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Mechanistic Insights into Hydrogen Evolution by Photocatalytic Reforming of Naphthalene

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Abstract

Heterogeneous photocatalysis has been widely considered, amongst other applications, for environmental remediation and hydrogen production. While these applications have been traditionally seen as well separated areas, recent examples have highlighted the possibility of coupling them. Here we demonstrate the simultaneous production of H₂ and naphthalene removal from aqueous solutions with (unoptimized) photonic efficiencies of 0.97% and 0.33%, respectively, over Pt-TiO₂ under simulated sunlight. Photocatalytic and spin trapping experiments in the presence of hydroxyl radical and hole scavengers evinced that only the photogenerated holes play a significant role in the oxidation of naphthalene. Isotopic labeling analyses showed that the evolved H₂ isotopologues match those of the solvent, and that deuterated water (but not deuterated naphthalene) decreases the reaction rate, suggesting its involvement in the rate-determining step. Moreover, the use of Ti¹⁸O₂ does not lead to the significant formation of ¹⁸O-enriched CO₂, suggesting that water is the source of the oxygen atoms. Ultimately, by considering the stable and transient reaction intermediates, we propose a plausible reaction pathway. Our work illustrates that environmental remediation can be effectively coupled to solar fuel production, providing a double purpose to photocatalytic reactions, while the mechanistic insights will be of utility for the further development of this strategy.

Keywords:

Polycyclic aromatic hydrocarbons, persistent organic pollutants, photoreforming, titania, H₂ production, EPR, isotopic study, reaction mechanism

1. Introduction

Achieving a fully sustainable energy production system based on sunlight involves the development of multiple and diverse technologies. Although solar light represents a huge untapped potential, it is intermittent in nature, making the use of energy vectors an unavoidable requirement ¹. In this regard, the photocatalytic production of molecular hydrogen (H₂) in the solar-driven process is a promising strategy to store sunlight as chemical energy *via* photoinduced reduction of water ^{2, 3}. As an energy vector, H₂ possesses the highest gravimetric gross calorific value among all fuels (142 MJ kg⁻¹), and burns cleanly yielding only pure water ⁴. Nonetheless, its photocatalytic production and achieve acceptable efficiencies^{2, 3}, in a process commonly called photocatalytic reforming of the SED. This entails, however, the consumption of compounds that may have a significant cost with respect to that of the produced H₂.

Lanterna and Scaiano have recently illustrated an interesting alternative ⁵. These authors utilized water samples from Canadian rivers to perform a photocatalytic reaction where both the reduction and oxidation half-reactions were purposeful: while water was reduced to form H₂, the accompanying half-reaction was exploited to oxidize dissolved pollutants, thus simultaneously improving the water quality. This strategy increases the H₂ production efficiency with respect to pure water, avoids the use of potentially costly SEDs, and achieves the above-mentioned two-fold purpose. Another attractive dual-purpose system was described by Horiuchi et al., ⁶ combining solar H₂ production with a plant factory. The use of plant biomass as SEDs aids the photocatalytic H₂ production, while the emitted CO₂ is useful for plant growth.

Industrial effluents are an attractive target to apply this approach. Although they commonly carry a broad range of pollutants, a particularly troublesome group is that of persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs). These compounds, mainly distributed by the incomplete combustion of fossil fuels and by accidental oil spills, are ubiquitously found in the environment, have a great tendency to bioaccumulate, and, importantly, present a broad range of deleterious health effects ^{7, 8}. Among the different PAHs, naphthalene is a particularly noxious member due to its relatively large solubility in water, which leads to increased bioavailability and ultimately to adverse effects in the environment and human health.

As for many other pollutants, oxidative processes based on photocatalysis have often been considered for the removal of PAHs. Nevertheless, while several studies have explored their photocatalytic oxidation in aerobic conditions (where the reduction half-reaction is the conversion of molecular oxygen to the superoxide radical anion) $^{9-13}$, there are no reports on the remediation of PAHs with the simultaneous production of H₂. At the same time, reports on simpler aromatic compounds such as benzene and its derivatives have indeed shown that coupling their photocatalytic degradation to H₂ production could be a viable strategy $^{14-16}$. In comparison to relatively simpler SEDs like methanol, however, the involvement of the oxidation intermediates may play an important and undesired role 17 ; to unravel these, mechanistic investigations on both the reductive and oxidative half-reactions are desired 18 .

In the present study, we report the investigation of the removal of naphthalene concurrently with the H_2 production reaction, using a platinized TiO_2 photocatalyst under anaerobic irradiation with simulated sunlight. Moreover, we delve into the underlying mechanism and possible degradation pathways by monitoring the formation

of organic intermediates, performing isotopic substitution experiments, and studying the reaction in the presence of active species scavengers and spin traps.

2. Experimental section

2.1 Raw materials

The commercial titanium dioxide (TiO₂) Hombikat UV100 was supplied by Sachtleben Chemie GmbH. Naphthalene (\geq 99%), naphthalen-1-ol (97%), naphthalen-2-ol (99%), 1,1'-binaphthalene (97%), naphthalene-1,4-dione (97%), 1,2,3,4-tetrahydro-1-naphthalenone (97%), 3,4-dihydronaphthalen-1(2H)-one (97%), 5-hydroxynaphthalene-1,4-dione (97%), dimethyl phthalate (99%), diethyl phthalate (99%), potassium iodide (99.5%), deuterium oxide (D₂O, 99.9 atom % D), 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 97%), and chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, 99.9%) were purchased from Sigma-Aldrich. Methanol (HPLC grade), acetone (GC grade), dichloromethane (GC grade), and ethyl acetate (GC grade) were purchased from Carl-Roth. All reagents were used as received without any further purification. All solutions were prepared with deionized water obtained from a Millipore Mill-Q system (18.2 M Ω cm, 25 °C).

2.2 Preparation and characterization of the photocatalysts

Platinum-loaded TiO₂ samples were prepared by a photodeposition method following the procedure of Melvin et al. ¹⁹. The TiO₂ powder (1.5 g) was dispersed in 150 mL of a 10% aqueous methanol solution with 3.86 mL of 0.01M platinum precursor (H₂PtCl₆) and stirred for 1 h prior to its purging for 1 h with argon. The obtained suspension was then illuminated for 4 h with UV(A) light employing a Philips CLEO 15W lamp inside a climatic chamber with an adjusted temperature of 18°C. The solid was then collected by centrifugation, washed once with methanol and four times with distilled water, and finally dried at 100 °C for 24 h. Ti¹⁸O₂ was kindly provided by Dr. Juan Felipe Montoya and synthesized according to a previously reported procedure.²⁰ The synthesized Ti¹⁸O₂ was mixed with the proper volume of a platinum nanoparticles suspension prepared by laser ablation and kindly provided by Particular GmbH, Germany. Then it was stirred for 1h, and finally dried overnight to prepare 0.5 wt% Pt-Ti¹⁸O₂.

The synthesized platinized TiO_2 and pristine UV100 photocatalysts were characterized with the Brunauer– Emmett–Teller technique (**Table S1**), X-ray diffraction (XRD) (**Figure S1**), transmission electron microscopy (TEM) (**Figure S2**), and electron paramagnetic resonance spectroscopy (EPR) (**Figure S3**). A detailed discussion of the physicochemical characterization can be found in the supplementary information file.

