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Effect of electron acceptors H_2O_2 and O_2 on the generated reactive oxygen species $^1\text{O}_2$ and $\text{OH}^\bullet$ in TiO_2 -catalyzed photocatalytic oxidation of glycerol

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ABSTRACT

The effect of the electron acceptors H_2O_2 and O_2 on the type of generated reactive oxygen species (ROS), and glycerol conversion and product distribution in the TiO_2 -catalyzed photocatalytic oxidation of glycerol was studied at ambient conditions. In the absence of an electron acceptor, only $\text{HO}^\bullet$ radicals were generated by irradiated UV light and TiO_2 . However, in the presence of the two electron acceptors, both $\text{HO}^\bullet$ radical and $^1\text{O}_2$ were produced by irradiated UV light and TiO_2 in different concentrations that depended on the concentration of the electron acceptor. The use of H_2O_2 as an electron acceptor enhanced glycerol conversion more than O_2 . The type of generated value-added compounds depended on the concentration of the generated ROS.

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1. Introduction

Glycerol is a chemical that can be applied in various industries such as pharmaceutical, cosmetic, and food industries [1]. It is also a building block chemical that can be converted to high-valued chemical substances such as lactic acid [2–4], acrylic acid [5–7], dihydroxyacetone [8–11], acrolein [12–14], and propanedial [15] using processes such as hydrothermal [3,4], oxidation [5–7, 9–11], dehydration [12–14], and electrochemical treatment [8,15,16]. Photocatalytic oxidation is a process that can convert glycerol to various value-added compounds. Although various semiconductor metal oxides can be used in a photocatalytic reaction, including TiO_2 , ZnO , Al_2O_3 , SiO_2 , ZrO_2 , CeO_2 , SnO_2 , Fe_2O_3 , SrTiO_3 and BaTiO_3 , TiO_2 is the most widely used because of its high photocatalytic activity,

stability, and suitable band gap energy [17]. Recently, it was reported that the use of TiO_2 in either an anatase or rutile/anatase-rutile phase can enhance the partial photocatalytic oxidation of glycerol to dihydroxyacetone (DHA) and glycer-aldehyde (GCD) to give selectivities of 4.5%–8% and 6.5%–13%, respectively [18]. It was also reported that a cylindrical photoreactor was more efficient than an annular photoreactor. The transformation of glycerol in the presence of TiO_2 Degussa P25 was a function of the substrate concentration, and the generated products were derived from a direct electron transfer [19]. TiO_2 in the rutile phase with a high percentage of [110] facets enhanced glycerol conversion and achieved over 90% selectivity to hydroxyacetadehyde (HAA), while anatase with [001] or [101] facets gave only 16% and 49% selectivity for HAA, respectively [20].

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Nevertheless, the use of bare TiO_2 as a photocatalyst still gave a slow rate of glycerol conversion, probably due to the recombination of $\text{h}^+\text{-e}^-$ that occurred after the charge separation when TiO_2 absorbed light with photon energy equal to or higher than its band gap energy. This caused a decrease in the photoinduced h^+ [21]. Two strategies that can reduce this recombination problem are the use of a metal-doped TiO_2 photocatalyst and the use of an electron acceptor. By using a metal-doped TiO_2 , it was reported that peroxide is the main oxidation product over irradiated aqueous Pt/TiO_2 under conditions of glycerol photoreforming from two routes involving (1) the oxidation of surface hydroxyl groups by photogenerated holes and the subsequent dimerization of the so-formed hydroxyl radicals and (2) the consecutive reduction of surface-trapped oxygen by conduction band electrons [22]. A high production rate of the hydroxyl radical can enhance a high conversion of glycerol and product generation. A nanotube-structured TiO_2 (TiNT) can enhance a conversion of glycerol to H_2 to twice that of nanoparticle TiO_2 (P25). The doping of TiNT with Pt and N (Pt-N-TiNT) can improve the activity for glycerol conversion up to 13 times compared with P25 [23]. The rate of the photoreforming of glycerol to H_2 and CO_2 was increased by a factor of 25 and 60, respectively, over Pt/TiO_2 compared to the TiO_2 photocatalyst, which was due to the increased separation of $\text{h}^+\text{-e}^-$ pairs and the promotion of the rate limiting cathodic half reactions in the presence of metallic Pt [24].

