments on photooxidation of *EB*, and we ran two experiments, one with irradiation and photosensitization and the other without irradiation, keeping constant the rest of the operating variables of the reactor (temperature, stirring speed, oxygen flow, reactor tank). Figure 1 shows the *EBHP* ($\%w/w$) *versus* time (h) for both experiments. Clearly, the kinetic rate of *EBHP* formation (w_{EBHP}) is much better for the photochemical experiment ($w_{EBHP} = 1.54 \times 10^{-5}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$) than for the experiment without photocatalysis ($w_{EBHP} = 4.3 \times 10^{-6}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$).

An experiment was carried out with irradiation in absence of a catalyst. The results showed that the rate of reaction was very slow. Therefore, in order to get a good kinetic rate the reaction must be carried out photocatalytically (Fig. 2).

The overall radical chain mechanism of the oxygen photooxidation of EB can be outlined as shown in Scheme 2.

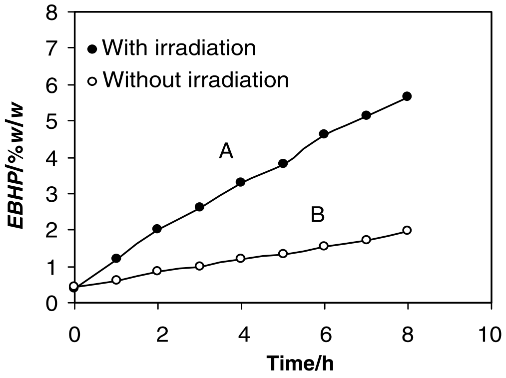

Fig. 1. Kinetic plots of *EBHP* (%*w*/*w*) *vs.* time (h) for 0.01 g of TiO_2 catalyst and 10 g of *EB* at 120°C; (A) with irradiation; (B) without irradiation

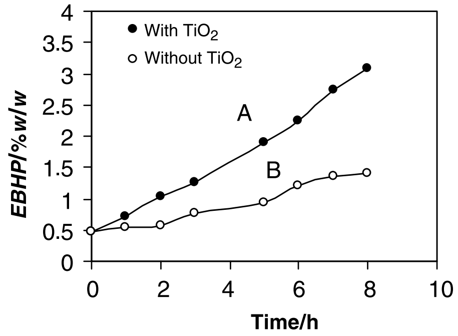

Fig. 2. Kinetic plots of *EBHP* (%*w*/*w*) *vs.* time (h) at 120°C; 10 g of *EB* (A) with 0.01 g of TiO_2 catalyst and (B) without TiO_2 catalyst

Initiation $S \xrightarrow{UV} S^*(h^+ + e^-)$

$S^* + {}^3O_2 \xrightarrow{k_i} [S\ldots O_2] \rightarrow {}^1O_2 + S$

$RH + {}^1O_2 \rightarrow R^0 + {}^0OOH$

$R^0 + O_2 \rightarrow RO_2^0$

Propagation $RO_2^0 + RH \xrightarrow{k_p} ROOH + R^0$

$R^0 + O_2 \rightarrow RO_2^0$

Termination $RO_2^0 + RO_2^0 \xrightarrow{k_t}$ coupling by-product

(S = Catalyst, RH = EB)

Scheme 2

Effect of the Temperature

We tried to keep the thermal initiation process at a minimum level by lowering the temperature and we ran experiments with irradiation and photosensitization at 120,

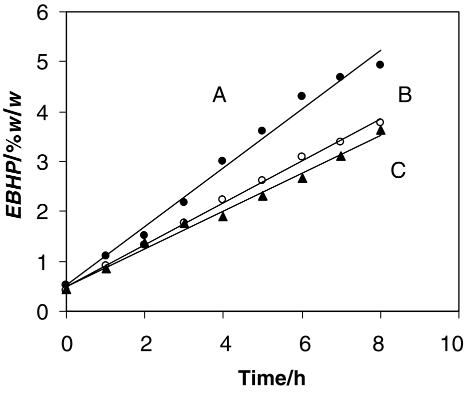

Fig. 3. Kinetic plots of *EBHP* (%*w*/*w*) *vs.* time (h) for 0.01 g of Ag/TiO_2 (2%) catalyst at three temperatures; (A) 120°C; (B) 95°C; (C) 85°C