2.3 Sample preparation and photocatalytic experiments

Due to the low solubility of naphthalene in water $(2.44 \times 10^{-4} \text{ mol L}^{-1} \text{ at } 25 \text{ °C}^{-21})$ and its high vapor pressure, special care was taken to prepare deaerated solutions of known concentrations, as summarized in **Scheme S1**. As a first step, a stock saturated and the deaerated solution was prepared in deionized water. In brief, 0.100 g of naphthalene was introduced in a double-jacket two-necked container with airtight screw caps, containing 200 mL of Milli-Q water. The mixture was purged with a gentle stream of argon for 1 h at room temperature. The temperature was then maintained at 40 °C by using a thermostatic water bath with continuous magnetic stirring for 2 h to increase

the solubility of naphthalene (4.30×10^{-4} mol L⁻¹ at 40 °C ²¹). Subsequently, the temperature was decreased and maintained at 25 °C with continuous stirring for 4 h. Afterward, the stirring was stopped, and the solution was left for 2 h to settle the undissolved naphthalene crystals. This procedure results in a solution with an estimated concentration of 2.44×10^{-4} mol L⁻¹ (31ppm); the exact value was determined via HPLC-UV.

The photocatalytic experiments were carried out in batch mode. The photocatalytic H₂ evolution experiments were performed in 20 mL glass vials tightly closed with crimp caps and silicone septa. In a typical experiment, 15 mg of the photocatalyst powder was suspended in ca. ~9.5 mL of deionized water inside a vial. The vial was then closed with the crimp septum and purged with argon for 30 min. Afterward, the necessary volume from the stock naphthalene solution was injected inside the vial by using a pre-purged (with argon) needle and syringe, in order to reach a final 1.56×10^{-4} mol L⁻¹ (20 ppm) naphthalene concentration. The total reaction volume was 15.0 mL, with a photocatalyst mass concentration of 1.0 g L⁻¹. Finally, the vials were horizontally fixed inside an orbital shaker and left in the dark for 1 h to establish the adsorption equilibrium. Afterward, the orbital shaker was placed at a 30 cm distance below a solar simulator consisting of a 1000 W xenon lamp (Hönle UV Technology, Sol 1200) equipped with a filter to mimic the emission profile of sunlight. The temperature of the vials was maintained at 25 ± 2 °C by using a water bath. From the measurement of the lamp irradiance in the wavelength range between 320 nm and 380 nm at the irradiated area, the photon flux density was found to be I_0 = 3.31 × 10⁻⁴ mol m⁻² s⁻¹. Ignoring light losses due to reflection and scattering, 2.18 × 10⁻⁷ mole of photons entered the irradiated suspension per second.

The photocatalytic experiments in the presence of scavengers were performed under the same conditions, using a 20 mmol L⁻¹ concentration of either potassium iodide (KI) as the hole scavenger or tert-butyl alcohol (TBA) as the hydroxyl radical scavenger. For the radical trapping experiments, the necessary amount of the spin trapping agent 5,5-dimethyl-1-pyrroline N-oxide (DMPO, Aldrich) to achieve a 20 mmol L⁻¹ final concentration was also added. The suspensions were then transferred under an argon stream to a small quartz flat cell cuvette (FZK 160-7x0.3, Magnettech GmbH, Germany) designed for EPR analysis. The samples were irradiated at room temperature (~ 25 °C) directly in the EPR spectrometer microwave cavity, and the spectra were recorded before and during irradiation.

Identical experimental conditions were used for intermediates identification. However, a 250 mL borosilicate reactor was chosen to perform these experiments in a higher volume of the reaction suspension, to guarantee a detectable amount of these intermediates. All the photocatalytic tests were done by triplicate, yielding relative standard deviations (RSD) between 4% and 8%.

2.4 Mineralization measurements

The extent of naphthalene mineralization was monitored by total organic carbon (TOC) measurements, using a Shimadzu TOC-5000A analyzer. Different concentrations of standard potassium hydrogen phthalate and sodium bicarbonate solutions were used for the calibration of the instruments before the analyses. The initial concentration was measured after the equilibrium adsorption of the naphthalene on the Pt/TiO_2 surface for 1h, and afterward, the TOC was recorded at regular intervals. All samples were filtrated with syringe filters (0.2 µm) and immediately analyzed, to minimize the volatilization of naphthalene.

A HIDEN HPR-20 QIC gas analyzer equipped with a quadrupole mass spectrometer (QMS) was used to identify the evolved gases during the photocatalytic tests. The experiments were carried out in a 65 mL cylindrical air-tight reactor with a quartz window. A continuous flow of 5 mL.min⁻¹ of argon carried the headspace into the QMS system. In all experiments, the aqueous suspension volume was 50 mL, while the temperature was kept constant at 25 ± 1 °C. Blank experiments showed no detectable gases evolution in the absence of either light, the photocatalyst or naphthalene. The same setup was employed for the isotopic substitution experiments. In this case, however, irradiation was performed in the vials in an identical way to the photocatalytic experiments, and then the headspace was swept into the QMS using a 0.75 mL min⁻¹ argon flow. The quantitative of the evolved gases was done by calibrating the QMS with standard argon-diluted H₂ (Linde Gas, Germany) and D₂ (Sigma-Aldrich).

2.5 Extraction procedures

To ensure the complete extraction of stable intermediates, two complementary approaches were employed. In the liquid-liquid procedure, the irradiated suspension (250 mL) was transferred to a 500 mL separatory funnel and extracted with three 25 mL aliquots of dichloromethane. The organic layer was passed through a 0.45 mm filter paper containing anhydrous sodium sulfate to remove the TiO_2 particles and water. Finally, the organic layer was concentrated to 1 mL using a gentle stream of nitrogen.

In the solid-phase extraction procedure, the irradiated suspension was immediately filtered through 0.2 µm PTFE syringe filters to remove the TiO₂ particles, then transferred to a brown glass bottle. The extraction was performed within 24 hours to avoid any losses or degradation of the by-products, using packed cartridges (OASIS HLB, 6 mL/500 mg, from Waters[®] Ireland). The cartridges were connected to a solid-phase extraction apparatus (Supelco, USA) and preconditioned with 6 mL of methanol, 6 mL of ethyl acetate and 6 mL of acidified deionized water (pH 2.0) at a flow rate of 1 mL min⁻¹. Then a sample's aliquot of 200 mL (pH adjusted to 2.0 with 1 M HCl) was loaded into the cartridge and passed through it at a 3-4 mL min⁻¹ rate. Subsequently, the cartridge was pre-dried under low pressure for 5 min to remove the excess of water. Finally, the retained analytes were eluted using three 4 mL aliquots of ethyl acetate at a flow rate of 1 mL min⁻¹. The collected extract was passed through anhydrous sodium sulfate to remove any remaining water and then concentrated to around 0.5 mL using a gentle stream of nitrogen.

2.6. Analytical methods

High-Performance Liquid Chromatography (HPLC) analyses were performed using an Ecom system equipped with a UV-vis detector operating at 276 nm and a Knauer Vertex Plus column packed with Eurospher II 100-5 C18 A material (length \times inner diameter 150 mm \times 4 mm with precolumn). The oven temperature was 30 °C and the mobile phase was a mixture of methanol and water. Different elution programs were applied for naphthalene and intermediates identification as described in **Table S2**.

The formation of short-chain organic acids was monitored via High-Performance Ion Chromatography (HPIC), using a Dionex ICS-1000 equipped with a conductivity detector and an electro-regenerator suppressor. The column was an anion exchange resin (IonPac AS9-HC, $L \times I.D.$ 250 mm \times 2 mm) and the eluent was a mixture of alkaline

solutions of 8×10^{-3} mol L⁻¹Na₂CO₃ and 1.5×10^{-3} mol L⁻¹NaHCO₃ with a flow rate of 0.3 mL min⁻¹. The temperature of the conductivity cell was kept constant at 35 °C during the analysis period (90 min).

Gas chromatography with thermal conductivity detection (GC-TCD) was used to quantify the photocatalytically evolved H_2 . For this purpose, a 50 μ L gas sample was periodically taken from the headspace over the suspension using a Valco gas-tight sampling syringe equipped with a push-button valve. The gas sample was then injected into the injection port of a Shimadzu GC-8A, equipped with a stainless-steel molecular sieve 5A GC column (Sigma-Aldrich, USA). The temperature of the injection port and the TCD detector was maintained at 120 °C, while the column temperature was fixed at 80 °C.