To enhance glycerol conversion, the second strategy was carried out. It was reported that different types of ROS were produced in the presence of different electron acceptors as well as the TiO_2 phase. In the presence of H_2O_2 , the rate of $\text{OH}^\bullet$ formation increased for rutile and anatase mixed with rutile of 10%–20%, while pure anatase exhibited an opposite trend [25]. A higher production rate of O_2^- was observed with the TiO_2 in the anatase phase than that in the rutile phase. However, in the presence of O_2 , a larger quantity of O_2^- was generated in the presence of TiO_2 in the rutile phase compared with the anatase phase. The use of O_2 as an electron acceptor could facilitate the photoreforming of glycerol toward CO_2 and H_2 more than an un-metallized TiO_2 , while the activity was extremely high with the Pt/TiO_2 photocatalyst [24]. However, the final production of $\text{OH}^\bullet$ and singlet oxygen ($^1\text{O}_2$), which are the main ROS that contribute to photodegradation, was more than one order of magnitude higher than O_2^- . [26]. The importance of the $\text{OH}^\bullet$ radical is understandable because of its high oxidizing power. However, with other ROS species such as $^1\text{O}_2$ and O_2^- , very little work has been carried out to understand their formation in a photocatalytic oxidation system. In addition, O_2^- can be quickly converted to $^1\text{O}_2$ [26], resulting in its lower concentration in the photocatalytic system. $^1\text{O}_2$ is a strong oxidation reagent for some organic compounds [27,28] due to its high quantum yield [25]. This suggests that it is an important species for the photocatalytic TiO_2 aqueous suspension [25–29].

In the present study, both H_2O_2 and O_2 were used as electron acceptors in the photocatalytic oxidation of glycerol with nanoparticle TiO_2 . The effects of these electron acceptors on the type of generated ROS (especially $\text{OH}^\bullet$ and $^1\text{O}_2$), glycerol conversion, and product distribution were explored on the labora-

tory scale at ambient conditions. On addition, the reaction pathway for glycerol conversion via TiO_2 -induced photocatalytic oxidation in the presence of H_2O_2 and O_2 as an electron acceptor was also proposed.

2. Experimental

2.1. Chemicals and catalyst

All chemicals used were analytical grade, including glycerol (GLY, 99.5%, QReC), H_2O_2 (30 wt%, QReC), O_2 (99.5% Praxair), DHA (98%, Merck), glyceric acid (GCA, 20 wt%, TCI), GCD (98%, Sigma Aldrich), glycoric acid (GCOA, 70 wt%, Ajax Finechem), formic acid (FMA, 98%, Merck), hydroxypyruvic acid (HPA, $\geq 95\%$, Sigma Aldrich), and formaldehyde (FMD, 37%, Merck). The photocatalyst used was commercial anatase TiO_2 powder (Sigma Aldrich). The probe compounds used to monitor the generation of the oxidizing species were *para*-chlorobenzoic acid (*p*CBA, Sigma Aldrich) and furfuryl alcohol (FFA, Sigma Aldrich).

2.2. Characterization

The BET surface area of the utilized commercial TiO_2 was measured by N_2 adsorption by the Brunauer-Emmett-Teller (BET) technique with a surface area analyzer (Quantachrome, Autosorb-1). Its band gap energy was determined by a UV-Visible spectrophotometer (Shimadzu UV-3600) in the wavelength range of 300–800 nm at room temperature. The bonding and valence state of the metals in the photocatalyst were determined using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II with monochromated Al K_α radiation).

