



Catalytic routes and oxidation mechanisms in photoreforming of polyols



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ABSTRACT

Photocatalytic reforming of biomass-derived oxygenates leads to H₂ generation and evolution of CO₂ via parallel formation of organic intermediates through anodic oxidations on a Rh/TiO₂ photocatalyst. The reaction pathways and kinetics in the photoreforming of C₃–C₆ polyols were explored. Polyols are converted via direct and indirect hole transfer pathways resulting in (i) oxidative rupture of C–C bonds, (ii) oxidation to α -oxygen functionalized aldoses and ketoses (carbonyl group formation) and (iii) light-driven dehydration. Direct hole transfer to chemisorbed oxygenates on terminal Ti(IV)-OH groups, generating alkoxy-radicals that undergo β -C–C-cleavage, is proposed for the oxidative C–C rupture. Carbonyl group formation and dehydration are attributed to indirect hole transfer at surface lattice oxygen sites [Ti···O···Ti] followed by the generation of carbon-centered radicals. Polyol chain length impacts the contribution of the oxidation mechanisms favoring the C–C bond cleavage (internal preferred over terminal) as the dominant pathway with higher polyol carbon number.

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1. Introduction

Photocatalytic H₂ generation from bio-derived oxygenates ('photoreforming') is a desired pathway for the production of a chemical energy carrier utilizing solar energy as it lowers the energy requirements compared to water cleavage [1–5]. Aqueous glycerol, an abundant by-product from triglyceride transesterification, and polyol-containing wastewaters, e.g. from industry or catalytic upgrading conceptually, could be suitable feedstocks for photoreforming [1–4,6]. Thereby valorization and/or purification of those resources are coupled to the production of H₂. Photoreforming benefits from a narrow energetic separation of the two redox half-reactions ($E^0(\text{H}^+/\text{H}_2) = 0 \text{ V}$; e.g. for glycerol photoreforming $E^0(\text{CO}_2/\text{C}_3\text{H}_8\text{O}_3) = -0.004 \text{ V}$ vs. NHE [7]), which provides a large overpotential at the anode facilitating cathodic H₂ evolution. Moreover, compared to overall water splitting, substitution of the oxygen evolution reaction for anodic oxygenate oxidation to CO₂ eliminates the need of separation and the back-reaction of H₂ and O₂ [8].

While the electron-hole recombination and charge carrier transport to the surface and their relation to physicochemical properties of the photocatalyst have been explored with great

depth [9–12], the role of the chemically coupled reactions have been hardly explored mechanistically and kinetically. In such reactions, the co-catalyst decorated semiconductor acts as coupled micro-electrochemical cell [13–15]. Anodic half-reactions are thought to occur on the semiconductor surface as a consequence of interfacial transfer of photogenerated holes through either direct transfer to the oxygenate or via an indirect mechanism, e.g. mediated by $\cdot\text{O}(\text{H})$ -radicals [6,16,17]. The co-catalyst serves as cathode, electron trap, and, thus, H₂ evolution site and does not participate in the anodic half-reactions [18,19]. Yet, H₂-evolution and thus oxygenate degradation rates (due to charge balance) are influenced by co-catalyst nature [7], loading and particle size [7,20] as well as its composition and morphology [21,22]. The co-catalyst could even aid the suppression of surface back-reactions at the cathode [8,23]. These factors provide essential means for optimization of the efficiency of electron transfer at the semiconductor/co-catalyst interface.

It is established that H₂-evolution rates over TiO₂-based photocatalysts depend on oxygenate nature and coverage [3,7,24–28]. However, there is ambiguity in the anodic pathways and mechanisms toward full oxidation to CO₂. Initial anodic transformations of polyols over metal/metal oxide loaded TiO₂ were proposed to result in the formation of the corresponding aldehydes, which undergo either decarbonylation followed by water-gas shift [17] or cleavage of formic acid [19]. Oxidation to carboxylic acids that decarboxylate [6,16] or initial polyol dehydration to compounds with non-functionalized carbon atoms [17] was also suggested

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prior to C–C-cleavage. On the other hand, photoreforming of linear aldehydes was reported to involve sequential cleavage of formic acid to form the C₁-deficient aldehyde in a single reaction pathway [19,29].

During aerobic photooxidation of oxygenates, multiple reaction pathways were accounted for by a two-site model for direct and indirect mechanisms [30–32]. Holes trapped at surface lattice oxygen sites [Ti···O···Ti] abstract a H-atom from a C–H bond whereas direct hole transfer yields alkoxy radicals chemisorbed on terminal OH-groups. We hypothesize that under photoreforming conditions (anaerobic environment and hydrogen evolving) similar mechanisms operate, which determine the routes toward complete oxidation. We have shown in a preceding contribution that the anodic transformations of ethylene glycol during photoreforming may be rationalized on this basis [18]. We further propose that identical anodic transformations are followed across families of compounds. However, the impact of molecular polyol structure and associated surface adsorption complexes on the contribution of the different reaction pathways to the complete oxidation is largely unknown.

Here, we explore the mechanisms and kinetics of photoreforming of C₃–C₆ polyols on benchmark TiO₂ P 25 with Rh as co-catalyst. On the basis of quantitative analysis of gas- and liquid-phase species we establish general relationships between structural reactant functional groups, anodic reaction pathways and oxidation mechanisms. We provide rationalization of the impact of anodic surface chemistry on the photoreforming kinetics in terms of oxygenate conversion and associated H₂-evolution rates.

