

Article

H₂ Photoproduction Efficiency: Implications of the Reaction Mechanism as a Function of the Methanol/Water Mixture

Irene Barba-Nieto ^{1,2}, Gerardo Colón ³, Anna Kubacka ^{1,*} and Marcos Fernández-García ^{1,*} 

¹ Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, 28049 Madrid, Spain; irene.barba.n@gmail.com

² Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

³ Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, C/Américo Vespucio 49, 41092 Sevilla, Spain; gcolon@icmse.csic.es

* Correspondence: ak@icp.csic.es (A.K.); mfg@icp.csic.es (M.F.-G.)

Abstract: The influence of the reaction pathway of the sacrificial molecule oxidation to generate hydrogen is here investigated for lean and rich methanol reaction mixtures. Pt-TiO₂ powders promoted or not with tin sulfide were used as catalysts. With the help of in situ infrared experiments under reaction conditions, methanol evolution was shown to take place by hole-related oxidation steps, with alkoxy and carbon-centered species as key radical species. The study analyzed quantitatively the fate and chemical use of the photons absorbed by the solids with the help of the quantum efficiency and the useful fraction of photons observables. Within this framework, the role of the sulfide component to promote photoactivity is interpreted, braiding chemical and photonic information.

Keywords: H₂; quantum efficiency; fraction of useful photons; mechanism



Citation: Barba-Nieto, I.; Colón, G.; Kubacka, A.; Fernández-García, M.

H₂ Photoproduction Efficiency: Implications of the Reaction Mechanism as a Function of the Methanol/Water Mixture. *Catalysts* **2022**, *12*, 402. <https://doi.org/10.3390/catal12040402>

Academic Editors: Hugo de Lasa and Salvador Escobedo

Received: 22 February 2022

Accepted: 2 April 2022

Published: 6 April 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Hydrogen is considered as an energy vector with importance for achieving a more sustainable future. The production of this molecule using light as the energy source and methanol/water mixtures is a hot topic within the catalysis field. In fact, photocatalytic generation of such an energy vector from bio-derived molecules as methanol corresponds to an environmentally benign and carbon-neutral process, deserving intensive research. Within the field of hydrogen photoproduction, the use of titania-based platinum-promoted catalysts appeared as one of the most interesting materials to promote the enhancement of activity and optimize performance [1–4].

For a photocatalytic reaction, a well-known measure of the efficiency is proposed by the IUPAC through the definition of the quantum efficiency parameter (η_q) [5]. This parameter, if correctly calculated, can provide a quantitative measure of the number of hydrogen molecules obtained per photon absorbed by the catalyst [6]. In brief, Equation (1) provides the mathematical formulation of the observable.

$$\eta_q(\%) = \frac{\langle r \rangle_A}{\langle e^a \rangle_A} \times 100 \quad (1)$$

In this equation and considering the liquid-phase hydrogen photoproduction from methanol/water mixtures, r is the photoproduction reaction rate and e^a is the local volumetric rate of photon absorption. These two last observables correspond to average values (A subindex), which are calculated over the entire volume of the reactor and wavelength range of the illumination source [5]. In addition, a closely related and recently proposed parameter is the fraction of useful photons, η_u , which is obtained using Equation (2) [7,8].

$$\eta_u = \frac{\langle r \rangle_A}{\langle e^a \rangle_A S} \quad (2)$$

Equation (2) can be also expressed in percentage. The S factor is defined as Equation (3):

$$S = \sum_i n_i S_i \quad (3)$$

In Equation (3), i runs over all products of the reaction, S_i is the fractional selectivity to product i , and $1/n_i$ is the number of charge carrier species required to obtain 1 mole of the molecule utilized to express the reaction rate. The equation can handle two possible cases: a target molecule forming several products and/or a product obtained from different reaction intermediates (the latter being the case of hydrogen photogeneration). Equation (3) allows to account for the fate of the charge carrier species ending up in the generation of chemical products. Considering that one photon generates one hole–electron pair, comparison between Equations (1) and (2) indicates that the S factor allows to calculate the fraction of the absorbed photons utilized to run the chemical reaction. Therefore, η_u is a chemically-sensitive parameter that provides additional input with respect to the quantum efficiency. In brief, it provides a true measurement of the photon use in any photo-catalytic reaction. Here, it has been formulated in relation to the quantum efficiency but can also be trivially formulated with respect to the photonic efficiency [6].

The S factor has been used previously for a significant number of gas and liquid-phase photo-catalytic reactions [7–12]. Nonetheless, for hydrogen production, we will use it here for the first time. Of course, to analyze the implications of the mechanism in the hydrogen production (and utilize Equation (3)) from a wide range of methanol/water mixtures, a first (obvious) point is to provide a chemical connection of the hydrogen production with the carbon-containing molecules obtained from methanol. This will allow to track the associated number of charge carrier species utilized per hydrogen molecule generated.

The corresponding chemical steps of the reaction mechanism here studied concern the methanol evolution by attack of radical species. Protons (and at the end hydrogen) are formed concomitantly to each oxidation step of the sacrificial molecule. As mentioned in numerous contributions and reviews, the mechanism is defined by the initial hole-related attack to the carbon-containing performance [1–3,13,14]. Normally, an alkoxy (methoxy)-type radical is proposed as the initial methanol-derived radical and evolves, by successive oxidation steps, to formaldehyde, formic acid, and carbon dioxide. Numerous publications also detected the formation of methyl formate from the interaction of the alkoxy-type radical and surface formate-type species as well as carbon monoxide coming from several decarbonylation processes of formaldehyde and/or carboxylate-type surface species [9,13,15]. In addition, in some works, ethylene glycol and the subsequent oxidation products (such as acetaldehyde and acetic acid) are observed [16,17]. Ethylene glycol is formed with participation of a carbon-centered radical instead of an alkoxy one. Obviously, this radical promotes the formation of carbon–carbon bond(s), and this has been exploited using sulfide-based photocatalysts [18,19]. The carbon-centered route can also generate carbon monoxide and dioxide products, using similar (decarbonylation, total oxidation) steps to the ones mentioned for alkoxy type radical. Finally, some additional products can be formed by the subsequent attack of electron-rich hydrogen-type species to some carbon-based adsorbed species leading to hydrocarbon species [1,15,20]. Of course, the last type of chemical steps competes with the use of electrons to generate the hydrogen molecule from protons formed concomitantly to the oxidized carbon-containing species. So, a crucial point to understand how the efficiency of the reaction is optimized is to rationalize and interpret the influence of the mechanism on the consumption of charge carrier species and, finally, on hydrogen production.

Here, we attempt to accomplish such a task for both methanol-rich and lean mixtures, as, potentially, quite different results may be expected as a function of the methanol content of the reaction mixture. Thus, such a study will be of general application. In particular, we would calculate how the efficiency of the reaction, as measured by the quantum efficiency and, particularly, the useful fraction of photons, evolves as a function of the methanol/water mixture for two titania-based catalysts. The bare promoting effect of the platinum metal

is selected as one of the studied catalysts. The additional presence of a sulfide-phase, attempting to promote specific routes for methanol radical species, is considered for a second system. The work shows that hydrogen photoproduction is optimized by an efficient balance of the different routes to activate the methanol molecule.

2. Results and Discussion

As described previously, our two systems are nearly identical in terms of BET surface area (in the $124\text{--}128\text{ m}^2\text{ g}^{-1}$ range), anatase and platinum primary particle size (ca. 11.5 and 4.1 nm, respectively), and (anatase) band gap energy (3.2 eV) [21]. So, their comparison would allow extracting the effect of the additional semiconductor phase in the photocatalytic activity. In Figures 1 and 2, we display the optical properties and the volumetric rate of photon absorption observables for, respectively, the T and T-S samples. Note that the origin (0, 0) of the volumetric rate of photon absorption plot is positioned at the lower left corner of the panel. This point corresponds to the (z, height coordinate) surface of the liquid closer to the light source and the (x, radial coordinate) center of the cylindrical reaction vessel (Figure 3).