2.3. Glycerol oxidation

The conversion of commercial glycerol gave value-added compounds that included DHA, GCA, GCD, GCOA, FMA, HPA, and FMD, and was carried out in a hollow cylindrical glass reactor having a diameter of 10 cm. The reactor was placed in the middle of a UV-protected box with the dimensions of 0.68 m $\times$ 0.68 m $\times$ 0.78 m. A 120 W UV high pressure mercury lamp (RUV 533 BC, Holland) was placed on the roof of the UV-protected box as previously described [30].

In each experiment, 100 mL of glycerol (0.3 mol/L) was irradiated with UV light having the intensity of 4.7 mW/cm² and with a TiO_2 dosage of 3 g/L for 20 h. The solution was agitated continuously by a magnetic stirrer at 300 r/min to achieve complete mixing. Two types of electron acceptor including H_2O_2 and O_2 were used for their effect on glycerol conversion and product distribution. The feeding procedure of the two chemicals was slightly different due to their different chemical phases. The total required volume of H_2O_2 (0.765 mL for 0.075 mol/L and 3.06 mL for 0.3 mol/L) was added into the glycerol solution prior to starting the reaction, while O_2 was fed continuously at a constant flow rate of 200 mL/min. As the experiment progressed, 2 mL samples were collected and quenched in an ice-water trap at 0 °C to terminate the reaction and then

centrifuged on a KUBOTA KC-25 Digital Laboratory Centrifuge to separate the solid catalyst from the aqueous product.

The concentrations of glycerol and generated products were analyzed by a high performance liquid chromatography (HPLC) with a RID-10A refractive index detector (Agilent 1100). The stationary phase was Aminex HPX-87H ion exclusion (300 mm $\times$ 7.8 mm), and the mobile phase was a water-acetonitrile solution (65:35 V/V) with H_2SO_4 (0.5 mmol/L) at a constant flow rate of 0.5 mL/min. Standard solutions of glycerol and expected major product compounds were used to identify the retention time and determine the relationship between the peak area and concentration.

The conversion of glycerol (X) and the yield of the monitored products (Y) of the photocatalytic oxidation were calculated based on carbon using Eqs. (1) and (2), respectively. The data reported were the average values obtained from at least three experiments and the error in this work was 3%.

$$X = \frac{\text{Moles of glycerol converted}}{\text{Total Moles of glycerol in reactant}} \times 100\% \quad (1)$$

$$Y = \frac{\text{Moles of glycerol converted to product } j}{\text{Total Moles of glycerol in reactant}} \times 100\% \quad (2)$$

2.4. Measurement of ROS

Both ROS, including the $\text{OH}^\bullet$ radical and $^1\text{O}_2$, were determined by using specific scavengers. The production of the $\text{OH}^\bullet$ radical was monitored by the loss of $p\text{CBA}$ [31,32]. The production of $^1\text{O}_2$ was monitored by the loss of FFA [32]. The concentration variation of $p\text{CBA}$ and FFA was analyzed by HPLC equipped with a Pinnacle II C18 column (240 mm $\times$ 4.6 mm). The mobile phase was methanol-water-acetonitrile (55:35:10 V/V) with H_2SO_4 (10 mmol/L) for $p\text{CBA}$ detection. A 50/50 (V/V) solvent mixture of water-ethanol was used as the mobile phase for FFA determination. The 10 μL sample injected passed through the column with a constant flow rate of 0.5 mL/min.

3. Results and discussion

3.1. Catalyst characterization

The photocatalyst utilized was commercial TiO_2 having a BET surface area of 22.84 m^2/g and particle size of less than 25 nm. Figure 1 exhibits the optical absorption spectra of TiO_2 recorded using a UV-visible spectrophotometer in the wavelength range of 300–800 nm at room temperature. A decrease of absorbance to a zero value was observed in the visible light region at wavelengths above 450 nm, showing its UV light absorption ability. By using the linear portion of the fundamental absorption edge of its spectra, the plot of $(\alpha h\nu)^{1/n}$ against $(h\nu)$ (inset of Fig. 1), where α is the optical absorption coefficient determined from the obtained absorbance and $h\nu$ is the energy of the incident photons, provided the value of the band gap energy (E_g). The band gap energy of TiO_2 was 3.2 eV, which agreed with the theoretical band gap energy of anatase TiO_2 .