2. Experimental

A comprehensive list of compounds used during the study, and detailed experimental procedures regarding the characterization of the photocatalyst are compiled in the [Supporting Information](#). Briefly, experiments are conducted over AEROXIDE® TiO₂ P 25 (referred to as TiO₂ hereafter), commonly employed as benchmark semiconductor, decorated with nanoparticulate Rh as a co-catalyst (1 wt.% loading, particle size 1.9 nm (±0.7 nm), dispersion 57%). Further physicochemical properties of the materials are described in the [Supporting Information](#).

2.1. Photocatalyst preparation

The 1 wt.% Rh-decorated P 25 photocatalyst, hereafter referred to as Rh/TiO₂, was prepared *via* incipient wetness impregnation. TiO₂ P 25 was dried under a static air atmosphere at 473 K for 2 h prior to impregnation. Subsequently, the semiconductor was treated with appropriate amounts of an aqueous solution of RhCl₃·xH₂O in ultrapure water. The resulting precursor was kept in synthetic air at 383 K for 1 h (100 mL min⁻¹, 5 K min⁻¹) and heated to 623 K (100 mL min⁻¹, 5 K min⁻¹) for 1 h. The material was allowed to cool to room temperature before treatment in H₂ at 623 K (100 mL min⁻¹, 5 K min⁻¹) for 1 h. A TiO₂ reference was prepared subjecting as-received TiO₂ P 25 to the same temperature and gas treatments described before.

2.2. Photocatalytic test

2.2.1. Photoreforming experiments

Kinetic experiments were performed in a Pyrex top-irradiation photo-reactor connected to a closed gas-circulation system [18]. The setup is equipped with facilities for *online* gas-analysis and liquid-phase sampling. Irradiation is provided by a 300 W Xe lamp with a cold mirror 1 (CM 1). A water filter with quartz windows closes the top of the photo-reactor. The photon flux within the

reactor at water level is $8.08 \cdot 10^{17} \text{ s}^{-1}$ ($\lambda < 390 \text{ nm}$). Typically, 75 mg of photocatalyst were ultrasonically dispersed in 100 mL of a 20 mM aqueous reactant solution. The system was deaerated by four consecutive evacuations and Ar filling cycles. All reactions were carried out at 288 K and an Ar pressure of 1 bar.

Evolved gases during photocatalytic reactions were analyzed *online* *via* gas chromatography (Shimadzu, GC 2010 Plus) on a Chromosorb 101 and a Molsieve 5 Å column with a TCD, FID and a methanizer catalyst unit. Ar was used as a carrier gas.

Aliquots of the liquid-phase were manually taken at regular times from the photocatalyst suspension *via* a sample valve. The solid was separated by filtering through 0.2 μm nylon filters. Liquid-phase species were quantitatively analyzed by ¹H NMR spectroscopy. Additionally, high-performance liquid chromatography (HPLC) analysis was performed for photoreforming experiments with C₄–C₆ oxygenates.

Reactant conversions X_A were calculated according to $X_A(\%) = (1 - \frac{N_A(t)}{N_{A,0}}) \cdot 100$, where N_A(t) is the time-dependent molar amount of reactant A and N_{A,0} is the initial molar amount of reactant A, i.e. present at the beginning of the reaction.

2.2.2. ¹H NMR analysis

For quantitative ¹H NMR measurements reactor aliquots were mixed in a 1:1 volume ratio with an external standard that contained 20 mM 1,3,5-trihydroxybenzene in D₂O adjusted to pH 3 with DCl. ¹H NMR spectra with water signal suppression were recorded at 305 K using an Avance III HD 500 System (Bruker Biospin, Rheinstetten, Germany) with an UltraShield 500 MHz magnet (11.75 T) and a BBI 500 S2 probe head (5 mm, inverse ¹H/X with Z-gradient). The resonance frequency of ¹H was 500.13 MHz. The spectra were acquired using the one-dimensional NOESY sequence from the Bruker library “noesygppr1d” with presaturation of the residual water signal during the relaxation delay and the mixing time using spoil gradients. Longitudinal relaxation times (T₁) were determined by the inversion recovery pulse method. Relaxation delay and acquisition time were set to 26 s and 4.1 s, respectively. The sum of the latter corresponds to at least three times T₁ of the slowest relaxing ¹H-nucleus (formic acid) and ensures quantitative analysis. Typically, 64 or 128 scans, with 64 k data points were collected. An exponential window function with a line broadening of 0.2 Hz was applied prior to Fourier transformation and the spectra were manually phased, baseline corrected and integrated using Mestre-C 8.1.1 software package. Liquid-phase species were identified according to their chemical shifts (referenced to the internal standard, see [SI-Table 1](#)) and in comparison with spectra of commercial references recorded under identical conditions. Overlapping signals were deconvoluted using Lorentzian-Gaussian shape type fitting functions. Quantification was done on the basis of the integrated signal intensities which were further calibrated against prepared solutions of known concentration in order to account for signal damping due to the water-suppression in close proximity to the water resonance frequency.

2.2.3. ¹³C NMR analysis

For ¹³C NMR measurements, reactor aliquots were again mixed in a 1:1 volume ratio with D₂O adjusted to pH 3 with DCl. ¹³C NMR spectra were recorded at 300 K using an Avance III 500 System (Bruker Biospin, Rheinstetten, Germany) with an UltraShield 500 MHz magnet (11.75 T) and a Cryo-QNP probe head (5 mm, direct ¹³C/³¹P/²⁹Si/¹⁹F with Z-gradient). The resonance frequency of ¹³C was 125.07 MHz. The spectra were acquired using the one-dimensional “zgpg” sequence from the Bruker library using waltz16 ¹H-decoupling and a 30° ¹³C-pulse. Relaxation delay and acquisition time were set to 4 s and 1.2 s, respectively. Typically, 1024 scans with 64 k data points were collected. An exponential

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