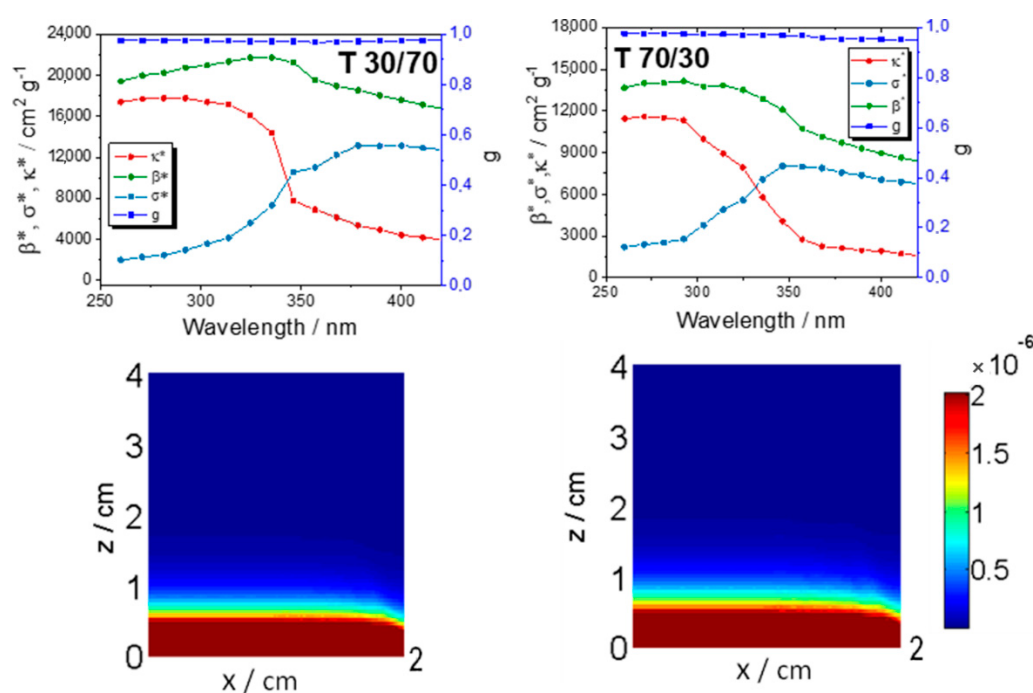


Figure 1. T sample optical properties and volumetric rate of photon absorption ($\text{Einstein cm}^{-3}\text{ s}^{-1}$) for lean and rich methanol mixtures.

For simplicity, Figures 1 and 2 illustrate the results using the methanol lean and rich cases. Differences in optical properties mainly correspond to the different aggregation state (secondary particle size) of the solids [22–24]. As a main effect, we can highlight the decrease in the extinction coefficient observed as the methanol content of the mixture grows. The extinction coefficient has also a slightly different behavior with wavelength for the two samples under study. Such differences, particularly the first, lead to a (modestly) higher penetration depth along the “z” coordinate of the reaction vessel (see the bottom part of the figures). The samples display a g value above 0.95, indicating that in all cases, we have a dominating forward-scattering phenomenon. This could be characteristic of high surface area pure anatase samples [25], which here renders a rather uniform rate of photon absorption value along the perpendicular coordinate to the light main propagation path (x coordinate in the plots of Figures 1 and 2).

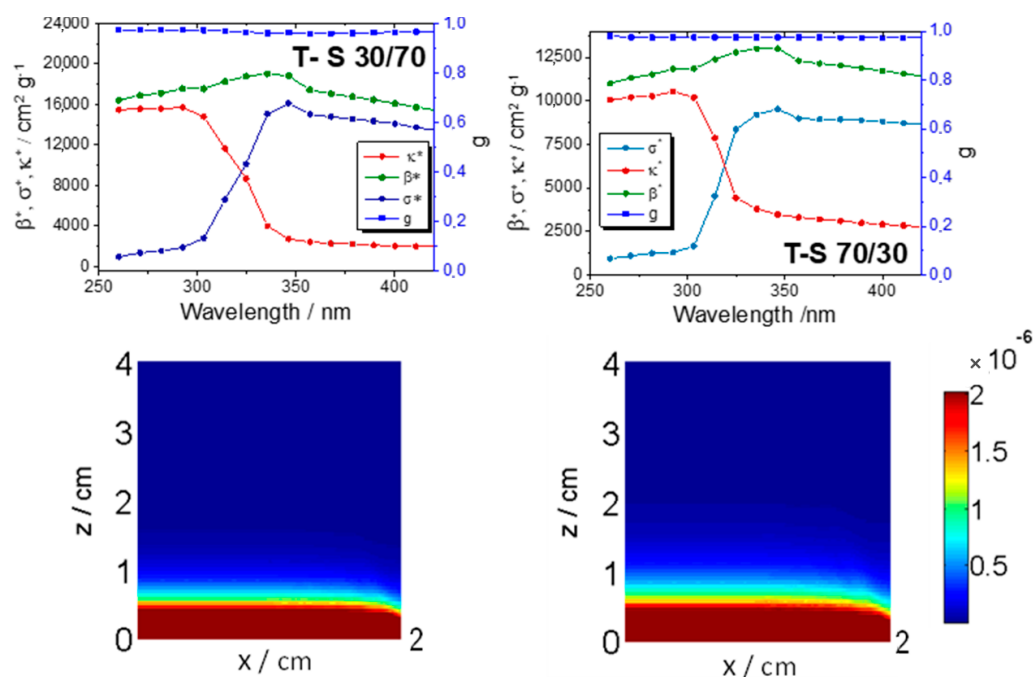


Figure 2. T-S sample optical properties and volumetric rate of photon absorption ($\text{Einstein cm}^{-3} \text{s}^{-1}$) for lean and rich methanol mixtures.



Figure 3. Experimental reactor utilized in the experiments. Elements: (1) Hg lamp, (2) water filter, (3) dichroic filter (280–400 nm), (4) methanol–water/catalyst suspension, (5) argon carrier inlet, (6) argon carrier and gas products outlet, and (7) neutral filter. Red dotted arrows indicate inlet and outlet cooling water.

In Table 1, we summarize all products detected in the experiments. The two samples provide the same products although with different selectivity. The alkoxy route generates carboxylate-types species, formic acid, and methyl formate. These are typical main products of Pt-TiO₂ composites [9,17,25,26]. However, the less studied, carbon-centered radical route renders a larger number of products such as ethylene glycol, acetaldehyde, acetic acid, and also C₃ products such as 2-methoxyacetaldehyde [27]. Carbon dioxide can be produced by any route; however, an analysis of adding increasing quantities of ethylene glycol to methanol/water mixtures indicates that it is dominantly produced though the alkoxy route. The reaction mechanism is investigated in detail using infrared spectroscopy.

Table 1. Products generated in the reaction and corresponding balance equations. Products from alkoxy (in blue) and carbon-centered (in red) type radical species are presented in Equations (18)–(23), respectively. Carbon dioxide can be generated from all radical species. Equation number in parentheses.

Molecule	Balance Equation	
Formic acid	$\text{CH}_3\text{OH} + \text{H}_2\text{O} + 4\text{h}^+ + 4\text{e}^- \rightarrow \text{CH}_2\text{O}_2 + 2 \text{H}_2$	(18)
Methyl formate	$2 \text{CH}_3\text{OH} + 4\text{h}^+ + 4\text{e}^- \rightarrow \text{C}_2\text{H}_4\text{O}_2 + 2 \text{H}_2$	(19)
Ethylene glycol	$2 \text{CH}_3\text{OH} + 2\text{h}^+ + 2\text{e}^- \rightarrow \text{C}_2\text{H}_6\text{O}_2 + \text{H}_2$	(20)
Acetaldehyde	$2 \text{CH}_3\text{OH} + 2\text{h}^+ + 2\text{e}^- \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + \text{H}_2$	(21)
Acetic acid	$2 \text{CH}_3\text{OH} + 4\text{h}^+ + 4\text{e}^- \rightarrow \text{CH}_3\text{COOH} + 2 \text{H}_2$	(22)
2-methoxyacetaldehyde	$3 \text{CH}_3\text{OH} + 4\text{h}^+ + 4\text{e}^- \rightarrow \text{C}_3\text{H}_6\text{O}_2 + \text{H}_2\text{O} + 2 \text{H}_2$	(23)
Carbon dioxide	$\text{CH}_3\text{OH} + \text{H}_2\text{O} + 6\text{h}^+ + 6\text{e}^- \rightarrow \text{CO}_2 + 3 \text{H}_2$	(24)