With regard to the bonding and valence state of Ti, as shown in Fig. 2, the XPS spectra of the TiO_2 showed two symmetric

Fig. 1. UV-visible spectra and (inset) the dependence of $(\alpha h\nu)^{1/2}$ on the photon energy of TiO_2 powder.

peak shape of Ti 2p assigned to the component of $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$ at the binding energies of 465.2 and 459.4 eV, respectively, which confirmed the state of Ti as Ti^{4+} in the TiO_2 structure. In the O 1s XPS spectra (insert of Fig. 2), the main O 1s peak appeared at the binding energies between 530.2–530.6 eV, 531.8–532.0 eV and 533.0 eV, assigned to the O 1s peaks characteristic of O^{2-} , OH^- and adsorbed H_2O , respectively.

3.2. Glycerol conversion and product distribution

To explore the effect of electron acceptor on the TiO_2 -induced photocatalytic oxidation of glycerol, two types of electron acceptors, H_2O_2 and O_2 , were utilized. A blank experiment was first carried out with the presence of either H_2O_2 or O_2 , but the absence of both UV light and TiO_2 . It was found that the presence of only H_2O_2 or O_2 cannot facilitate the conversion of glycerol. However, the presence of irradiated UV light and TiO_2 in the absence of H_2O_2 or O_2 promoted the conversion of glycerol to four value-added compounds, DHA, GCA, GCD and GCOA (Fig. 3(a)). The addition of H_2O_2 into the irradiated UV light and TiO_2 system further enhanced the conversion of glycerol and gave one additional product, FMA (Fig. 3(b)). Using O_2 as electron acceptor instead of H_2O_2 decreased the glycerol conversion to almost half (Fig. 3(c)). The glycerol conversion was about 50% at 20 h. The same three value-added compounds, DHA, GCD and GCOA, were still observed, while two more

Fig. 2. XPS spectra of the commercial TiO_2 powder.

Fig. 3. Photocatalytic conversion of glycerol (0.3 mol/L) and yield of products versus time over (a) UV light/TiO₂, (b) UV light/TiO₂/H₂O₂ (0.3 mol/L) and (c) UV light/TiO₂/O₂.

compounds were generated in this system: HPA and FMD.

3.3. Oxygen species

As previously reported, the oxidation of glycerol proceeded via the photogenerated oxidizing species, including photogenerated holes (h⁺) [33], HO[•] radical [34], and oxide radicals (¹O₂/O₂^{•−}) [35] formed in the photo-cleavage of water and H₂O₂ [22]. To monitor the type of ROS generated in the system in the presence of both H₂O₂ and O₂, parallel reactions were carried out to monitor the production of the two strong ROS, including the HO[•] radicals and ¹O₂. The production of the former species was traced by the concentration loss of pCBA [31,32], while the generation of the latter species was monitored by the concentration loss of FFA [32]. More decrease of the pCBA and FFA concentrations indicated a higher generation rate of HO[•] radical and ¹O₂, respectively.

As demonstrated in Fig. 4(a), under irradiated UV light and TiO₂ and the absence of an electron acceptor, the concentration

Fig. 4. Variation of (a) pCBA and (b) FFA as a function of time in the irradiated UV light and TiO₂ system in the presence of H₂O₂ and O₂ as electron acceptors.

of pCBA decreased slightly as the reaction time increased, while that of FFA remained constant (Fig. 4(b)). This suggested the formation of HO[•] radicals in the irradiated UV light and TiO₂ system, but no ¹O₂. When either H₂O₂ or O₂ was used as an electron acceptor, the concentration of pCBA and FFA decreased significantly, suggesting the formation of both HO[•] radical and ¹O₂ in the system.