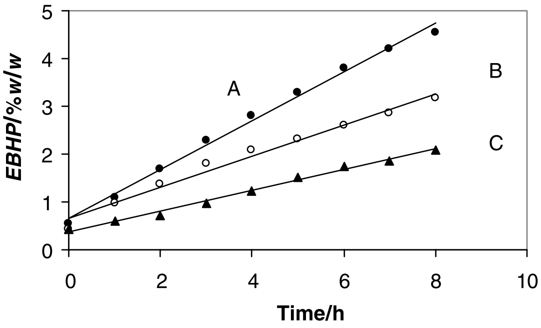

Fig. 4. Kinetic plots of *EBHP* (%*w*/*w*) *vs.* time (h) for 0.01 g of Cu/TiO_2 (2%) catalyst at three temperatures; (A) 120°C; (B) 95°C; (C) 85°C

95, and 85°C. Figures 3 and 4 show the kinetic plots of *EBHP* (%*w*/*w*) *versus* time (h) for the three temperatures for two catalysts. The effect of the temperature is very important, and the *EBHP* formation kinetic rate drops dramatically at lower temperatures. The influence of temperature on *EBHP* formation with the Ag coated on TiO_2 catalyst was less than with Cu coated on TiO_2. By plotting the *EBHP* formation kinetic rates (mol dm^{-3} s^{-1}) *versus* 1/T (K^{-1}) we have found the activation energies (kJ mol^{-1}) for the oxidation reaction using different catalysts (Table 1).

Effect of the Amount of Photosensitizer

The effect of the amount of metal (Ag or Cu) coated on TiO_2 on kinetic rate of *EBHP* formation is shown in Fig. 5. The three experiments were carried out under the same conditions, irradiating externally with the mercury lamp and using 0.5, 1, and 2 g of the catalyst to 1000 g of *EB*.

The effect of the amount of metals (Ag or Cu) coated on TiO_2 on the kinetic rate of *EBHP* formation shows that the rate of formation of *EBHP* is increased by

Table 1. Activation energies of *EBHP* formation in presence of catalysts

Type of catalyst	$Ea/\mathrm{kJ\,mol^{-1}}$
Anatase	22.055
Rutile	28.664
TiO_2	43.912
Cu/TiO_2 (2%)	31.604
Cu/TiO_2 (4%)	30.837
Cu/TiO_2 (5%)	22.759
Cu/TiO_2 (6%)	41.701
Cu/TiO_2 (8%)	53.698
Ag/TiO_2 (2%)	26.117
Ag/TiO_2 (4%)	16.792
Ag/TiO_2 (5%)	12.763
Ag/TiO_2 (6%)	12.179
Ag/TiO_2 (8%)	17.095

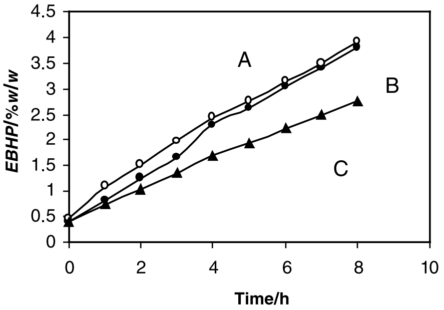

Fig. 5. Kinetic plot of *EBHP* (%*w*/*w*) *vs.* time (h) for 10 g of *EB* and three amounts of Rutile catalyst; (A) 0.01 g; (B) 0.005 g; (C) 0.02 g

increasing the amount of Cu coated on TiO_2 up to 4–5% Cu. By increasing the amount of Ag up to 6% the rate of formation of *EBHP* is increased.

Experimental

Ethylbenzene was oxidized with oxygen at 120, 95, and 85°C in a stirred reactor at a pressure of 2 bar in the presence of TiO_2 powder and metal coated on TiO_2 as photosensitizer irradiating with a 400 W high-pressure mercury lamp.