The extracted reaction intermediates were analyzed by GC-MS using a GCMS-QP5050 (Shimadzu) coupled with AOC-5000 Plus autosampler and a capillary Agilent DB-5ms column (L × I.D. × film thickness 30 m × 0.1 μ m × 0.32 mm). The carrier gas was helium at a constant flow of 1.25 ml min⁻¹. The oven temperature was programmed at 70 °C for 3 min, followed by a raise to 180 °C at a rate of 10 °C min⁻¹, held for 2 min, and then a final raise at a rate of 20 °C min⁻¹ to 315 °C and held for 10 min. The injection port and the interface temperatures were set at 250 °C and 280 °C, respectively. The mass spectrometer was operated in the positive electron impact mode with ionization energy of 70 eV; the detection was performed in scan mode and peaks were identified according to the NIST library.

2.7 EPR in situ experiments

The electron paramagnetic resonance (EPR) spin-trapping technique was applied to detect and monitor the formation of paramagnetic intermediates. Such intermediates were detected upon in situ irradiation using an X-band EPR MiniScope MS400 (Magnettech GmbH, Germany) spectrometer operating at a 9.51 GHz field and equipped with a UV spot-light (LC8, Hamamatsu, 200 W super-quiet mercury-xenon lamp). The acquisition parameters were as follows: center field: 335.4086 mT, sweep time 15 s, number of points: 4096, number of scans: 1, modulation amplitude: 0.2 mT, power: 10 mW, gain: 5. The EPR spectra simulations were carried out using EasySpin ²².

2.8. Transient Absorption Spectroscopy

The transient absorption spectroscopy (TAS) measurements were carried out in diffuse reflectance mode by means of an Applied Photophysics equipment, employing an LKS80 nanosecond Laser Flash Photolysis Spectrometer with a pulsed Nd:YAG laser (Quantel, Brilliant B). Samples were measured as aqueous slurries inside flat quartz cells. Prior to the measurements, the samples were purged with argon for 30 min. The excitation wavelength was 355 nm, with an average energy per pulse of 6 mJ cm⁻². The obtained transient signal is detected upon measuring the change in reflectance (ΔJ) before (J₀) and after the laser excitation (J), according to Equation 1.

$$\Delta J = \frac{J_0 - J}{J_0} \tag{1}$$

3. **Results and discussion**

3.1 Naphthalene degradation and photoreforming

We start our analysis by considering the requirements for the photocatalytic production of H₂ over bare and platinized Hombikat UV100 TiO₂ (from here on, UV100 or Pt-UV100, respectively). First, as expected from the known lack of water splitting activity of bare TiO₂²³, no H₂ is evolved in the absence of naphthalene. Similarly, there is no H₂ production in the absence of either light or a photocatalyst. However, the naphthalene concentration moderately decreases under irradiation in the absence of the photocatalyst (32% after 4 h), possibly due to the photolysis of the probe compound ¹³. The direct photolysis of PAHs has been reported previously ^{13, 24}, and it is considered as one possible method for eliminating these compounds from the environment.²⁵ For the photolysis to occur the absorption spectra of the organic molecules must overlap with the emission spectra of the source. In the present case only a limited overlap occurs in the range 300-315nm (Figure S4), which results in a relatively slow photolysis of naphthalene. It has been reported that, upon irradiation, naphthalene undergoes oxidation to its radical cation,^{24, 25} which reacts with water or O₂ to mainly yield naphthol, quinone, and aldehyde.²⁶ The detection of byproducts in our system proved unsuccessful, most likely due to the low concentration and the sequential photooxidation of these products²⁷ in our system. The estimated photonic efficiency for the direct photolysis of naphthalene after 4 h irradiation is 2.3×10^{-3} %. This value is low compared to that reported by Vialaton et al. ²⁸ of 2.5×10^{-1} % for the photolysis of naphthalene under aerobic conditions at 313 nm irradiation. On the other hand, the absorption coefficient of TiO₂ is much higher in the range of the light source emission, and thus we expect that, when TiO₂ and naphthalene are both present, most light is absorbed by TiO₂, significantly decreasing the photolysis rate.

The degradation of naphthalene is greatly enhanced in the presence of UV100 and Pt-UV100 (**Figure 1**). After irradiating the aqueous suspension for 4 h, the naphthalene concentration decreases by 71% and 86%, respectively. However, we only observe H_2 evolution in the presence of Pt-UV100. The lack of H_2 evolution over bare TiO₂ is a known issue, ascribed to the high overpotential for this reaction on the TiO₂ surface ²⁹. In the present case, whilst photogenerated holes in TiO₂ may be consumed by naphthalene, the absence of molecular oxygen as the electron acceptor necessitates that the accompanying electrons either reduce one of the organic species present in the system or accumulate in the form of trivalent titanium (Ti³⁺) inside the photocatalyst.³⁰

Regarding the choice of the photocatalyst, we exclusively employ here the pure-anatase Hombikat UV100, either bare or loaded with 0.5 wt% of platinum (prepared by photodeposition). Although the photocatalyst optimization is out of the scope of this study, we mention that this selection is not arbitrary but is based on experimental results showing that i) UV100 is more active than Aeroxide P25; ii) the photodeposition method of Pt on TiO_2 surface results in a higher activity than other deposition methods such as physical mixing of titania with Pt nanoparticles, and iii) a 0.5 wt% Pt loading seems to be optimal for the reaction under investigation. We show the detailed characterization of UV100 and Pt-UV100 in the Supporting Information.

The analysis of the kinetic profiles reveals some interesting features. As shown in **Figure 1**, during the prior dark period around 14% of the initial naphthalene amount adsorbs on the surface of the photocatalysts. Although the compound is not expected to strongly interact with the TiO₂ surface, it is apparent that the high specific surface area of UV100 results in significant adsorption ³¹. The adsorption kinetics of naphthalene on the surface of 0.5 w% Pt-UV100 are shown in **Figure S5**. We observe that the adsorption equilibrium is attained within 1h. The adsorbed amount at the equilibrium corresponds to a coverage of around 0.05 molecule nm⁻². A similar value for naphthalene

on the surface TiO₂ (anatase) has been reported by Mahmoodi and Sargolzaei, with the difference that the dynamic equilibrium was established after 5 min in that case.³². The adsorption of aromatic compounds on the TiO₂ surface was studied by Nagao and Suda ³³, who suggested that the adsorption involves the formation of Ti⁺⁴··· π -electron and/or OH_(surface)··· π -electron type complexes.



Figure 1. Kinetic profiles for the photocatalytic degradation of naphthalene and molecular hydrogen evolution over UV100 and Pt-UV100. Conditions: batch reactor, reaction volume = 15 mL; [Naphthalene] = 156 μ mol L⁻¹; [catalyst] = 1 g L⁻¹; T = 25 °C; illumination under simulated solar light. Lines are guides for the eye.

Upon irradiation, we observe a rapid decrease of the naphthalene amount in the presence of both photocatalysts during the first 30 min of illumination. This decrease is found to be accompanied by rapid H₂ evolution only in the presence of Pt-UV100. After this initial 30 min period, the changes in the amounts of naphthalene as well as evolved H₂ became significantly slower, suggesting the depredation of accumulated intermediates at the photocatalyst surface and the competition of naphthalene and intermediates for the holes during the photocatalytic process. This hypothesis of a poisoning of the photocatalyst surface is supported by the observation of a color change of the photocatalyst from light gray to brown after 1 h of illumination (**Figure S6**). This observation is in agreement with previous reports which have shown that the photocatalytic degradation of naphthalene and other aromatic compounds may yield intermediates, likely of polymeric nature, that deactivate the catalyst surface ^{34, 35}. Additionally, we performed recycling experiments by collecting the photocatalyst and irradiating it in the presence of molecular oxygen for 1 h to remove the adsorbed organic compounds (**Figure S6**) for overcoming possible poisoning problems.