Figures 4 and 5 display the infrared results for the T sample and the 30/70 and 70/30 methanol/water mixtures, respectively. Figures 6 and 7 summarize the same type of results for the T-S sample. The presence of methoxy species is pointed out by the C-O stretch frequency observed, in all cases, between 1030 and 1040 cm^{-1} . A side (less intense) band at ca. 1090 cm^{-1} may indicate the presence of bridged methoxy species [28–30]. The methoxy species shows increasing intensity as the methanol content of the reaction mixture increases for the two samples under study. As observed in the absorption step of the experiment (dark conditions at Figures 4–7), the surface contact of methanol with the catalysts generated carbon-containing adsorbed species concomitantly to displacement of water from the surface (negative band in our difference spectra at ca. 1625–1640 cm^{-1} , which was accompanied with two broad positive bumps under illumination, one at each size of the negative signal ascribable to water desorption). So, a significant number of species appear in the catalyst(s) surface even at dark conditions. Specifically, bands at ca. 1500–1520, 1450, and 1410 cm^{-1} can be ascribed to bidentate and other (likely monodentate, indicated by the 1450 cm^{-1} band) carboxylates [8,30–32]. The intensity of the carboxylate-type species always grows under illumination. The mentioned carboxylate moieties appear to be the main products detected at the surface of the samples and their presence demonstrates the existence of an alkoxy-based path to generated hole-related oxidized carbon-containing species, as stated previously in several publications [8,33–36]. This path would be dominated here by the chemical step displayed in Equation (18) of Table 1, describing the formation of formic acid. We also detected CO species adsorbed on the noble metal particles at ca. 2025–2031 and (a weak shoulder at ca.) 2055 cm^{-1} [16,17,30]. As mentioned in the introduction section, CO is not detected as reaction product, which indicates, in first place, the existence of decarbonylation reactions to generate the chemical species and, also, the consumption of carbon monoxide through a water gas shift reaction, which further promotes the formation of hydrogen with the co-generation of carbon dioxide. The water gas shift efficiency to generate hydrogen depends critically on the Pt particle size and metal-support interface, as CO can act as a poison or not depending on the adsorption enthalpy, surface coverage, and degree of activation [9,26,35,37]. In our case, infrared CO signals display a marked dependence on the sample (sulfide inhibits to a significant extent the formation) and methanol content of the reaction mixture. Methyl formate is also detected as (liquid phase) product (Equation (19) in Table 1), but we cannot provide an unambiguous presence at the surface under reaction conditions using infrared due to the broad and ill-defined bands appearing at the carboxylate region. A reasonable similarity is observed in the overall shape of the IR spectra and thus between adsorbed species located at the surface of T and T-S samples, although obvious differences are observed in the carbonyl region. The last species is significantly suppressed in the presence of the sulfide. On the other hand, noticeable differences are detected for both samples as a function of the methanol content of the samples. These at least concern (i) the facility of methanol interaction with the catalyst(s) surface (and thus the methanol surface coverage under reaction conditions), (ii) the above-mentioned differences concerning CO signals, as well as (iii) those at the carboxylate region. Methanol interaction is always favored with

the increasing concentration of the molecule in the reaction mixture while, apparently, the formation of carboxylate-type species is diminished as the methanol content grows.

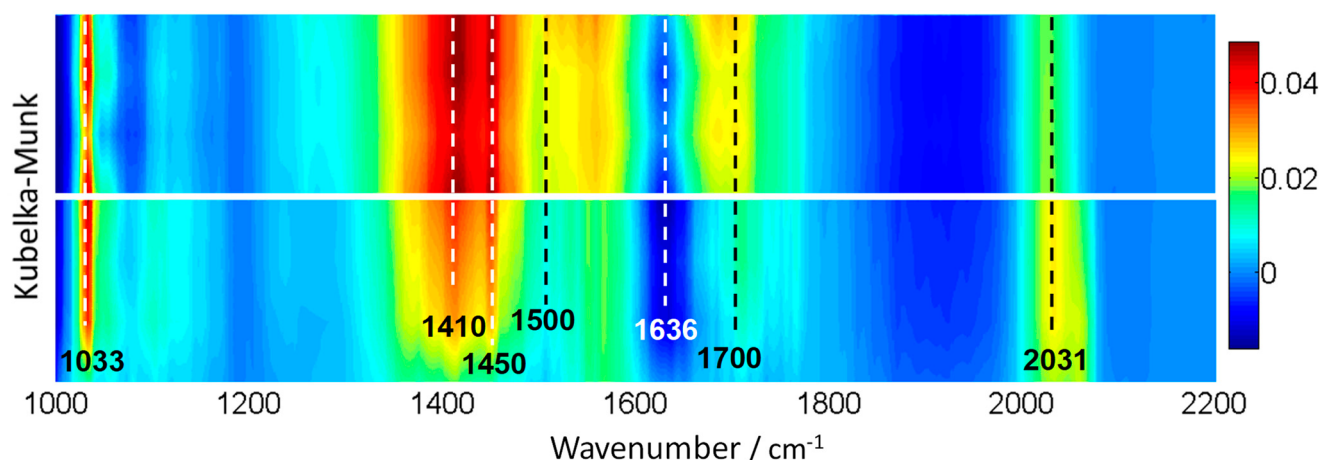


Figure 4. Difference infrared spectra of the T sample using a 30/70 methanol/water reaction mixture under dark (**bottom panel**) and illumination (**upper panel**).

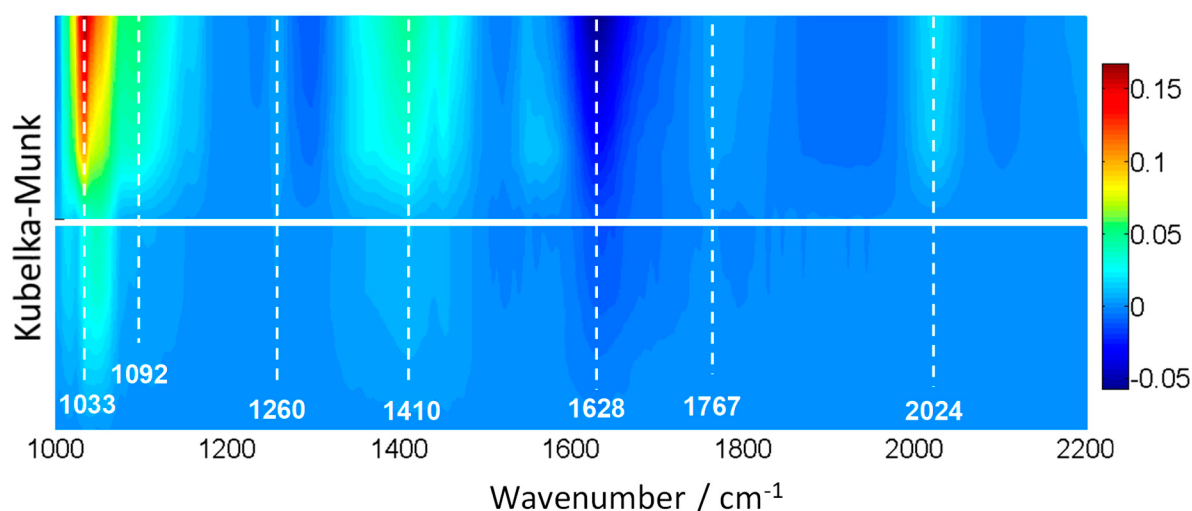


Figure 5. Difference infrared spectra of the T sample using a 70/30 methanol/water reaction mixture under dark (**bottom panel**) and illumination (**upper panel**).

As mentioned in the introduction section, Equation (1) (quantum efficiency, η_p) and Equation (2) (fraction of photon use, η_u) allow comparing the performance of the samples quantitatively from different perspectives. In Figure 8, we present these two observables and the reaction rate as a function of the methanol content of the mixture. From 30/70 to 70/30 methanol/water mixtures, the reaction rate shows a moderate increasing value for both samples. The quantum efficiency measures differences accurately. As can be seen in the corresponding plots, the T-S sample triples (on average) the performance of the T sample. As a function of the methanol content of the mixture, both samples show enhancing activity, with a more or less constant behavior for methanol-lean mixtures and an increasing trend for methanol-rich mixtures and starting at the 50/50 mixture. Going from methanol-lean to methanol-rich mixtures, the T sample increases by ca. 50%, but the T-S sample only does it by ca. 10%. So, on a relative basis, the two samples display evident differences. Considering the photon use (now expressed in percentage), we can observe that the magnitude is higher than in the case of the quantum efficiency. The higher values of the “photon use” come from S factors below unity. Nevertheless, the overall trend is similar to the quantum efficiency both in terms of the comparison between samples as

well as the methanol content of the reaction mixture. Yet fine (identifiable and significant) details differentiate the behavior of the two efficiency observables, as previously discussed.