Materials

Ethylbenzene obtained from Merck contains about 0.4%*w*/*w* of *EBHP*. Sodium iodide, glacial acetic acid, sodium thiosulphate, ethanol, and isopropanol were of analytical grade from Merck. TiO_2 anatase and rutile, with surface areas of 50 and 47 $m^2\,g^{-1}$, respectively, were purchased from Aldrich and they had a mean particle size of 30 nm. The Ag/TiO_2 2, 4, 5, 6, and 8% catalysts were prepared according to the following experimental procedure: 0.5 g of TiO_2 in 9, 8, 7.5, 7, and 6 cm^3 of ethanol were added to 1, 2, 2.5, 3, and 4 cm^3 of a 0.0927 *M* $AgNO_3$ solution, N_2 was bubbled through the mixtures for 15 min, it was irradiated with a mercury lamp for 45–60 h, then filtered, and finally heated to 90°C for 15 h. The Cu/TiO_2 2, 4, 5, 6, and 8% catalysts were prepared according to the following experimental procedure: 0.5 g of TiO_2 in 9, 8, 7.5, 7, and 6 cm^3 of ethanol, were added to 1, 2, 2.5, 3, and 4 cm^3 of a 0.1574 *M* $CuSO_4$ solution, N_2 was bubbled through the mixtures for 15 min, it was irradiated with a mercury lamp for 45–60 h, then filtered, and finally heated to 90°C for 15 h.

Photoreaction Equipment

The reactor was a round-bottomed glass tank connected to a SH-12 type stirrer, a water thermostat (Haake model F-122), an oxygen gas inlet system, and a 400 W high-pressure mercury lamp. The set up of the photooxidation experiments is shown in Fig. 6.

General Procedure for Photooxidation of EB

EB (10 g) was charged into the reactor with 0.010 g of catalyst. When the temperature stabilized at the value previously set for the experiment, the oxygen flow (0.4 cm^3/s) was set and kept constant during the experiment, and the mercury lamp was switched on. Samples (about 0.7 cm^3) were taken from the reactor at regular intervals (typically 1 h) during the experiment that lasted for about 8 h.

Analysis

For determination of *EBHP* in *EB* we chose a volumetric determination method. The weight percent (*%w/w*) of *EBHP* in the samples taken from the reactor was determined by iodometric analysis, in the following way: 0.5 cm^3 of glacial acetic acid was added to 5 cm^3 of isopropanol in a 100 cm^3 *Erlenmeyer* flask. Later, 2 cm^3 of sodium iodide–isopropanol reagent (prepared by refluxing 8.8 g of sodium iodide in 40 cm^3 of isopropanol, cooling, and filtering) and about 0.5 g of the sample were added. The mixture was refluxed gently for 5 min, and later 20 cm^3 of distilled cold water were added through the reflux condenser. The samples, and the blank, were later titrated using 0.05 *N* sodium thiosulphate (previously standardized against potassium iodide) until the yellow reddish colour of the

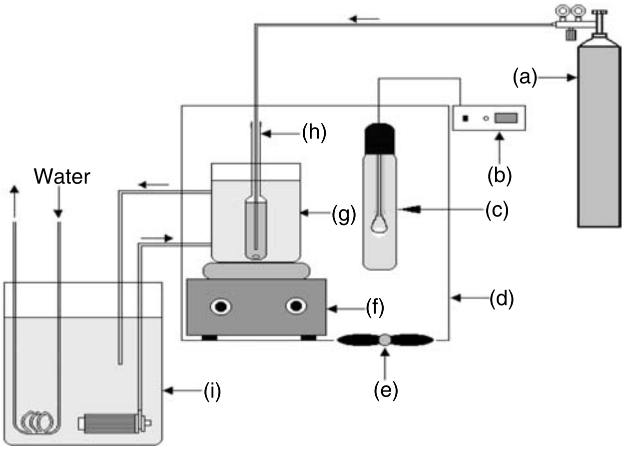

Fig. 6. Photooxidation set up for ethylbenzene; (a) oxygen cylinder; (b) power supply; (c) 400 W high-pressure Hg lamp; (d) photoreactor with aluminum foil as reflector for complete irradiation of catalyst; (e) fan; (f) magnetic stirrer; (g) 2 dm^3 pyrex beaker; (h) photooxidation cell; (i) water thermostat Hake model F.122

iodine disappears [17]. The *EBHP* (%*w*/*w* was calculated from Eq. (1), where *S* is the volume of sodium thiosulphate for the titration of the sample, *B* the volume of sodium thiosulphate for the titration of the blank, *N* the normality of sodium thiosulphate, *F* the factor of the sodium thiosulphate solution, *MW* the molecular weight of *EBHP*, and *G* the sample weight.

$$EBHP\ \%w/w = \frac{(S - B) \times N \times F \times MW \times 100}{G \times 2000} \tag{1}$$

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