As illustrated in **Figure 1**, the loading of platinum nanoparticles on TiO_2 not only enables the evolution of H_2 possibly through the reduction of the overpotential for the electron transfer to the proton ³⁶, but also promotes the degradation of naphthalene. We ascribe this observation to the charge separation effect caused by the Schottky barrier between TiO_2 and platinum, which results in a lower recombination rate of the photogenerated electron-hole pairs ^{37, 38}. On another hand, the reduction of the adsorbed protons on the surface of the TiO_2 by depletion of the photogenerated electrons could be another factor for enhancing the photocatalytic activity of the Pt/TiO_2 and lessening the charge carrier recombination. Since the reduced protons (i.e., hydrogen atoms) migrate to the Pt islands to combine yielding H_2 molecules, the degradation of the naphthalene is enhanced on the positively charged TiO_2 surface ³⁹. Similarly,

Sun et al.⁴⁰ have reported that the rates of light-induced phenol decomposition and total carbon removal increased by a factor of 1.5 when UV100 was loaded with 1 wt% Pt.

From the photocatalytic naphthalene reforming experiments over Pt-UV100, we determined the initial (< 30 min) photonic efficiencies, ξ , to be (0.97 ± 0.06) % for H₂ formation (3.8 µmol / 30 min) and (0.33 ± 0.01) % for naphthalene degradation (1.3 µmol / 30 min) after correction by subtracting the quantity of adsorbed naphthalene. The employed equations are detailed in the **SI file**. These are typical values for photocatalytic processes ⁴¹, although much lower than those reported, for instance, for the photocatalytic reforming of methanol over Pt-UV100 (between 20 and 30 %) ⁴². Methanol, however, gives rise to current-doubling effects, that in conjunction with its well-known hole scavenging properties results in a highly efficient H₂ evolution.

We observe a considerably higher ξ for H₂ production than for naphthalene degradation. This suggests that H₂ is not only produced in association with the direct oxidation of naphthalene but also with the oxidation of organic intermediates, as will be discussed below. The 30 min period in which the ξ was determined is long enough to reach a significant conversion for naphthalene accompanied by the formation of reaction intermediates.

Besides the disappearance of naphthalene, it is of high importance for practical applications to evaluate the extent of complete mineralization of the reactant yielding CO_2 and H_2O . Therefore, we monitored the concentration of the total organic carbon (TOC) being present in the aqueous solution after the removal of the photocatalyst Pt-UV100. The TOC data points in **Figure 2** showed a gradual decline to around 55 % after 4 h of irradiation. As mentioned above, the concentration of naphthalene decreases by 86 % in the same period of time, pointing to the formation of stable intermediates. By converting the amount of naphthalene to organic carbon, TOC_N, during the photocatalytic process in presence of the Pt-UV100 and subtracting its curve from that of measured TOC, we estimate the kinetic profile of all organic intermediates (**Figure 2**). This curve follows the expected profile for reaction intermediates by various analytical techniques and describe the results in Section 3.2, together with a plausible reaction pathway. We note, however, that a decrease in the TOC amount could possibly reflect the adsorption of the by-products on the TiO₂ surface, instead of mineralization.

To rule out this possibility, we performed in-line monitoring of the reaction atmosphere by means of the quadrupole mass spectrometry (QMS) technique. Blank experiments showed no detectable evolution of gases in the absence of either irradiation, the photocatalyst, or naphthalene. Additionally, no significant signals were detected for the formation of CO, CH_4 , and other small alkanes and alkenes. We show the time course of the QMS signals for H_2 and CO_2 which are proportional to the amount of produced gases in **Figure S7**. We note here that experimental limitations (namely, a significant evaporation of naphthalene) prevent us from quantifying the absolute amounts of generated CO_2 and H_2 . The following description is thus only qualitative. The observation of a CO_2 formation shows an increasing rate over time during the analyzed period. Contrarily, after a fast-initial growth, the H_2 QMS signal shows a marked decrease in its formation rate, in accordance with the results of **Figure 1.** On the other hand, the loss of naphthalene due to its large vapor pressure during these experimental runs, which were performed in an open

system, prevents us to perform a direct comparison between the evolved amount of CO_2 and the decrease in the TOC. However, the brownish color of the recovered photocatalyst and its disappearance during the irradiation in the presence of O_2 could indicate that at least part of the TOC decrease is related to the adsorption of by-products on the TiO₂ surface.



Figure 2. *Kinetic profile for the relative amount of total organic carbon (TOC) during the photocatalytic reforming of naphthalene over Pt-UV100.*

3.2 Identification of intermediates

We investigated the intermediates formed during the photocatalytic reforming of naphthalene over Pt-UV100 using a combination of chromatographic techniques. Firstly, we employed liquid-liquid and solid-liquid extraction procedures followed by gas chromatography-mass spectrometry (GC-MS) to obtain an overview of the stable intermediates. The identified by-products are shown in **Chart 1**, while the details of their detection (retention times, molecular ion peaks, and mass fragmentation patterns) are listed in **Table S3**. Among these compounds, we found that naphthalen-1-ol and naphthalen-2-ol are the main constituents after 4 h of irradiation (0.25 ± 0.01 and $0.13 \pm 0.01 \mu$ mol, respectively). In contrast, we detected naphthalene-1,4-dione in a lower amount ($0.030 \pm 0.003 \mu$ mol), and only traces of the remaining compounds. Complementarily, we also analyzed the samples for short-chain organic acids using high-performance ion chromatography (HPIC). From these analyses, we determined the presence of formic acid and acetic acid in low concentrations (0.051 ± 0.008 and $0.029 \pm 0.005 \mu$ mol, respectively).

Although these are, to the best of our knowledge, the first results concerning the photoreforming of naphthalene, we can perform a meaningful comparison with the intermediates previously observed during its aerobic photocatalytic oxidation, summarized in **Table S4**. Although there is some degree of coincidence, it is revealing that in the present case most detected intermediates correspond to earlier stages of the degradation process. This is consistent with the poisoning effect discussed above, that may limit the extent of mineralization under anaerobic conditions. Similarly, we find short-chain acids, produced from ring cleavage reactions,^{10, 12, 43} in very low concentrations.

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Chart 1. Detectable intermediates during the photocatalytic reforming of naphthalene using Pt-UV100.

Considering that naphthalen-1-ol and naphthalen-2-ol are the main detected intermediates, we now focus on the time dependence of their concentrations, as monitored by high-performance liquid chromatography (HPLC). The kinetic profiles, shown in **Figure 3**, closely match the degradation of naphthalene (**Figure 1**) with a high formation rate during the first 30 min, and a significant retarding at longer times. The detected amounts, however, are considerably smaller than those expected from the complete conversion of naphthalene. While, around 1.5 μ mol of naphthalene was degraded after 4 h, only a combined amount of 0.39 μ mol of naphthalen-1-ol and naphthalen-2-ol was formed. In the first stage of the reaction (**Figure 3**), the formation rate of these naphthalenols is larger than the rate of their consumption, thus, increased their amount in the medium. Subsequently, in the second stage, the formed amount becomes almost constant as both rates nearly equivalent. This may suggest the formation of a relatively large quantity of unidentified intermediates, consistent with the hypothesis of polymeric species poisoning the TiO₂ ⁴⁴. have suggested that the structurally similar phenol and 4-chlorophenol may indeed show strong binding to TiO₂⁴⁴.