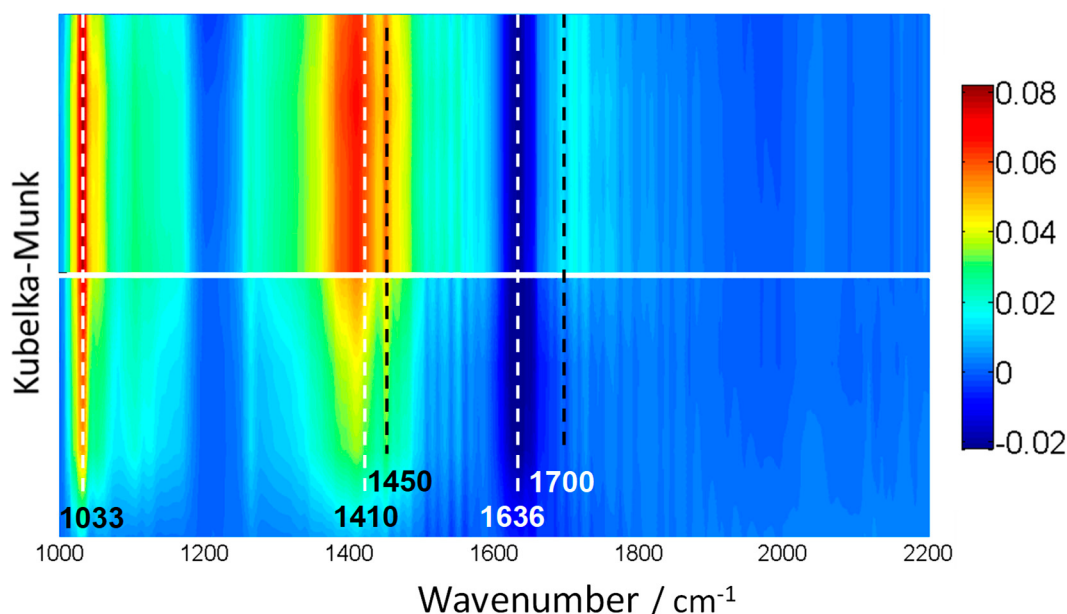


Figure 6. Difference infrared spectra of the T-S sample using a 30/70 methanol/water reaction mixture under dark (**bottom panel**) and illumination (**upper panel**).

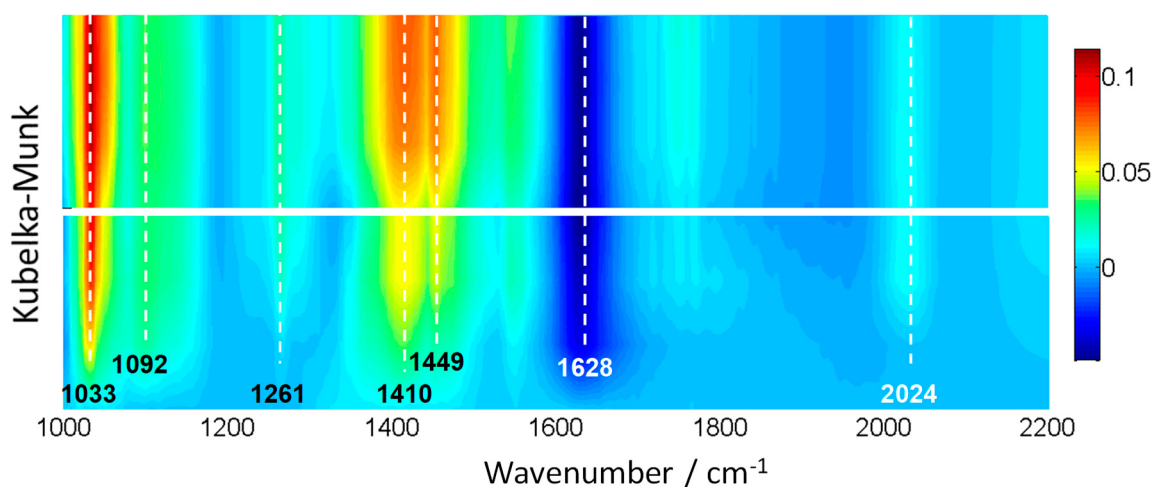


Figure 7. Difference infrared spectra of the T-S sample using a 70/30 methanol/water reaction mixture under dark (**bottom panel**) and illumination (**upper panel**).

An additional frequency appearing at 1261–1266 cm^{-1} for all samples in the presence of methanol-rich mixtures (Figures 4–7) can be ascribed to ethylene glycol [27]. This species is not observed or strongly suppressed for methanol-lean mixtures. To provide evidence of the assignment, Figure 9 shows an infrared study of the ethylene glycol/water mixture (ethylene glycol of ca. 1%) for the T-S sample. Similar results are obtained for the T sample (result not shown). Ethylene glycol is formed through a step summarized in Equation (20) of Table 1. As mentioned, this is the primary product of the carbon-centered radical species. Interestingly, we observe the formation of other carboxylate species (1410 and 1500 cm^{-1}), which are also generated in the alkoxy radical route, indicating the relatively unspecific nature of the bands ascribed to carboxylate species. However, the intensity of the carboxylate-type species is significantly lower than the observed under methanol/water mixtures. From ethylene glycol, the successive oxidation steps of the

molecule leads initially to acetaldehyde and acetic acid (Equations (21) and (22) of Table 1) generation. The 2-methoxyacetaldehyde is formed by absorbed methoxyl and acetyl-type species (Equation (23) of Table 1 describes the formation from methanol, the original reactant) [27,38].

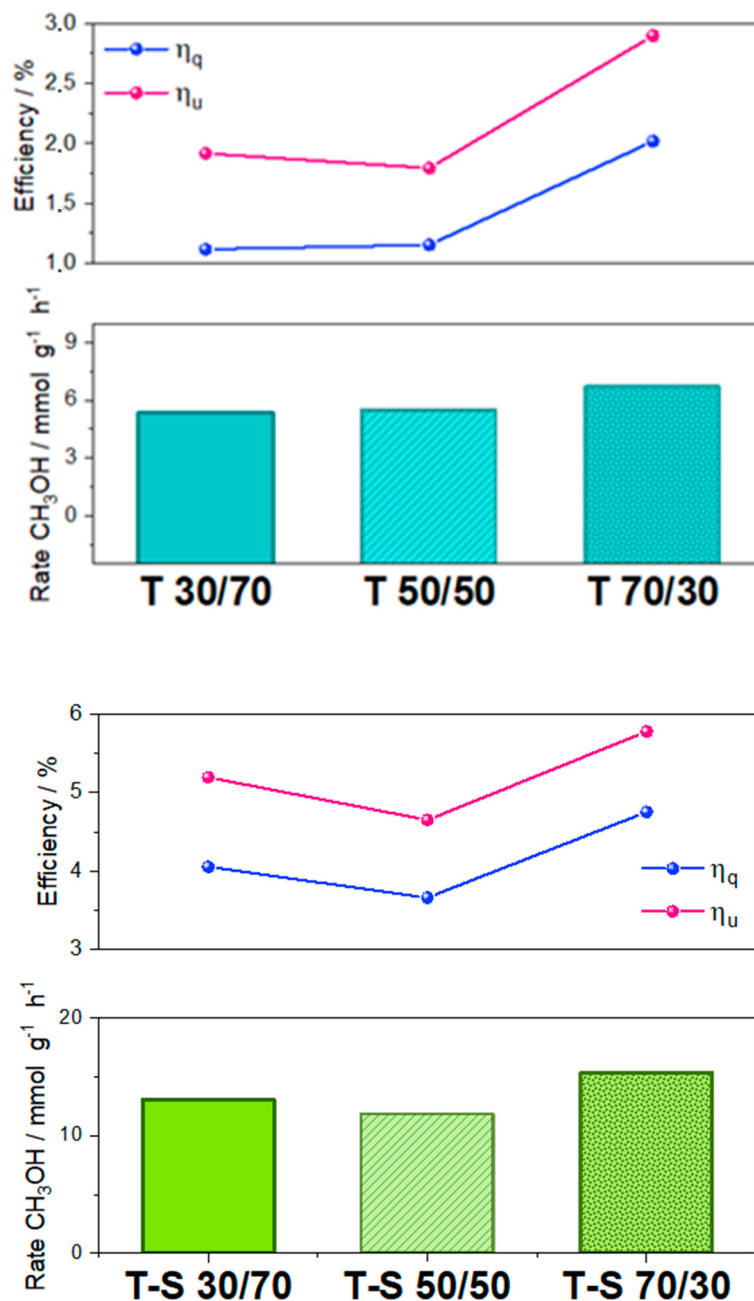


Figure 8. Reaction rate and efficiency observables (quantum efficiency, η_q , and photon usage, η_u) for the T and T-S samples as a function of the methanol content of the reaction mixture.