Based on the results and literature reports, the generation of HO[•] radicals and ¹O₂ in this study can be proposed as follows. When TiO₂ absorbed light having energy equal to or greater than its band gap energy (E_{bg}), an electron (e[−]) is excited from the valence band into the conduction band, leaving a positive hole (h⁺) in the valence band according to Eq. (3) [22].

In the absence of an electron acceptor, the photogenerated hole oxidized surface bonded water molecules to produce highly reactive OH[•] radicals, while the generated e[−] can further react with proton (H⁺) to form gaseous H₂ according to Eqs. (4) and (5) [22,36,37].

As exhibited in Fig. 4(a), a small quantity of OH[•] radicals was produced in this case, probably due to the recombination of h⁺-e[−] pairs, which usually occurred in the absence of an electron acceptor. This was confirmed by a low glycerol conversion and product yield as demonstrated in Fig. 3(a).

In the presence of an electron acceptor, e.g. H₂O₂, both OH[•] radicals and ¹O₂ were generated. Various elementary reactions can then proceed as follows. The H₂O₂ can break down to form OH[•] radicals (Eq. (6)) when it absorbs UV light [38,39]. It can also react via the photogenerated electrons or photogenerated holes according to Eqs. (7) and (8) to form OH[•] radicals [40].

Furthermore, it can oxidize via the formed HO^- and the photogenerated holes as well as the $\text{OH}^\bullet$ radicals to form $\text{O}_2^{\bullet-}$ radicals, which readily react with H_2O_2 to form $\text{HO}^\bullet$ radicals according to Eqs. (9)–(11), respectively [25,41]. Also, the generated $\text{O}_2^{\bullet-}$ radicals can further react with h^+ and H^+ as well as H_2O_2 to form $^1\text{O}_2$ and $\text{HO}^\bullet$ radicals as described above (Eqs. (12)–(14)). Both generated ROS have the ability to oxidize glycerol to form various products as shown in Fig. 3(b).

Regarding the use of O_2 as an electron acceptor, various possible reactions can be proposed. Initially, the supplied O_2 can react with the photogenerated e^- to form $\text{O}_2^{\bullet-}$ (Eq. (15)) and H_2O_2 (Eq. (16)) [26, 36]. The generated $\text{O}_2^{\bullet-}$ radicals can further react with h^+ and H^+ as well as H_2O_2 to form $^1\text{O}_2$ and $\text{HO}^\bullet$ radicals (Eqs. (12)–(14)). Besides, the generated H_2O_2 can dissociate after absorbing UV light or react with either photogenerated h^+ or e^- to form $\text{OH}^\bullet$ radicals according to Eqs. (9)–(11).

The mechanism of glycerol conversion to value-added compounds under irradiated UV light and TiO_2 in the absence and presence of H_2O_2 has already been proposed in published work [30,43]. In brief, in the absence of H_2O_2 , the photogenerated h^+ and the $\text{OH}^\bullet$ radicals can attach to the 1° - or 2° -C atom of glycerol to form GCD or DHA, respectively [44]. Then, they can further oxidize the generated GCD to form GCA as well as cleave the C–C bond of GCA to form GCOA [45]. Our previous work demonstrated that DHA can be oxidized to GCA and GCOA [36]. High glycerol conversion and yield of value-added compounds were observed in the presence of H_2O_2 , which was probably due to the large amounts of both $\text{OH}^\bullet$ radical and $^1\text{O}_2$ generated as well as their high oxidizing power.

In the presence of O_2 , different value-added compounds were produced, particularly HPA and FMD. From the results, it seems that the type of generated ROS, including $\text{OH}^\bullet$ radical and $^1\text{O}_2$, did not affect the types of value-added compounds produced from glycerol conversion because both species were produced when either H_2O_2 or O_2 was used as the electron acceptor. This difference was probably due to the difference in the ROS concentration produced in the system.