A further interesting observation is that the concentration ratio of naphthalen-1-ol to naphthalen-2-ol is not unity but instead ranges from 1.7 to 2 throughout the reaction. We find a plausible explanation for this behavior on the basis of Dewar's molecular orbital theory ⁴⁵ and the adsorption of naphthalene on the surface of the TiO₂. Briefly, this theory predicts that the difference in the activation energy of two related aromatic substitution reactions is mainly determined by the difference in the so-called localization energies of the extended π -systems. Of relevance here, the localization energies have been quantified in the form of *Dewar's reactivity numbers*; a lower reactivity number corresponds to a faster aromatic substitution reaction, and vice versa. The reported values for the 1- and 2- positions

in naphthalene are 1.81 and 2.12, respectively. Moreover, as determined from near edge x-ray absorption spectroscopy (NEXAFS), naphthalene molecules adsorb on the surface of rutile (110) in a flat-lying geometry with tilt angles about 24°, at relatively high altitudes that reach 3–4 Å from the substrate surface ⁴⁶. Matsuura et al,⁴⁷ demonstrated that position 1 on the naphthalene molecule is more reactive for removing an electron than that of position 2 due to the higher charge density in this position. Thus, hydroxylation at position 1 results in a more stable product than hydroxylation at position 2, which has been confirmed by Hückel-McLachlan molecular orbital calculations by Steenken ⁴⁸ and experimentally by Hykrdova et al.,³⁴ who reported the preferred formation of naphthalen-1-ol in the TiO₂ (heterogeneous) and Fe⁺³ (homogenous) systems. This becomes congruent with *Dewar's reactivity numbers* hypothesis and thus explains the preferential formation of naphthalen-1-ol. Considering these results, it can be concluded that the interaction of the naphthalene molecules with the TiO₂ surface does not significantly change its electronic distribution in naphthalene. Hence, the electronic density at the carbon atoms (C₁ > C₂ > C_{9,10}) of the naphthalene molecule governs the position of hydroxylation ³⁴.



Figure 3. Kinetic profile for the formation of naphthalen-1-ol and naphthalen-2-ol during the photocatalytic reforming of naphthalene over Pt-UV100.

Although the mechanism for the formation of naphthalen-1-ol and naphthalen-2-ol will be discussed in section 3.4, we mention here that the overall reaction is given by Equation 2. Consequently, the expected H_2 to naphthalenols ratio is 1:1, thus being at odds with our observation of a >10:1 ratio, as deduced from **Figure 1** and **Figure 3**. This discrepancy can be explained from two perspectives. On the one hand, there may be parallel channels by which naphthalene is degraded. One such example is given by Equation 3, that results in one of the detected intermediates, 1,1'-binaphthalene, and the formation of hydrogen. Additionally, the kinetic profile of naphthalenols in **Figure 3** not only reflects their formation rate but also their simultaneous consumption rate by a photoreforming reaction, skewing the ratio towards higher H_2 values. This is illustrated by Equations 4 and 5, that result in the formation of two equivalents of H_2 via the successive transformation of naphthalene-1-ol into two of the detected intermediates, napthalen-1,4-diol, and naphthalene-1,4-dione. Moreover, the strong binding of the naphthalenols to the TiO₂ surface could also explain their low observed amounts.





$$2 \underbrace{\qquad hv \qquad }_{Pt/TiO_2} + H_2(t)$$
(3)

$$\begin{array}{c} OH \\ H_2O \end{array} + H_2O \end{array} \xrightarrow{hv} Pt/TiO_2 + H_2(f) \\ OH \end{array}$$
 (4)

3.3 Mechanistic study

3.3.1 Participation of the TiO₂ surface as a source of oxygen atoms

Recently, besides photogenerated holes and hydroxyl radicals as active species in photocatalytic processes, the role of bridging oxygen radicals at the TiO₂ surface (\bigcirc) has been discussed^{14,49,50}. Holes could be trapped by bridging oxygen atoms on the TiO₂ surface (\equiv Ti-O_s-Ti \equiv) to produce the active species oxygen radical (\equiv Ti-O_s-Ti \equiv), which ultimately can be incorporated into the reaction products, creating oxygen vacancies that are subsequently healed by water. Therefore, isotope labeling is a useful strategy to evaluate such mechanism, e.g. by using mass spectroscopy to monitor the isotopic composition of the evolved species. As we demonstrated in section 3.1, CO₂ was one of the final products during the photocatalytic reforming of naphthalene. Thus, if the bridging oxygens are the oxygen source for hydroxylation of naphthalene, in this case, we expect that the isotopic composition of the evolved CO₂ should (partially) reflect that of TiO₂. To investigate the participation of bridging oxygens, we performed the reaction over isotopically labeled Pt-Ti¹⁸O₂ and monitored different CO₂ isotopologues before and during the illumination by means of QMS.

Figure 4 illustrates the time evolution of the QMS signals of different CO_2 isotopologues and their fragments during the photocatalytic reforming of naphthalene over Pt-Ti¹⁸O₂. Before illumination, no changes in the background signals were observed for one hour; i.e., no catalytic reaction occurred between naphthalene and Pt-Ti¹⁸O₂ in the absence of light. Upon irradiation, only the signal of $C^{16}O_2$ (m/z = 44) significantly increased, indicating the photocatalytic mineralization of naphthalene without the incorporation of oxygen atoms from the lattice. However, it should also be mentioned that oxides readily undergo lattice oxygen exchange with gaseous O₂, not only under UV irradiation but in dark conditions as well ⁵¹. The absence of ¹⁸O-labelled CO₂ was also observed in batch reactor experiments where we increased the catalyst mass concentration 5-fold, collected the evolved gases in the headspace

of the reaction vial and analyzed them via injection to the QMS to increase sensitivity. Civis and co-workers⁵² studied the photocatalytic decomposition of formic acid on the surface of $Ti^{18}O_2$ by the means of Fourier-transform infrared absorption spectroscopy, and found that the process does not lead to the evolution of either C¹⁶O¹⁸O nor C¹⁸O₂. On the contrary, Montoya and co-workers^{20, 50} did observe C¹⁶O¹⁸O evolution during the photocatalytic oxidation of benzene over Ti¹⁸O₂ in anaerobic conditions. Although we investigated the same kind of organic compounds, namely aromatic hydrocarbons, we believe that naphthalene could be photocatalytically oxidized by a different mechanism. This can be argued from several angles, first, we observe a significant production of 1,1'-binaphthalene, which cannot be accounted for by the bridging oxygen mechanism. Second, the one-electron standard redox potentials for the oxidation of benzene and naphthalene in acetonitrile are 2.65 and 1.85 V vs. NHE respectively 53. Thus, neglecting the slight variation in aqueous solution, the one-electron oxidation of naphthalene by its direct reaction with holes (valence band potential: 2.68 V vs. NHE at pH 7)⁵⁴ is thermodynamically favored with respect to the same reaction for benzene. Hence, as long as the reaction does not fall into the Marcus inverted region, it will be significantly faster. The observation by Fox et al. of increasing photocatalytic oxidation rates for substituted naphthalenes as the exergonicity increased supports this notion ⁵⁵. Accordingly, abstraction of an electron from naphthalene by the valance band hole, which has a more positive potential, is likely to take place. And third, as shown in Figure 1, naphthalene adsorbed significantly on the TiO₂ surface, unlike benzene ⁵⁶. Indeed, temperature programmed desorption measurements over rutile single crystals have shown a significantly stronger binding by naphthalene ⁴⁶. Notably, the direct-indirect hole transfer model (DT-IT) of Salvador et al ⁵⁷, proposes that the specific pathway depends on the degree of electronic interaction of the dissolved molecules with the semiconductor surface. The relatively strong interaction of naphthalene with TiO₂ leads us to conjecture that, although both mechanisms may be operative, in contrast with benzene, the direct transfer of holes to naphthalene is favored with respect to the indirect, bridging oxygen mediated transfer.⁵⁶. Therefore, according to what we presented above; we propose that naphthalenols are the product of naphthyl radical cation formation followed by its reaction with water. More experimental evidences supporting this argument will be presented in the following sections.