The acetic acid product may likely be the main product responsible for the carboxylate absorbed species detected in the absence of methanol and thus may contribute to the infrared spectra reported over the methanol/water mixture. In any case, the significance of the carbon-centered route for titania-based materials is here clearly demonstrated using infrared spectroscopy. We finally note that competition of ethylene glycol with water is different than the one taking place with methanol. In the presence of methanol water, it is removed to a significant degree from the surface (leading to a negative band at ca. $1650\text{--}1670 \text{ cm}^{-1}$), while in Figure 9, the mentioned band is positive, indicating that ethylene

glycol is not displacing the water molecule (from the surface) as much as methanol. This is a consequence of the relatively low degree of interaction of the ethylene glycol with the surface of the materials (mainly titania). The competitive adsorption phenomena taking place under reaction is evidenced with infrared. This means that methanol is the most akin molecule to be absorbed, followed by water and ethylene glycol. Both methanol and ethylene glycol are able to capture holes under illumination and generate oxidized species with the concomitant generation of protons. The presence of the sulfide component makes clear effects in the chemistry, as summarized in the previous paragraph for the alkoxy-type radical and, additionally, favors the generation of ethylene glycol (please, pay attention to the different scales in Figures 4–7). The influence of the complex reaction mechanism and different initial (methanol-derived) radical species derived from methanol on the catalytic performance of the solids is explored subsequently.

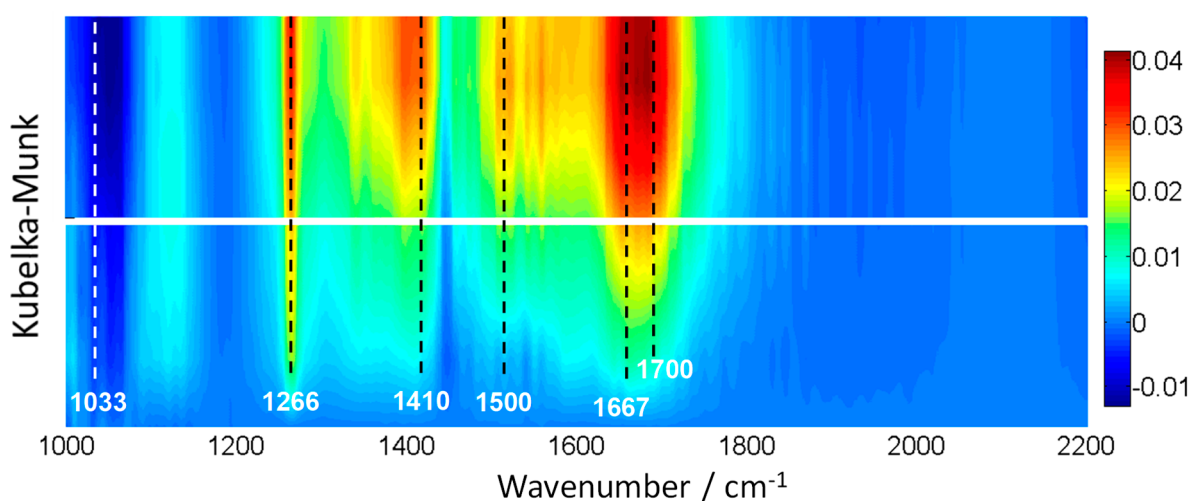


Figure 9. Difference infrared spectra of the T-S sample using an ethylene glycol/water mixture under dark (**bottom panel**) and illumination (**upper panel**).

To interpret the mechanism influence in the efficiency observables, Figure 10 displays the comparison between the contributions of the carbon-centered and alkoxy radical-derived species to the quantum efficiency and fraction of photon use. The corresponding products are enumerated in Table 1, and the chemical “balance” equations presented in the table are used to approach the problem. From the infrared study, we learned the increasing significance of the carbon-centered radical path as the methanol content of the reaction mixture grows, irrespective of the sample. An initial perspective would hold that the higher methanol content would favor the increasing importance of reaction routes implying two methanol molecules from the initial steps. The quantum efficiency ratio (which is equal to the reaction rate ratio between carbon-centered and alkoxy radical-derived species, Table 1) is below 1 for the T sample and above 1 for the T-S sample, and it increases rather smoothly as a function of the methanol content in both cases. Increasing factors of the ratio (along with methanol content growth) of 1.67 to 1.40 were obtained for, respectively, the T and T-S sample. Considering jointly the magnitude (ratio above/below 1 for the two samples, see right axis of Figure 10) as well as the behavior of the quantum efficiency ratio with methanol (content of the reaction mixture), the set of data indicates that in all experimental conditions tested (from methanol-lean to rich reaction mixtures), the carbon-centered derived species are significantly more important in the presence of the sulfide for all experimental conditions tested. When comparing the usage of the absorbed photons by the different methanol-derived radicals as a function of the methanol content of the mixture, we observed significantly lower variations than in the corresponding quantum efficiency ratio. This clearly indicates that the variation previously described for the quantum efficiency is modulated (significantly counteracted) by the one of the selectivity factor as a function of

the methanol content of the reaction mixtures. Going from methanol-lean to rich mixtures, the corresponding ratio (now, such ratio corresponds to the “carbon-centered rate” $\times$ “methoxy S factor” divided by the “methoxy rate” $\times$ “carbon-centered S factor”) goes from 1.13 to 1.00 (differences below 1% in the last case) for, respectively, the T and T-S samples. The T-S behavior is essentially constant for the photon usage but not for quantum efficiency. So, the photon usage and the quantum efficiency ratios provide different information when comparing samples (T vs. T-S) and their behavior as a function of the methanol content. Note that the result cannot be directly extracted from the number of charge carriers present in Table 1, and the chemical driving of the selectivity (as can be outlined in the infrared) is critical in order to express specific methanol-radical derived products. Summarizing, the here-described analytical scheme to interpret efficiency observables allows understanding the chemical bases of the catalytic use of photons in the production of hydrogen using methanol as a sacrificial molecule. In other words, the present study highlights the fact that in addition to the common morphological and optoelectronic properties of the solids typically considered in photocatalysis [39], the chemical properties of the materials should be considered in order to optimize hydrogen photoproduction and to extract information about the chemical use of photons by catalysts.

