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Photoinduced transformation of glycerol in titania suspensions. (An EPR spin trapping study of radical intermediates)

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ABSTRACT

Formation of radical intermediates upon photocatalytic (UVA) glycerol transformation in aerated aqueous TiO_2 (P25) suspensions was followed by EPR spin trapping technique. Character and concentration of the spin-adducts generated by the addition of the radical species to 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) spin trap are significantly affected by the UVA radiation dose and by the initial composition of the photocatalytic system. The DMPO spin-adducts of hydroxyalkyl radicals $^{\bullet}$R1 and $^{\bullet}$R2 detected in the aerated aqueous P25 suspensions containing glycerol are compatible with the H-abstraction processes attributed to the interaction of physisorbed glycerol molecules with the trapped holes or to the reaction of free hydroxyl radicals with glycerol in solution. Addition of fluoride at various concentrations has no effect on the character and concentration of DMPO spin-adducts observed upon *in situ* UVA photoexcitation of photocatalytic system P25/DMPO/glycerol under given experimental conditions ($pH > 7$).

1. Introduction

Glycerol (GLY) represents a substance with unique physical and chemical properties, which are exploited in a variety of commercial applications including over 2000 end-uses in cosmetics, personal care products, pharmaceutical and food industry, where it serves as a humectant, thickener, lubricant, sweetener or anti-freezer [1,2]. Traditionally, glycerol is involved in the synthesis of trinitroglycerine, alkyd resins and polyurethanes [1]. Recently the global glycerol market has dramatically changed due to an exponential increase in the production of biodiesel, yielding large volume of glycerol as a concomitant representing about 10 % of the total output [2]. Consequently, the global oversupply of glycerol coming from the biodiesel industry has evoked an intensive effort to develop alternative applications or transformations of glycerol into valuable chemicals or hydrogen using various techniques including photocatalysis [3–8].

Investigations of the photoinduced processes of glycerol on the semiconducting photocatalysts are mainly oriented on two areas: (*i*) photooxidation of glycerol to valuable chemical substances, *e.g.* glyceraldehyde (GAD) and 1,3-dihydroxyacetone (DHA), with high rate and selectivity; (*ii*) glycerol photoreforming to produce H_2 and CO_2 under anaerobic conditions using metal modified semiconductor nanostructuctures [5–9].

The photocatalytic oxidative transformation of glycerol in TiO_2 aqueous systems represents a complex function of reaction parameters including pH, substrate concentration, the type of the catalyst or its surface modification, as demonstrated by Minero et al. revealing different transformation rates for glycerol on pristine P25 and Merck photocatalysts [6]. Under given experimental conditions the photocatalytic oxidation of glycerol was rather selective toward DHA and GAD production with the highest conversion found for P25 at pH 7 [6]. The key glycerol oxidation products are determined by the initial glycerol concentration, and a detailed analysis of the intermediates produced upon glycerol photooxidation in P25 suspensions was performed to distinguish between the direct electron transfer and $^{\bullet}$OH-mediated mechanism [10]. The C_3-products GAD and DHA, produced mainly at low glycerol concentrations, were attributed to $^{\bullet}$OH-mediated mechanism, while C_1- and C_2-products (formaldehyde (FORM) and glycolaldehyde (GLC)) were assigned to the direct electron transfer, despite the attempts to measure the adsorption isotherm were not successful on pristine P25 [10]. Modification of P25 surface by fluoride ions, which exclude the glycerol adsorption, lead to the formation of GAD and DHA as the major oxidation products, while the production of FORM and GLC is coupled with direct electron transfer to glycerol chemisorbed on P25 surface [10]. The product analysis upon photocatalytic oxidation of glycerol in aqueous TiO_2 suspensions using commercial (Degussa P25 or Sigma-Aldrich) and home-prepared anatase, rutile or anatase-rutile allotropes evidenced the production of