Figure 4. QMS signals for isotopologues of CO, CO₂, and O₂ from the reforming of naphthalene over Pt-Ti¹⁸O₂. Experimental conditions: reaction volume: 5 ml; [Naphthalene] = 230 μ mol L⁻¹, light intensity I₂₅₀-I₄₅₀ = 30 mWcm⁻², [catalyst] = 2 g L⁻¹, T = 25 °C, and irradiation with an Osram XBO 1000-Watt xenon arc lamp as a solar simulator

3.3.2 Scavengers and electron paramagnetic resonance (EPR) spin-trapping technique

To determine the involvement of different active species in the photoreforming of naphthalene, we performed the reaction in the presence of two scavengers: potassium iodide (KI), which acts as a hole scavenger ⁵⁸, and 2methylpropan-2-ol ((CH₃)₃COH, TBA), a known hydroxyl radical (*'OH*) scavenger ⁵⁹. As shown in **Figure 5 (a)**, the photocatalytic conversion of naphthalene is completely inhibited in the presence of KI, with a degradation rate identical to that of the photolytic process. In contrast, the addition of TBA does not appreciably affect the photocatalytic process, yielding a kinetic profile virtually identical to that in the absence of scavengers. These results suggest that free hydroxyl radicals (*'OH*_{free}) present, have a minor contribution in the process. In contrast, the use of a hole scavenger leads to a halt in the photocatalytic process, confirming that naphthalene's disappearance is initiated by an oxidative half-reaction. Miller and Olejnik²⁵, as well as Beltran *et al.*⁶⁰, showed that neither TBA nor bicarbonate ions, respectively, affect the degradation rate of different PAH compounds in the presence of hydroxyl radicals in homogeneous systems. Therefore, they concluded that the photooxidation of these compounds was initiated via the formation of a radical cation, without involving free hydroxyl radicals. Accordingly, our results are in good agreement with their findings, despite the difference between both types of systems.

Complementarily, we monitored the formation of naphthalen-1-ol and naphthalen-2-ol during these experiments, as shown in **Figure 5 (b) and (c)**. Their kinetic profiles are consistent with those of naphthalene degradation: while the addition of TBA does not significantly affect the formation of naphthalenols, the addition of KI hinders naphthalene degradation almost completely due to the consumption of holes by this scavenger, highlighting their role in the photoreforming process. This result is not only important from the mechanistic point of view, but also for potential applications, since the simultaneous presence of hole-scavenging species in industrial effluents may completely inhibit naphthalene reforming.

The involvement of ${}^{OH}_{free}$ in photocatalytic reactions is the subject of a long-standing debate. Salvador has provided strong arguments against the oxidative formation of ${}^{OH}_{free}$ on the grounds of thermodynamic and kinetic arguments, stating that their observation in photocatalytic systems must respond to the reduction of molecular oxygen ⁶¹. However, recent works have challenged this idea, suggesting that the irradiation of anatase TiO₂ does lead to the formation of ${}^{OH}_{free}$, although this is not the case for the rutile polymorph ⁶². We thus employed electron paramagnetic resonance (EPR) spectroscopy to obtain additional insights regarding the role of ${}^{OH}_{free}$ in our system. To this end, we performed in-situ naphthalene photoreforming experiments in the presence of either TBA or KI, and the spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO). As expected, under dark conditions no radicals are detected. Upon irradiation, however, the tested samples under all conditions lead to the appearance of a signal attributable to the DMPO-OH adduct (four lines with relative intensities of 1:2:2:1), **Figure 6**. The simulation of the EPR spectrum (**Figure S8**) yields the spin Hamiltonian parameters $a_N = 1.453 \text{ mT}$, $a_H = 1.494 \text{ mT}$ and g = 2.0059, in accordance with previously reported values for this adduct 63 , 64 . Notably, we observe the production of the OH adduct in the absence of molecular oxygen, providing evidence in favor of their formation from the oxidation of water 65 . Additionally, we could detect neither organic radicals nor their DMPO adducts, likely due to a relatively low concentration of naphthalene and its intermediate radicals inside the EPR cell, together with a large multiplicity for

the hyperfine splitting of the adducts. A similar conclusion was reached by Steenken *et al.*,⁴⁸ who could not detect any signal from organic radicals during the reaction of naphthalene (and some of its derivatives) with both '*OH* and SO_4 ' in aqueous solution, both in the presence and the absence of spin trapping agents.

By performing the same experiment (i.e. aqueous DMPO with Pt-UV100) either in the absence or presence of naphthalene, we obtained similar signals (**Figure S9**), showing that, under these conditions, naphthalene is not strong $^{\circ}OH$ scavenger. In the presence of TBA, however, the adduct signal shows a decrease of 35 % (**Figure 6**) and vanished within 90 sec comparing to more than 240 sec in its absence (**Figure S10**), confirming TBA's $^{\circ}OH$ scavenging properties. Nevertheless, this lower quantity of available $^{\circ}OH$ radicals does not impact on naphthalene's degradation (**Figure 5**), providing evidence against a degradation mechanism initiated by the attack of $^{\circ}OH_{free}$.

The addition of KI to the system, on the other hand, practically nullifies the adduct formation, as could be expected from the efficient hole consumption by this scavenger. Regarding the role of holes, although we can confirm their importance, we cannot distinguish between a direct hole (h^+) transfer to naphthalene or its indirect oxidation via surface-trapped holes ($-OH_s^-$).

2.5

(a)



Naphthalene conversion / µmol 2.0 1.5 1.0 Photolysis Naphthalene 0.50 Naphthalene-TBA Naphthalene-KI 0.0 0.30 (b) 0.25 0.20 0.15 0.10 0.050 0.0 0.15 (c) 0.12 0.090 0.060 0.030 0.0 ò Time / min

Figure 5. Kinetic profiles for the disappearance of naphthalene (a), the formation of naphthalen-1-ol (b), and the formation of naphthalen-2-ol (c) during the photocatalytic reforming of naphthalene in the presence of different scavengers over Pt-UV100. [catalyst] = 1 g L⁻¹; 156 μ mol L⁻¹ aqueous solution of naphthalene; 20 mmol/L of KI and TBA; UV illumination. The initial amount of naphthalene for all reactions was considered after 1 h dark adsorption. Lines are guides for the eye.

Moreover, by means of an electrochemical degradation process, Li and Goel ⁶⁶ showed that naphthalene degradation was not affected by the presence of acetone and methanol as an OH competitor, suggesting that naphthalene degradation occurred as a result of direct electron transfer. Thus, they excluded the indirect oxidation via the OH. We applied a simple model by Luo *et al.*⁶⁷ to determine the Gibbs free energy (ΔG°) for the single electron transfer reaction from benzene, naphthalene, and anthracene to OH to produce the corresponding radical

cation and hydroxide ions. The calculated values are +24.6, +1.7, and -21.5 kcal mol⁻¹, respectively. It is thus apparent that by increasing the number of aromatic rings in the organic compound the reaction becomes more spontaneous. Hence, naphthalene has a higher tendency to react with OH forming a radical cation, rather than an adduct, as is the case for benzene.



Figure 6. EPR spectra recorded during the photocatalytic reforming of naphthalene after 15 seconds in the presence of DMPO, DMPO- TBA, and DMPO-KI. [catalyst] = 1 g/L; 156 µmol/L aqueous solution of naphthalene; 20 mmol/L of KI and TBA; irradiation using UV(A); microwave frequency: 9.51 GHz.