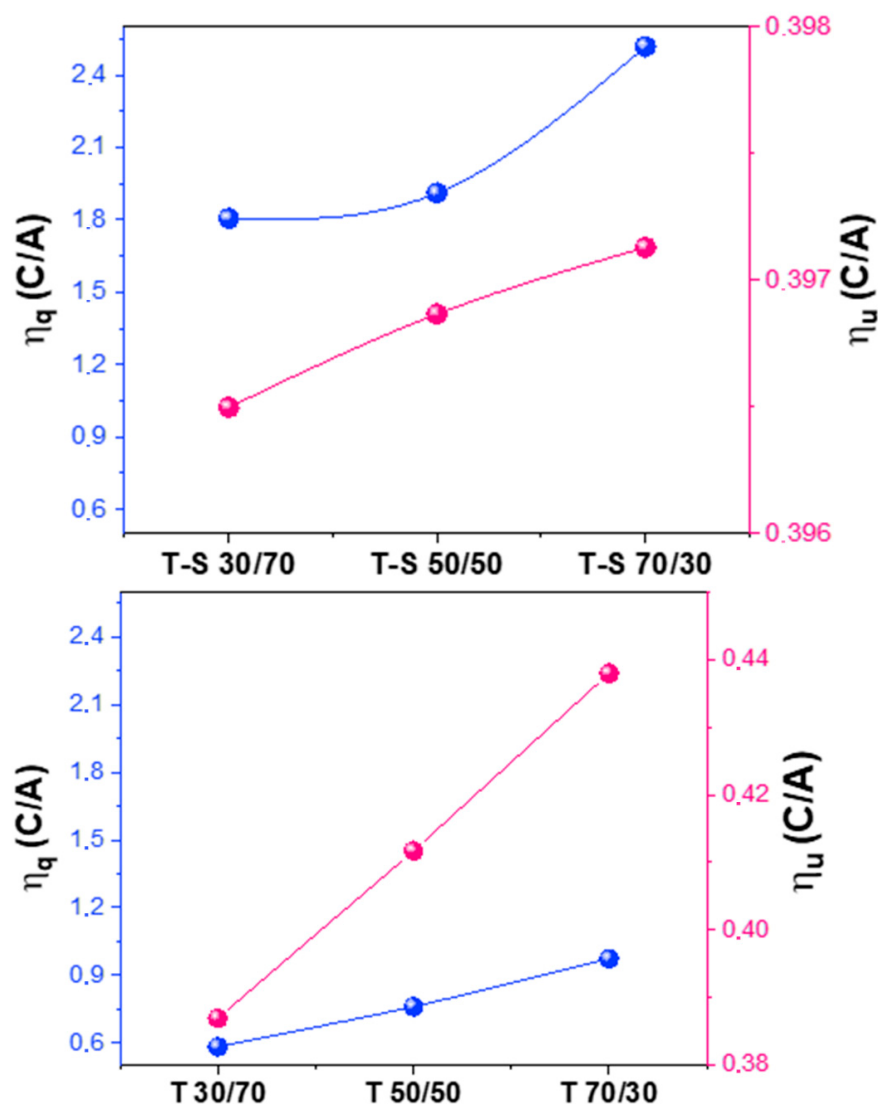


Figure 10. Ratio of efficiency observables (quantum efficiency, η_q , and photon usage, η_u) between the contribution of carbon-centered (C in the figure) and alkoxy (A in the figure)-derived reaction products. T and T-S samples are presented (see OX axis labels).

3. Materials and Methods

3.1. Catalysts Preparation

The titania-based support preparation was carried out following a sequential procedure. Titanium tetra-isopropoxide was added drop by drop to a reverse emulsion, with n-heptane as a non-polar component, water as a polar component, Triton X-100 (Aldrich, Wyoming, IL, USA) as surfactant, and hexanol as cosurfactant. Water/Ti and water/surfactant molar ratios were maintained constant for all samples, taking values of 110 and 18, respectively. The resulting liquid was stirred for 24 h, centrifuged, decanted, and rinsed with methanol. Then, the solid was dried at 110 °C for 12 h. After drying, the solids were calcined using a heating ramp (1 °C min^{−1}) up to 450 °C, maintaining this temperature for 2 h. In subsequent steps, we include tin sulfide (SnS_x) as the second semiconductor and Pt as co-catalyst in an order to optimize activity [21]. So, the co-catalyst was introduced by a deposition method over titania-based powders using a H₂PtCl₆ (Aldrich, Wyoming, IL, USA) in solution. First, the titania component was suspended in a deionized water solution for 30 min. After that, the proper quantity of H₂PtCl₆ was added to the solution and kept on stirring. Precipitation was carried out using NaBH₄ (Aldrich, Wyoming, IL, USA) (Pt/NaBH₄ molar ratio 1/5). Pt loading was adjusted to obtain throughout the samples a constant 0.4 mol% of Pt on metal basis [21]. After drying the solid at room temperature, the semiconductor was finally deposited on the powder using SnCl₄ (Aldrich, Wyoming, IL, USA) and thioacetamide (TTA, Aldrich, 99%) and a hydrothermal method in a Teflon-lined stainless-steel autoclave at 160 °C for 16 h. The SnCl₄/TTA molar ratio was constant and equal to 0.5, and a 0.5 mol% SnS_x was utilized. After idle cooling of the autoclave to room temperature, the solid was washed with distilled water and dried at 100 °C.

3.2. Catalytic Measurements

The liquid-phase production of hydrogen was measured using a liquid-phase semi-continuous reactor depicted in Figure 3. The system allows a continuous-mode production of the energy vector through the use of a carrier gas stream. Catalyst suspensions (optimized at 0.5 mg mL^{−1}) were tested from a complete series of water/methanol mixtures. The reactor was degassed with an Ar stream for 15 min. Subsequently, the Ar flow was settled down to 10 mL min^{−1} and stabilized before reaction. Ar is used as a carrier to displace reaction gases in a continuous mode from the reactor to the detection system. The solution inside a reactor was irradiated using a Hg-Xe lamp (500 W) and dichroic filters (LOT Quantum Design, Darmstadt, Germany) allowing exposure of the catalysts to the UV (280–420 nm). Reaction rates and efficiency observables were reported according to the IUPAC recommendations [5]. Analysis of reaction products was performed by means of GC-MS analysis (Agilent 7000D GC-MS Triple Quad, Colorado Springs, CO, USA) using a CP-Wax52 column (Agilent, Colorado Springs, CO, USA).

3.3. Efficiency Calculations: Volumetric Rate of Photon Absorption

The average volumetric rate of photon absorption (required in Equations (1) and (2)) can be obtained by solving the Radiative Transfer Equation (RTE) in the reaction system. The nomenclature utilized in this section is presented at the end of the manuscript.

Figure 3 displays the reactor. The RTE is presented in Equation (4). This assumes: (i) the emission radiation is negligible and (ii) steady-state condition (light emittance and chemical reaction) during the photocatalytic processes [22].

$$\frac{dI_{\lambda,\underline{\Omega}}(\underline{x})}{ds} = -\kappa_{\lambda}I_{\lambda,\underline{\Omega}}(\underline{x}) - \sigma_{\lambda}I_{\lambda,\underline{\Omega}}(\underline{x}) + \frac{\sigma_{\lambda}}{4\pi} \int_{\Omega'=4\pi} p(\underline{\Omega}' \rightarrow \underline{\Omega}) I_{\lambda,\underline{\Omega}'} d\Omega' \quad (4)$$

To solve Equation (4), a first step requires determining the optical properties of the photocatalysts suspensions. Specifically, the spectral absorption coefficient (κ_{λ}), the spectral scattering coefficient (σ_{λ}), and the scattering phase ($p(\underline{\Omega}' \rightarrow \underline{\Omega})$) are to be obtained. For TiO₂-based catalysts, the Henyey and Greenstein phase function (Equation (5)) was customarily used to calculate the scattering phase function [22,23].

$$p(\underline{\Omega}' \rightarrow \underline{\Omega}) = \frac{1 - g_\lambda^2}{(1 + g_\lambda^2 - 2g_\lambda u_0)^{3/2}} \quad (5)$$

where g_λ is the so-called asymmetry factor and u_0 is the director cosine between incoming and outgoing light.

The optical properties of the systems were collected with the help of a spectrophotometric cell. The corresponding RTE (which considers radiation absorption and scattering effects at the reaction medium) was solved using the discrete ordinate method (DOM). Before that, the extinction coefficients (β^* ; sum of absorption and scattering coefficients) were (experimentally) obtained by applying a standard linear regression to the plots of β_λ versus catalyst concentration, C . To carry out such a task, the rectangular cell is represented as an infinite plane parallel medium with azimuthal symmetry. The corresponding one-dimensional, one-directional radiation transport model can be used to solve the RTE (Figure 11A).