To prove this hypothesis, an additional experiment was carried out with a low H_2O_2 concentration (0.075 mol/L). As demonstrated in Fig. 5, both $\text{OH}^\bullet$ radical and $^1\text{O}_2$ were still generated in the presence of both low and high H_2O_2 concentrations but in different quantities as shown by the different decreases of $p\text{CBA}$ and FFA concentrations. Large quantities of ROS were produced in the presence of a high H_2O_2 concentration.

In the glycerol conversion and yield of value-added com-

Fig. 5. Variation of $p\text{CBA}$ and FFA as a function of time in the presence of H_2O_2 at different concentrations.

Fig. 6. Photocatalytic and catalytic conversion of glycerol (0.3 mol/L) and yield of products versus time in the presence of (a) UV light/ $\text{TiO}_2/\text{H}_2\text{O}_2$ (0.075 mol/L) and (b) UV light/ $\text{TiO}_2/\text{H}_2\text{O}_2$ (0.3 mol/L).

pounds produced at low H_2O_2 concentrations (Fig. 6(a)), the types of value-added compounds was almost the same as those generated in the presence of a high H_2O_2 concentration (Fig. 6(b)) but in low quantities except for FMA. Surprisingly, HPA was observed in this system, which indicated that the quantity of the ROS present affected the route of glycerol conversion as well as the type of generated products. In the presence of a low $\text{OH}^\bullet$ radical quantity, $^1\text{O}_2$ probably was as the main ROS that attack the 1° -C atom of DHA to form HPA [46].

In any event, a glycerol conversion route can be proposed with the pathways possible for this system as demonstrated in Scheme 1. The threshold quantity of ROS that controls which route of glycerol conversion to form the different value-added compounds in the TiO_2 -catalyzed photocatalytic oxidation cannot be determined at this stage. More extensive and expanded studies will be carried out to determine the threshold quantity of the ROS. The results will be reported in the future.

Scheme 1. Proposed reaction pathways for glycerol conversion over TiO_2 catalyst in the presence of H_2O_2 and O_2 as electron acceptors.

4. Conclusions

Two types of chemical agents, namely, H_2O_2 and O_2 , were used as the electron acceptor for the photocatalytic oxidation of glycerol with TiO_2 at ambient conditions. $\text{HO}^\bullet$ radicals were generated in the system having irradiated UV light and TiO_2 both in the absence and presence of an electron acceptor, while $^1\text{O}_2$ can only be produced in the system with an electron acceptor. The use of both chemicals as the electron acceptor enhanced the generation of both $\text{OH}^\bullet$ radicals and $^1\text{O}_2$. The types of product compounds were not affected by the type of ROS generated in the system but was affected by the ROS concentration. At least four compounds, namely, DHA, GCA, GCD, and GCOA, were produced in the photocatalytic oxidation of glycerol by TiO_2 in the presence of ROS in both low and high concentrations, while HPA and FMD were produced only at low ROS concentration.