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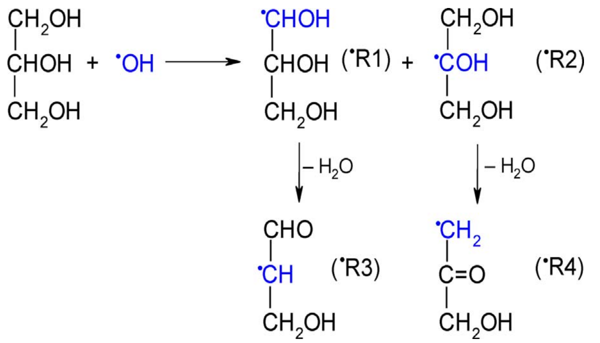
DHA, GAD, formic acid (FA) and CO_2 as the major products, showing that different TiO_2 nanostructures exhibit the diverse selectivity toward glycerol transformation. The best performance concerning the production rate and selectivity was obtained for the commercial samples P25 and Sigma-Aldrich [11].

TiO_2 photocatalysts modified with metal nanoparticles (Pt, Pd, Ru, Au, Cu, Ni) are applied to provide an efficient and low-cost method to produce renewable hydrogen by the photoinduced reforming of glycerol under anaerobic conditions [5,8,12], which can be coupled with the desired production of C_2- or C_1-products [8,13]. Also in these processes the product selectivity reveals a strong dependence on the character of TiO_2, *i.e.* crystal allotrope and crystal facets [14]. A detailed study on the catalytic routes and oxidation mechanisms in the photoreforming of glycerol on irradiated Rh/TiO_2 photocatalyst was published recently considering the anodic transformation of glycerol *via* direct or indirect hole transfer pathways [15]. C_3-products detected at low concentration represent GAD, DHA and hydroxyacetone (HA), and their transformation *via* parallel reactions yielded C_2- (glycolaldehyde, glycolic acid, acetic acid) and C_1-products (formic acid, formaldehyde) [15].

The analysis and quantification of glycerol and its photoproducts upon exposure has been the main aim of the studies dealing with the photocatalytic glycerol transformation so far, and only a little attention has been devoted to the detection of radicals generated [14].

A comprehensive effort was aimed to the characterization of the trapping sites for the photogenerated holes in titanium dioxide, with the discussion focused especially on the ability of superficially adsorbed hydroxyl groups to trap the photogenerated charge carriers and to produce the hydroxyl radicals [16–18]. The pioneering EPR studies of water oxidation on irradiated TiO_2 evidenced the formation of hydroxyl radicals [19,20], while further investigations on the TiO_2 colloids and aqueous suspensions confirmed that the photogenerated holes migrate from the lattice to the surface and are trapped directly on the oxygen atoms bound to the surface Ti(IV) atom. Most likely, Ti(IV)-O-Ti(IV)-O$^{\bullet}$ radicals representing deep hole traps are formed and the generation of surface hydroxyl radicals was not detected [21,22]. Despite the hydroxyl radicals are not the primary products of hole trapping [21,22], their generation during the photoexcitation of TiO_2 in aqueous systems cannot be excluded [17,18]. The hydroxyl radicals previously detected using EPR spin trapping technique [23–25] (although inverted spin trapping mechanism was also considered [23,26]) or fluorometric assay [18,23] are most probably generated in the alternative photocatalytic/photochemical processes of hydrogen peroxide produced *via* the electroreduction of dissolved oxygen by the photogenerated electrons in aqueous media [17,18]. The hydroxyl radicals react non-selectively with high, essentially diffusion-controlled, reaction rates with most organic compounds [27]; the bimolecular rate constant published for the reaction of hydroxyl radical with glycerol in aqueous solutions is in the range of $1.5–2.1 \times 10^9$ L mol^{-1} s^{-1} [27]. The interaction of hydroxyl radicals with glycerol leads to the abstraction of carbon-bond hydrogen atoms from two different positions in the glycerol molecule (Scheme 1). The radical reactions of glycerol in the homogeneous $^{\bullet}$OH-generating systems were investigated previously, suggesting the transformation of the primary hydroxyalkyl radicals $^{\bullet}$R1 and $^{\bullet}$R2 to the radicals $^{\bullet}$R3 and $^{\bullet}$R4, respectively, *via* acid-catalyzed elimination of water [28–30] as is shown in Scheme 1, or the disproportionation reaction of $^{\bullet}$R1 and $^{\bullet}$R2 yielding the original glycerol and either glyceraldehyde or dihydroxyacetone [31]. If molecular oxygen is present in the system, the hydroxyalkyl radicals such as $^{\bullet}$R1 and $^{\bullet}$R2 readily generate hydroxyperoxyl radicals, rearrangement of which leads again to the production of oxidized C_3-products (GAD and DHA) and superoxide radical anion [32]. Additionally, radicals $^{\bullet}$R3 and $^{\bullet}$R4 may be reduced in the disproportionation reactions with other radicals or substrates to yield 3-hydroxypropanal and hydroxyacetone, respectively [31]. Consequently, due to the complex parallel reactions of hydroxyalkyl and hydroxyperoxyl radicals in the aerated aqueous solutions, the formation of C_3-products GAD, DHA and HA from glycerol can be interpreted considering different reaction pathways [28–31]. The photocatalytic reactions of glycerol in the TiO_2 suspensions are even more complex since the prompt reactions of chemi- and physisorbed glycerol with the photogenerated holes [33,34] and the reactions of free glycerol with hydroxyl radicals in the solution proceed most probably simultaneously in the irradiated system.