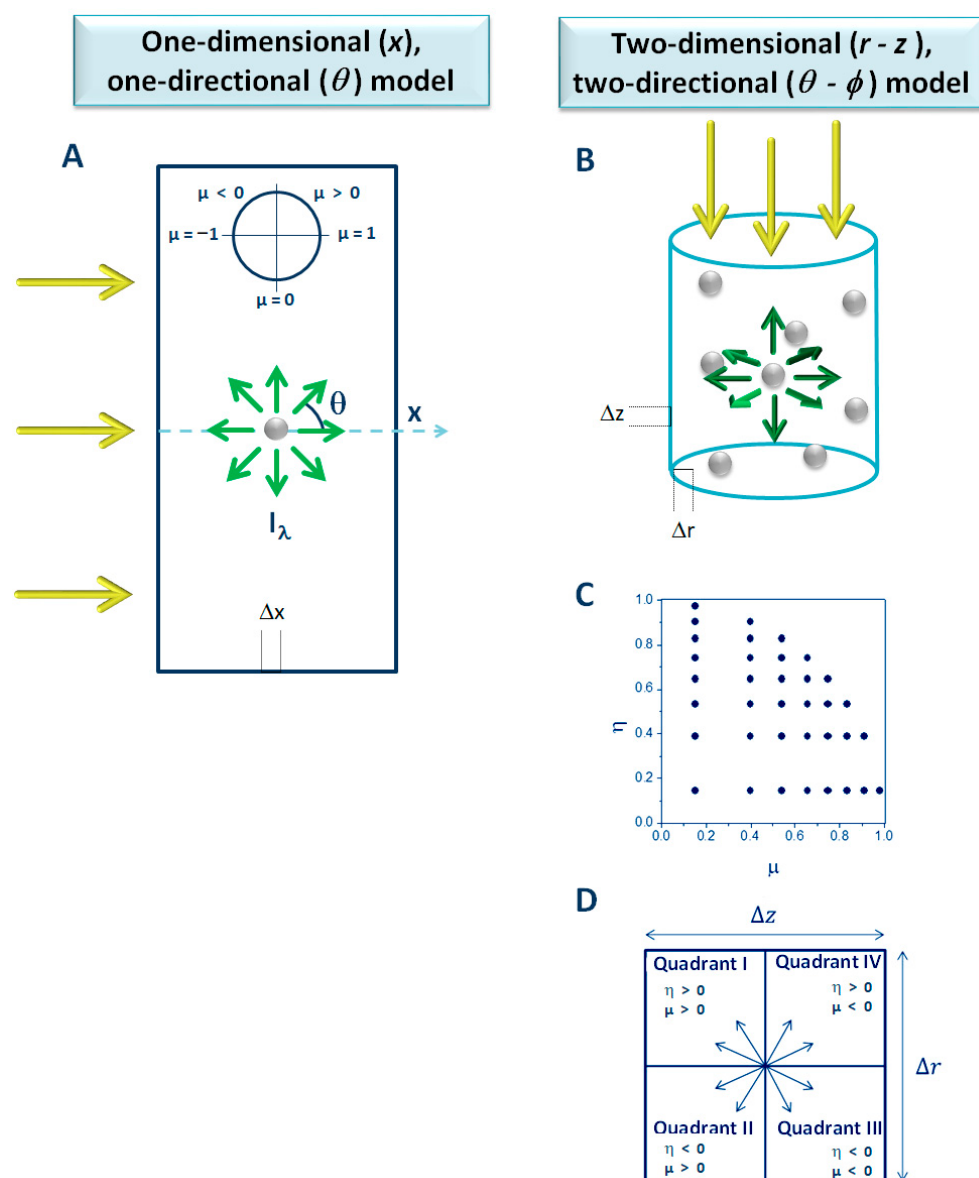


Figure 11. Spectrophotometric cell and one-dimensional, one-directional radiation model (A). Reactor vessel and two-dimensional, two-directional radiation model (B–D). The directional mess for quadrant I and the representation of the quadrants (at each spatial point) are presented in panels (C,D), respectively.

Figure 11A encloses a schematic representation of the spectrophotometer cell and the corresponding RTE solution scheme. The latter considers that each propagation path (departing from each point of the cell) of the net light intensity can be defined by a one angular-related variable ($\mu = \cos(\theta)$), one-dimensional (x variable) representation. For each x point and starting from the corresponding boundary condition, the light intensity for positive or negative μ values was obtained by solving a unidimensional DOM representation of Equation (4) in combination with a nonlinear, multiparameter least-square regression procedure (MATLAB lsqnonlin, Algorithm: Trust-Region-Reflective Optimization). An iterative process is carried out until error for all intensity values are lower than 1%. The output of the fitting provides values for ω_λ (the so-called albedo defined in Equation (6)) and g_λ (Equation (5)) parameters. To this end, the calculation carried out the minimization of the differences between the model and the experimental data corresponding to diffuse transmittance and reflectance measurements at the spectrophotometric cell. The corresponding data set is obtained for a range of catalyst concentrations, C , and considering the wavelength range of the light source [40]. The process renders the volumetric scattering and absorption coefficients:

$$\sigma_\lambda = \beta_\lambda * \omega_\lambda \quad (6)$$

$$\kappa_\lambda = \beta_\lambda - \omega_\lambda \quad (7)$$

Once the optical properties of the catalyst(s) have been obtained, we proceed to evaluate the radiation field inside the photoreactor. The DOM tool was used to transform the integro-differential Equation (4) into a system of algebraic equations that can be solved numerically. Our reactor configuration demands the use of a cylindrical two-dimensional ($r - z$ variables), two-directional ($\theta - \phi$ variables) model of the photoreactor radiation field (Figure 11B,C). The net radiation intensity at each $r - z$ point of the reactor is now represented using a discretized spatial mesh having two angular-related coordinates $\mu = \cos(\theta)$; $\eta = \cos(\phi)$. Figure 11C displays μ ; η unitary, basal projection(s) in a quadrant (quadrant I) of the space around an $r - z$ point calculated using the so-called S_{16} method [41]. For the two-dimensional representation of the space, the calculation of the intensity at each point of the reactor requires dividing the space into four quadrants as depicted in Figure 11D and the measurement of the incident light intensity at the boundary (liquid surface) using actinometry and potassium ferric oxalate [41]. Boundary intensity for UV illumination takes a value of 1.10×10^{-8} Einstein $\text{cm}^{-2} \text{s}^{-1} \text{sr}^{-1}$. Using Duderstadt and Martin's procedure [42] and numerical tools developed in previous contributions [41], the finite difference (DOM) was derived directly from the radiation balance for each mesh cell (Figure 11D). In this way, the central intensity at each cell (I_m^{ij}) can be calculated from the previous ones starting from the appropriate boundary values ($I_m^{1\pm 1/2,j}$, $I_m^{i,j\pm 1/2}$) as well as one "auxiliary" one coming from the directional mesh ($I_{m-1/2}^{ij}$) as:

$$I_m^{ij} = |\mu_m| \left(A_{i+1/2,j} - A_{i-1/2,j} \right) D^{-1} I_m^{1\pm 1/2,j} + 2|\eta_m| B_{i,j} D^{-1} I_m^{i,j\pm 1/2} + \left(A_{i+1/2,j} - A_{i-1/2,j} \right) \cdot (v_{m+1/2} + v_{m-1/2}) D^{-1} W_m^{-1} I_{m-1/2}^{ij} + \frac{\sigma_\lambda}{4\pi} \sum_{n=1}^M I_n^{ij} P_{nm} W_n V_{i,j} D^{-1} \quad (8)$$

where

$$D = |\mu_m| \left(A_{i+1/2,j} - A_{i-1/2,j} \right) + 2|\eta_m| B_{i,j} + \left(A_{i+1/2,j} - A_{i-1/2,j} \right) \cdot (v_{m+1/2} + v_{m-1/2}) W_m^{-1} + \kappa_\lambda V_{i,j} + \sigma_\lambda V_{i,j} \quad (9)$$

$$A_{i+1/2,j} = 2\pi r_{i+1/2} \Delta z_j \quad (10)$$

$$B_{i,j+1/2} = 2\pi \left(\frac{(r_{i+1/2} + r_{i-1/2})}{2} \right) \Delta r_i \quad (11)$$

$$V_{i,j} = 2\pi \left(\frac{(r_{i+1/2} + r_{i-1/2})}{2} \right) \Delta z_j \Delta r_i \quad (12)$$

The calculation at each of the four quadrants starts from the corner of the spatial mesh in which two of the four boundary conditions are in place. For our reactor, the four boundary conditions are: (i) known inlet radiation for quadrants I and II at $z = 0$; (ii) null reflection in the inner reactor wall surfaces (see Figures 3 and 11). The ascending m values are always utilized, selecting as $m = 1$ the angular direction more parallel to the r - z plane. For that, $I_m^{i,j-1/2}$ is approximated to zero [9,43]. Using this and Equation (13), the recursive Equation (8) can be applied to the cell closer to the boundary conditions and so forth.

$$\nu_{m+1/2} - \nu_{m-1/2} = -\mu_m W_m \quad (13)$$

For each quadrant, the intensities defined at each spatial mesh cell follow Equations (14)–(16).

$$I_m^{i,j} = \frac{(I_m^{i-1/2,j} + I_m^{i+1/2,j})}{2} \quad (14)$$

$$I_m^{i,j} = \frac{(I_m^{i,j-1/2} + I_m^{i,j+1/2})}{2} \quad (15)$$

For the directional mesh:

$$I_m^{i,j} = \frac{(I_{m-1/2}^{i,j} + I_{m+1/2}^{i,j})}{2} \quad (16)$$

The linear intensity variation inside each spatial mesh cell (an approximation with increasing accuracy as the finite, Δr and Δz elements approach zero) is assumed in these equations. After the observable is obtained, the local volumetric rate of photon absorption ($e^{a,v}$) was calculated at each $r - z$ point of the reactor according to:

$$e^{a,v} = \int_{\lambda} \kappa_{\lambda}(\underline{x}) \cdot \int_{\Omega=4\pi} I_{\lambda,\Omega}(\underline{x}) d\Omega d\lambda \quad (17)$$

The optical properties and volumetric rate of photon absorption were calculated for catalyst suspensions using three reaction mixtures (methanol/water ratio of 30/70, 50/50, and 70/30).