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References

- [1] H. Ueoka, T. Katayama, US Patent 6 288 287, **2001**.
- [2] J. Ftouni, N. Villandier, F. Auneau, M. Besson, L. Djakovitch, C. Pinel, *Catal. Today*, **2015**, 257, 267–273.
- [3] G. Y. Yang, Y. H. Ke, H. F. Ren, C. L. Liu, R. Z. Yang, W. S. Dong, *Chem. Eng. J.*, **2016**, 283, 759–767.
- [4] H. X. Yin, C. H. Zhang, H. B. Yin, D. Z. Gao, L. Q. Shen, A. L. Wang, *Chem. Eng. J.*, **2016**, 288, 332–343.
- [5] S. Thanasilp, J. W. Schwank, V. Meeyoo, S. Pengpanich, M. Hunsom, *Chem. Eng. J.*, **2015**, 275, 113–124.
- [6] S. Thanasilp, J. W. Schwank, V. Meeyoo, S. Pengpanich, M. Hunsom, *J. Mol. Catal. A*, **2013**, 380, 49–56.
- [7] K. Omata, K. Matsumoto, T. Murayama, W. Ueda, *Catal. Today*, **2016**, 259, 205–212.
- [8] R. Ciriminna, G. Palmisano, C. D. Pina, M. Rossi, M. Pagliaro, *Tetrahedron Lett.*, **2006**, 47, 6993–6995.
- [9] J. Luo, H. G. Li, N. Zhao, F. Wang, F. K. Xiao, *J. Fuel Chem. Technol.*, **2015**, 43, 677–683.
- [10] P. K. Dikshit, V. S. Moholkar, *Bioresour. Technol.*, **2016**, 216, 1058–1065.
- [11] X. M. Ning, Y. H. Li, H. Yu, F. Peng, H. J. Wang, Y. H. Yang, *J. Catal.*, **2016**, 335, 95–104.
- [12] R. Estevez, S. Lopez-Pedrajas, F. Blanco-Bonilla, D. Luna, F. M. Bautista, *Chem. Eng. J.*, **2015**, 282, 179–186.
- [13] C. García-Sancho, J. A. Cecilia, A. Moreno-Ruiz, J. M. Mérida-Robles,

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Effect of electron acceptors H_2O_2 and O_2 on the generated reactive oxygen species $^1\text{O}_2$ and $\text{OH}^\bullet$ in TiO_2 -catalyzed photocatalytic oxidation of glycerol

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The effect of the electron acceptor (O_2 or H_2O_2) on the photocatalytic oxidation of glycerol by TiO_2 was studied. H_2O_2 enhanced the conversion of glycerol more than O_2 . The type of generated compounds depended on the concentration of the formed ROS.