Scheme 1. H-abstraction reaction of glycerol with hydroxyl radical generating the primary hydroxyalkyl radicals $^{\bullet}$R1 and $^{\bullet}$R2 and their transformations *via* acid-catalyzed elimination of water [31].

The EPR spin trapping technique using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was successfully applied previously to detect non-persistent radicals produced in the homogeneous $^{\bullet}$OH-generating systems (*e.g.* H_2O_2 photolysis, radiolysis, Fenton) containing glycerol, glyceraldehyde or dihydroxyacetone [28–31]. However EPR investigations of non-persistent radical species formed in the presence of glycerol in the irradiated TiO_2 suspensions are still missing. Thus our EPR spin trapping study is oriented on the detection of radical intermediates generated in the aerated P25 suspensions containing glycerol, and the parameters influencing the spin-adduct formation including the initial concentration of glycerol and DMPO, TiO_2 loading, UVA irradiance or fluoride addition were investigated in detail.

2. Materials and methods

2.1. Chemicals

Titanium dioxide Aeroxide® P25 (Evonik) [35] was used as photocatalyst. Glycerol (GLY, ACS grade), sodium fluoride (ACS grade) and hydrogen peroxide ($\geq$30%, for trace analysis) were purchased from Sigma-Aldrich and used without further purification. The photoinduced generation of reactive radicals was monitored by EPR spin trapping technique using the 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, Sigma-Aldrich) distilled prior to the application or 3,5-dibromo-4-nitrosobenzenesulfonate sodium salt (DBNBS, Sigma-Aldrich) as the spin trapping agents. 4-Hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (Tempol, Sigma-Aldrich) was used as the calibration standard. All solutions and suspensions were prepared in deionized water.

2.2. Methods

2.2.1. EPR spin trapping experiments

The EPR experiments with P25 powder dispersed in water or in the homogeneous H_2O_2 solutions were carried out by means of EMX Plus X-band EPR spectrometer (Bruker) with a High Sensitivity Probe-head (Bruker) in the small quartz flat cell (WG 808-Q, Wilmad-LabGlass, optical cell length 0.045 cm). The samples containing TiO_2 or H_2O_2, spin trap, glycerol and NaF at different initial concentrations were prepared by adequate mixing of stock solutions immediately before measurements. The suspensions/solutions were then carefully aerated by a gentle air stream. The samples were irradiated at 295 K directly in the EPR resonator using UVA source (λ_{max} = 365 nm; Bluepoint LED,