3.3.3 Diffuse reflectance transient absorption spectroscopy

To evaluate the formation of short-lived species during the reaction, we turned to diffuse reflectance transient absorption spectroscopy. **Figure 7** shows the spectra obtained 300 ns after the laser excitation (355 nm, 6 mJ pulse⁻¹) of anaerobic Pt-TiO₂ slurries in the presence of (a) a (1:1) water/acetonitrile mixture and (b) naphthalene in the same solvent. In the absence of naphthalene, excitation of Pt-TiO₂ leads to a relatively featureless transient spectrum, slightly increasing at short wavelengths. Since Pt acts as an electron sink, this signal can be readily attributed to trapped holes, with an absorption maximum reported at around 430 nm.⁶⁸. On the contrary, in the presence of naphthalene, we could identify at least two distinct bands: a very broad one between 540 and 670 nm, and a narrow band at 685 nm. Since in this case, where both a hole scavenger (naphthalene) and an electron scavenger (Pt nanoparticles) are present, these bands can be ascribed to transient species related to naphthalene. Indeed, an absorption band at 685 nm has been attributed to the naphthalene radical cation in homogeneous photolysis experiments.^{48, 69} Moreover, due to its high reactivity, the radical cation can readily react with a second naphthalene molecule, giving rise to a naphthalene dimer radical cation which shows an absorption centered at 580 nm.⁶⁹ In addition, we also note that electronic interactions between polyaromatic radical cations and the TiO₂ surface have

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been attributed to the occurrence of new absorption bands, red-shifted with respect to the free species. ⁷⁰ Taking this into consideration, we attribute the broad transient spectrum of **Figure 7** to a convolution of the signals of the free naphthalene radical cation, the radical cation of its dimer, and the same ions interacting with the TiO₂ surface.



Figure 7. Diffuse reflectance transient absorption spectroscopy spectra obtained 300 ns after the laser excitation (355 nm, 6 mJ pulse⁻¹) of anaerobic Pt-TiO₂ slurries in the presence of (a) a (1:1) water/acetonitrile mixture and (b) naphthalene (NP) in the same solvent.

3.3.4 Origin of the evolved molecular hydrogen.

In order to identify the origin of the evolved H_2 , we performed isotopic substitution studies on the photoreforming of naphthalene, using in-line monitoring of H_2 , HD, and D_2 via quadrupole mass spectrometry (QMS), as shown in **Figure S11**.

The first evident effect of replacing H_2O by D_2O is a progressive decrease in the total amount of evolved gases as the D_2O fraction increases **Figure 8**. Considering the two extreme cases, pure H_2O and pure D_2O , the ratio between the amounts of evolved gases after 4h is ~1.3. Although we observed a smaller effect, similar behavior has been observed for the photocatalytic reforming of formaldehyde ⁷¹ and benzene ¹⁴ over platinized TiO₂ and interpreted on the basis of a hindered production of '*OH* radicals when using D_2O , which limited the rate of the reaction. In the present case, however, we rule out that these radicals play an important role in naphthalene's decomposition (**Figure 6**). In our interpretation, therefore, the observed kinetic isotope effect responds to a rate-determining step related to proton reduction ^{72, 73}, although further experiments are necessary to ascertain this hypothesis.

With respect to the identity of the evolved gases, it is remarkable that neither H_2 nor HD are detected when using 100% D₂O. We note that similar results have been previously interpreted as proof that water (and not the SED) is the source of H_2 in the photocatalytic reforming of methanol ²³. However, proton exchange reactions in aqueous media are extremely fast, and thus it is also possible that the hydrogen atoms originate from the sacrificial donor. Since the solvent's isotopic species are present in an overwhelming majority, the exchange reaction could mask the real origin of the atoms. On the other hand, recent reports have shown that in some photocatalytic systems the production of H_2 from SEDs can be sufficiently fast and spatially localized to avoid proton exchange, leading to isotopic compositions of the gases matching those of the sacrificial donor ⁷⁴. From our analysis, we can conclude that such effects are not operative in the present system.



Figure 8. Isotopic distribution of the evolved gases (H_2 , and D_2) from the photocatalytic reforming of aqueous naphthalene and deuterated naphthalene over Pt-UV100 employing D_2O and H_2O . Conditions: reaction volume, 15 mL; [Naphthalene] = 235 μ mol L⁻¹; [catalyst] = 1 g L⁻¹; T = 25 °C; illumination with simulated solar light.

In the experiments performed with intermediate fractions of H_2O and D_2O (**Figure S12**), we observe, as expected from these arguments, a mixture of gases that approximately follows the isotopic composition of the solvent. The distributions, however, are skewed towards protium-rich gases (i.e. primarily H_2 , and in second term HD), due to the above-mentioned preferential protium reduction. A clear illustration of this effect is given by the 50% $H_2O - 50\% D_2O$ composition, which yields H_2 and HD in almost a similar amount, but no D_2 .

Additionally, we studied the effect of using fully deuterated naphthalene, **Figure 8**. In agreement with the previous experiments, the ratio between the amounts of evolved gases after 4h is 1.4. The photoreforming of deuterated naphthalene in H_2O leads to the exclusive formation of H_2 . In D_2O , obviously, only D_2 is formed. Interestingly, the total amount of evolved gases in both solvents coincides, within experimental error, with the amounts observed using non-deuterated naphthalene. This suggests that, in contrast with water, hydrogen abstraction from naphthalene is not involved in the rate-determining step of the reaction. Similar conclusions have been drawn for the photocatalytic reforming of aqueous benzene over platinized TiO_2^{14} .

3.4 Mechanism of the photocatalytic reforming of naphthalene

We now unify the acquired knowledge into a plausible mechanism for the photocatalytic reforming of naphthalene, summarized in **Scheme 1**. Considering that naphthalene only absorbs light of wavelengths shorter than 315 nm (**Figure S4**) ⁹, the use of simulated sunlight leads to the exclusive excitation of TiO₂, with the concomitant generation of electron-hole pairs (Equation 6). From the EPR experiments and the associated photocatalytic runs in the presence of scavengers, we postulate that OH_{free} radicals do not play an important role in the initial reaction of naphthalene. Naphthalene's degradation, thus, is initiated either by a direct hole transfer or indirectly via its reaction

with surface trapped holes $(-OH_{S})$. This reaction can in principle follow two pathways: either a single electron transfer (SET) leading to the production of a radical cation (Equation 7), or a hydrogen abstraction reaction, leading to a naphthyl radical (Equation 8). If the latter were to occur, however, we would expect a strong effect from the presence of OH_{free} , since they would promptly react with the naphthyl radicals to yield naphthalenol (Equation 9). Instead, we propose the formation of the naphthalene radical cation (Equation 7), as we supported by the transient absorption spectroscopy experiments. This carbocation radical swiftly reacts with water to form an OH adduct (Equation 10)^{75,76}, in coincidence with the reported reactions of benzene with both persulfate and Pt-TiO₂ in aqueous media ^{77, 78}. The adduct itself reacts in either a further oxidation step (Equation 11), or a hydrogen abstraction by a hydrogen atom via a special type of "current doubling" (Equation 12) to form (as exemplified) naphthalen-1-ol (A), or naphthalene-2-ol (B). In this stage, we excluded the current doubling mechanism from either the naphthalene radical cation or the naphthalene radical for several reasons. The large difference between the oxidation potential of single electron transfer (1.85 V vs NHE) for naphthalene comparing with the conduction band (-0.5 V vs NHE)⁷⁹ of the TiO₂ does not allow the naphthyl radical cation to inject its unpaired electron in the conduction band of the TiO₂. Moreover, the ionization energy of the naphthalene radical cation is much larger than that for naphthalene (around 8.0 eV⁸⁰), which requires a much higher potential to transfer the unpaired electron⁸¹. This is in line with the observations of Hykaway et al., 82 who reported that naphthalene did not show any current doubling effect during its oxidation to a carbocation radical on the surface of the TiO₂ electrode.

Moreover, by using isotopically labeled TiO_2 we conclude that the surface oxygen atoms are not incorporated in the naphthalenols, thus leaving water as the source of oxygen in the products. We note that this mechanism is conceptually equivalent to that proposed by Yoshida et al. ¹⁴ for the photocatalytic reforming of benzene, although we consider here the TiO_2 surface only implicitly.