- J. Santamaría-González, R. Moreno-Tost, P. Maireles-Torres, *Appl. Catal. B*, **2015**, 179, 139–149.
- [14] A. Talebian-Kiakalaieh, N. A. S. Amin, Z. Y. Zakaria, *J. Ind. Eng. Chem.*, **2016**, 34, 300–312.
- [15] M. Hunsom, P. Saila, *Renew. Energy*, **2015**, 74, 227–236.
- [16] C. R. Zanata, P. S. Fernández, H. E. Troiani, A. L. Soldati, R. Landers, G. A. Camara, A. E. Carvalho, C. A. Martins, *Appl. Catal. B*, **2016**, 181, 445–455.
- [17] A. L. Linsebigler, G. Q. Lu, J. T. Yates, *J. Chem. Res.*, **1995**, 95, 735–758.
- [18] V. Augugliaro, H. A. Hamed El Nazer, V. Loddo, A. Mele, G. Palmisano, L. Palmisano, S. Yurdakal, *Catal. Today*, **2010**, 151, 21–28.
- [19] C. Minero, A. Bedini, V. Maurino, *Appl. Catal. B*, **2012**, 128, 135–143.
- [20] R. F. Chong, J. Li, X. Zhou, Y. Ma, J. X. Yang, L. Huang, H. X. Han, F. X. Zhang, C. Li, *Chem. Commun.*, **2014**, 50, 165–167.
- [21] C. H. Wu, *Chemosphere*, **2014**, 57, 601–608.
- [22] V. M. Daskalaki, P. Panagiotopoulou, D. I. Kondarides, *Chem. Eng. J.*, **2011**, 170, 433–439.
- [23] Slamet, D. Tristantini, Valentina, M. Ibadurrohman, *Int. J. Energy Res.*, **2013**, 37, 1372–1381.
- [24] P. Panagiotopoulou, E. E. Karamerou, D. I. Kondarides, *Catal. Today*, **2013**, 209, 91–98.
- [25] T. Hirakawa, K. Yawata, Y. Nosaka, *Appl. Catal. A*, **2007**, 325, 105–111.
- [26] X. Y. Guo, Q. L. Li, M. Zhang, M. C. Long, L. C. Kong, Q. X. Zhou, H. Q. Shao, W. L. Hu, T. T. Wei, *Chemosphere*, **2015**, 120, 521–526.
- [27] A. Maldotti, A. Molinari, R. Amadelli, *Chem. Rev.*, **2002**, 102, 3811–3836.
- [28] D. R. Kearns, *Chem. Rev.*, **1971**, 71, 395–427.
- [29] T. Daimon, T. Hirakawa, M. Kitazawa, J. Suetake, Y. Nosaka, *Appl. Catal. A*, **2008**, 340, 169–175.
- [30] T. Jedsukontorn, V. Meeyoo, N. Saito, M. Hunsom, *Chem. Eng. J.*, **2015**, 281, 252–264.
- [31] W. Y. Han, P. Y. Zhang, W. P. Zhu, J. J. Yin, L. S. Li, *Water Res.*, **2004**, 38, 4197–4203.
- [32] W. R. Haag, J. Hoigne, *Environ. Sci. Technol.*, **1986**, 20, 341–348.
- [33] A. Yamakata, T. A. Ishibashi, H. Onishi, *J. Phys. Chem. B*, **2003**, 107, 9820–9823.
- [34] R. M. Gao, J. Stark, D. W. Bahnemann, J. Rabani, *J. Photochem. Photobiol. A*, **2002**, 148, 387–391.
- [35] M. Styliadi, D. I. Kondarides, X. E. Verykios, *Appl. Catal. B*, **2004**, 47, 189–201.
- [36] D. H. Tseng, L. C. Juang, H. H. Huang, *Int. J. Photoenergy*, **2012**, 2012, 1–9.
- [37] G. N. Nomikos, P. Panagiotopoulou, D. I. Kondarides, X. E. Verykios, *Appl. Catal. B*, **2014**, 146, 249–257.
- [38] G. F. Jpelaar, D. J. H. Harmsen, M. Heringa, *Techneau*, D2.4.1.1, May **2007**.
- [39] E. F. Beerendonk, New Concepts of UV/H₂O₂ Oxidation, Project number B111.604BTO 2011.046, **2011**.
- [40] S. Parra, V. Sarria, S. Malato, P. Peringer, C. Pulgarin, *Appl. Catal. B*, **2000**, 27, 153–168.
- [41] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.*, **1995**, 95, 69–96.
- [42] A. Fujishima, X. T. Zhang, D. A. Tryk, *Surf. Sci. Rep.*, **2008**, 63, 515–582.
- [43] S. Demirel-Gülen, M. Lucas, P. Claus, *Catal. Today*, **2005**, 102–103, 166–172.
- [44] S. Carretin, P. McMorn, P. Johnston, K. Griffin, C. J. Kielly, G. J. Hutchings, *Phys. Chem. Chem. Phys.*, **2003**, 5, 1329–1336.
- [45] S. Gil, M. Marchena, L. Sánchez-Silva, A. Romero, P. Sánchez, J. L. Valverde, *Chem. Eng. J.*, **2011**, 178, 423–435.
- [46] J. Deleplanque, J. L. Dubois, J. F. Devaux, W. Ueda, *Catal. Today*, **2010**, 157, 351–358.

电子受体H₂O₂和O₂对TiO₂光催化甘油氧化反应中活性氧物种¹O₂和OH[•]的影响

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摘要: 在室温条件下研究了电子受体H₂O₂和O₂对TiO₂光催化甘油氧化反应中的活性氧物种、甘油转化率和产物分布的影响。当在紫外光辐射和TiO₂的体系中不存在电子受体时, 只产生HO[•]自由基。而当在此体系中有电子受体存在时, 则产生了HO[•]自由基和¹O₂, 但它们的浓度不同, 这取决于电子受体的浓度。以H₂O₂为电子受体时甘油转化率的提高大于以O₂为电子受体时。甘油转化生成有价值产物的类型则与体系中的活性氧物种浓度有关。

关键词: 甘油氧化; 二氧化钛; 光催化剂; 电子受体

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