The only non-oxygenated intermediated we observed during the photooxidation of naphthalene over Pt-UV100 is 1,1'-binaphthalene (**H**). Its formation can be explained by the coupling of two naphthyl radical cations accompanied by proton release (Equation 13), or of one radical cation with the mother compound (Equation 14) The equivalent compound biphenyl has previously been observed in the anaerobic photocatalytic oxidation of benzene by Hashimoto et al, ⁷⁷. Thus, the formation of this compound supports the SET mechanism.

The naphthalenols are susceptible to be further oxidized, by a similar mechanism, to different diols, of which we only observed naphthalene-1,4-diol (**C**) in significant amounts. In turn, the diols can be readily oxidized to form the respective naphthoquinones, such as the detected naphthalene-1,4-dione (**D**). A new hydroxylation step yields another of the detected intermediates, 5-hydroxynaphthalene-1,4-dione (**F**) ¹². Alternatively, **D** can after successive oxidation steps, undergo a ring cleavage reaction to produce phthalic acid (**K**), which upon alkylation with alkyl radicals (•**R**) can produce the detected dialkylphthalates (**E**). The formation of the esters could be aided by the production of carboxylate radicals in the first step of the photo-Kolbe reaction,⁸³ and their subsequent coupling with alkyl radicals (Equations 15 and 16).⁸⁴ In fact, Zhang et al. ¹¹ found that phthalate esters are the main intermediates during the photooxidation of phenanthrene over TiO₂ suspensions. Moreover, this reaction has been reported in the literature during the degradation of different PAHs in homogeneous systems ^{85, 86}. The ring-opening reactions and

further oxidations eventually lead to short-chain carboxylic acids, of which we observed formic and acetic acids. Their decarboxylation via a photo-Kolbe reaction ⁸⁷ can thus be the source of the alkyl radicals.

As noted above, we detected the 1,4-diol (C), but not the 1,2- isomer. The reactivity of such diols is however very high. In the case of the anaerobic degradation of benzene, it has been reported that the equivalent diol undergoes a rapid ring cleavage reaction to yield muconic acid, which upon successive oxidation yields CO_2^{77} . We thus interpret the absence of the 1,2-diol as proof of its high reactivity, instead of its lack of formation. A similar argument applies to naphthalene-1,2-dione (J).

$$Pt/TiO_2 + hv \longrightarrow Pt/TiO_2 | h^+ + e^{-1}$$
(6)

$$\frac{h^+ / -OH_S}{(+ \cdot)} \quad (+ OH_S)$$
(7)

$$(8)$$



$$H_{2} O H_{2}^{+} H_{2} O H_{2}^{+} H_{2} O H_{2}^{+} H_{2}^{+} H_{2}^{+} O H_{2}^{+} H_{2}^{+} H_{2}^{+} O H_{2}^{+} H_{2}^{+$$

$$\begin{array}{c} H \\ \hline \\ H \\ \hline \\ H \\ \hline \\ H \\ \hline \\ H \\ H_{(ads)} \end{array} \longrightarrow \begin{array}{c} OH \\ H \\ H_{2}(f) \end{array}$$
(12)

$$2 \underbrace{)}_{(++)} \longrightarrow \underbrace{}_{(++)} + 2H^{+}$$
(13)

$$(14)$$

Looking at the reductive side, the photogenerated electrons have a strong tendency to accumulate in the platinum particles. Once there, they can reduce protons to hydrogen atoms (Equation 17), which, upon dimerization, form H_2 (Equation 18). Notably, although the successive oxidation of naphthalene may yield protons (e.g. Equations

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Error! Reference source not found. and **Error! Reference source not found.**), the fast exchange reaction with water (Equation 19) implies that the origin of the protons that eventually are reduced may be indistinguishable.

In the same way, as the organic intermediates can compete with naphthalene for holes, they can also compete for the photogenerated electrons. This explains the observation of partially reduced compounds, such as 1,2,3,4-tetrahydro-1-naphthalenol (**G**) and 1,2,3,4-tetrahydro-1-naphthalenone (**I**). Additionally, the reduction may not be direct, but rather related to the hydrogen atoms produced by Equation 12. For instance, Yoshida et al. have shown their direct involvement in the photoreforming of benzene ¹⁴.

$$R'CO_2^- + h^+ \rightarrow [R'CO_2^-] \rightarrow \dot{R} + CO_2$$
(15)

$$RCO_2 + R' \rightarrow RCO_2 R$$
 (16)

 $Pt/TiO_2[e^-] + \dot{H}_{(ads)} \longrightarrow Pt/TiO_2 + \dot{H}_{(ads)}$ (17)

$$2\dot{H}_{(ads)} \rightarrow H_2(\uparrow) \tag{18}$$

$$H_2O + 'H_{(aq)} \longrightarrow HO'H + H_{(aq)}$$
(19)

4. Conclusions

We have studied the photocatalytic degradation of naphthalene, the most abundant polycyclic aromatic hydrocarbon in water, coupled with the production of molecular hydrogen, a potential energy vector for a sunlightbased economy. Although the photocatalyst TiO₂ initiates the degradation of naphthalene in anaerobic conditions under simulated sunlight irradiation, the evolution of molecular hydrogen requires the presence of a platinum cocatalyst. By applying a combination of chromatographic and mass spectroscopic techniques, we have performed close monitoring of the stable reaction intermediates, finding that 1- and 2-naphthalenol, acetic acid, and formic acid are the ones present in largest concentrations in the solution, while H₂ and CO₂ are the only gaseous products. Many possible pathways for photoinduced reforming of naphthalene involving different reactive species on the surface of photoexcited Pt/TiO₂ have been tested. The use of Ti¹⁸O₂ did not lead to a significant evolution of ¹⁸O-enriched CO₂, suggesting that lattice oxygen atoms are not incorporated into this product. In addition, experiments using solvents with variable H₂O - D₂O compositions and deuterated naphthalene led to an isotopic composition of the evolved hydrogen matching those of the solvent, and not that of naphthalene. By analyzing the reaction rates, we further determined that water (but not naphthalene) appears to be involved in the rate-determining step of the reaction. Furthermore, by performing photocatalytic experiments in the presence of a hole and hydroxyl radical scavengers, we determined that only the former plays a significant role in the oxidation of naphthalene. Complementary spin trapping experiments using electron paramagnetic resonance spectroscopy confirm this notion. Moreover, transient absorption spectroscopy allowed us to detect the radical cations of naphthalene and its dimer as short-lived species in the nanosecond time scale, in addition to their interaction with the Pt/TiO₂ surface. On the basis of the results, the most probable reaction route is the formation of naphthalene radical cation via SET from naphthalene, scavenging the photogenerated hole in the Pt/TiO₂ surface. This carbocation radical swiftly reacts with water to form an OH

adduct which furtherly oxidized by another hole to produce the hydroxylated naphthalene. Concomitantly, the photogenerated electrons reduced the proton originated mainly from water to molecular hydrogen.

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Scheme 1 Proposed mechanism for the photocatalytic reforming of naphthalene over Pt-UV100 under simulated sunlight. *Note: Compounds inside dashed square were not detected during the by-products identification.*

Supporting information

The Supporting Information is available free of charge at <u>https://pubs.acs.org</u>.

Material characterization (BET surface area, XRD, TEM and EPR), scheme of samples preparation, photonic efficiency determination, naphthalene dark adsorption, photocatalyst reusability, conditions for the HPLC separations, QMS signal of Photocatalytic CO₂ and H₂ evolution, retention time and ions peaks for the detected compounds by GC-MS, identified intermediates in aerobic conditions from previous study, EPR spectra, QMS signals for the photocatalytic H₂, HD, and D₂ evolution, and UV–Vis absorption spectra for naphthalene solution.

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