3.4. In Situ Infrared Experiments

A Bruker Vertex 80 FTIR spectrometer (Bruker, Santa Barbara, CA, USA) with an MCT detector (OPUS/IR software, v6.3, Bruker, Santa Barbara, CA, USA) was used to obtain infrared spectra. The set-up uses a praying mantis DRIFTS accessory (Harrick Scientific, Pleasantville, NY, USA) and a reaction cell (HVC, Harrick Scientific). The reaction mixture was prepared by injecting the appropriate methanol/water mixture in a N_2 flow before entering the DRIFTS cell. Parallel experiments were run with ethylene glycol. Inlet and outlet lines are heated at 130 °C. The DRIFTS spectra were collected in the range of 4000–600 cm^{-1} with a resolution of 1 cm^{-1} , by averaging 10 scans over a total of ca 15 s. In DRIFTS experiments, in situ light excitation was carried out using the same illumination source that the one of the reaction system. Each catalyst without pre-treatment was subjected to a single, multi-step experiment. Such an experiment proceeds as: (i) adsorption of the reactive mixture under dark conditions and subsequent (ii) evolution under illumination conditions. Each step of the treatment is carried out up to the absence of spectral evolution (ca. 30–35 min).

4. Conclusions

For the whole range of methanol/water mixtures, the performance of platinum promoted titania-based materials is analyzed in terms of the reaction mechanism for hydrogen photoproduction and, particularly, in connection with the different initial radical species formed by hole-type radical species to methanol. The existence of two routes of activation of the methanol molecule, originated from alkoxy and (a less studied) carbon-centered

radical species, is thoroughly investigated using in situ infrared spectroscopy. The catalytic effects in the absence/presence of an additional sulfide phase were interpreted with the help of the spectroscopic study and quantitatively analyzed using the quantum efficiency and fraction of photon use observables.

We provided evidence that the sulfide presence increases activity and, particularly, has a significant effect promoting the carbon-centered radical species and corresponding reaction products. Such catalytic effects are reflected to significantly higher values for the two efficiency observables here analyzed. Nonetheless, irrespective of the absence or presence of such a phase, the main trends presented by the quantum efficiency and photon usage as a function of the methanol content of the reaction mixture are broadly similar in the two samples. Yet, in the presence of the sulfide, photon usage shows a different trend than the quantum efficiency along with the increasing methanol content of the reaction mixture. So, in addition to increasing the values of the efficiency observables, the sulfide presence has also important consequences derived from the chemical selectivity factor, which in turn reflected on the chemical use of the absorbed photons. Thus, the new parameter allows including chemical effects in efficiency measurements and provides a quantitative estimation of them. In short, for all methanol-lean and rich mixtures, the study gives quantitative evidence that the sulfide phase not only enhances activity but also makes important effects in chemistry (favoring carbon-based radical formation) with direct influence in the “chemical use” of the photons absorbed by the solid.

Author Contributions: Conceptualization, A.K. and M.F.-G.; methodology, I.B.-N., G.C., A.K. and M.F.-G.; software, I.B.-N., G.C., A.K. and M.F.-G.; validation, I.B.-N., G.C., A.K. and M.F.-G.; formal analysis, I.B.-N., G.C., A.K. and M.F.-G.; investigation, I.B.-N., G.C., A.K. and M.F.-G.; resources, G.C., A.K. and M.F.-G.; data curation, I.B.-N., G.C., A.K. and M.F.-G.; writing—original draft preparation, I.B.-N., A.K. and M.F.-G.; writing—review and editing, I.B.-N., G.C., A.K. and M.F.-G.; visualization, I.B.-N., G.C., A.K. and M.F.-G.; supervision, A.K. and M.F.-G.; project administration, G.C., A.K. and M.F.-G.; funding acquisition, G.C., A.K. and M.F.-G. All authors have read and agreed to the published version of the manuscript.

Funding: Authors are thankful to MCIN/AEI/10.13039/501100011033 (Spain) for supporting the work carried out through the PID2019-105490RB-C31 and PID2020-119946RB-I00 grants. Financial support from the EU FEDER and Junta de Andalucía through P20-00156 I + D + i project is also acknowledged. I.B.-N. would like to thank MCIN/AEI/10.13039/501100011033 for an FPI doctoral fellowship (BES-2017-080069).

Data Availability Statement: Original data can be obtained from the corresponding authors upon request.

Acknowledgments: M.F.-G. is fully indebted to F. Fernández-Martín for general discussions. Authors also like to acknowledge the work of the “Unidad de Apoyo” at ICP-CSIC.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

$\underline{x}$	position vector (cm)
x	x coordinate (cm)
y	y coordinate (cm)
z	z coordinate (cm)
r	radial coordinate (cm)
I	specific radiation intensity (Einstein $\text{cm}^{-3} \text{s}^{-1} \text{sr}^{-1}$)
g	asymmetry factor of the Henyey–Greentein’s phase function (dimensionless)
$e^{a,v}$	local volumetric rate of photon absorption (Einstein $\text{cm}^{-3} \text{s}^{-1}$)
P	emission power (W)
V	volume (cm^3)
W	weight (dimensionless)
p	phase function (dimensionless)
S	selectivity factor (dimensionless)

Greek Letters

λ	wavelength (nm)
β^*	specific extinction coefficient ($\text{cm}^2 \text{g}^{-1}$)
κ^*	specific absorption coefficient (cm^{-1})
σ^*	specific scattering coefficient (cm^{-1})
μ	direction cosine (dimensionless)
η	direction cosine (dimensionless)
η_q	quantum efficiency
η_u	useful photon fraction
Ω	solid angle (sr)
$\underline{\Omega}$	unit vector in the direction of radiation propagation
θ	spherical coordinate (rad)
φ	spherical coordinate (rad)
β	volumetric extinction coefficient (cm^{-1})
κ	volumetric absorption coefficient (cm^{-1})
σ	volumetric scattering coefficient (cm^{-1})
ν	effective area for angular fluxes (cm^2)

Subscripts

λ	denotes wavelength dependence
m	denotes m position in a mesh

Special Symbols

$\underline{\quad}$	denotes vector
$\langle * \rangle$	average value over a defined space

References

- Chen, X.; Shen, S.; Guo, L.; Mao, S.S. Semiconductor-based Photocatalytic Hydrogen Generation. *Chem. Rev.* **2010**, *110*, 6503–6570. [\[CrossRef\]](#) [\[PubMed\]](#)
- Do, H.H.; Nguyen, D.L.T.; Nguyen, X.C.; Le, T.-H.; Nguyen, T.P.; Trinh, Q.T.; Ahn, S.H.; Vo, D.-V.N.; Kim, S.Y.; Le, Q.V. Recent progress in TiO₂-based photocatalysts for hydrogen evolution reaction: A review. *Arab. J. Chem.* **2020**, *13*, 3653–3671. [\[CrossRef\]](#)
- Fajrina, N.; Tahir, M. A critical review in strategies to improve photocatalytic water splitting towards hydrogen production. *Int. J. Hydrogen Energy* **2019**, *44*, 540–577. [\[CrossRef\]](#)
- Imizcoz, M.; Puga, A.V. Assessment of Photocatalytic Hydrogen Production from Biomass or Wastewaters Depending on the Metal Co-Catalyst and Its Deposition Method on TiO₂. *Catalysts* **2019**, *9*, 584. [\[CrossRef\]](#)
- Braslavsky, S.E.; Braun, A.M.; Cassano, A.E.; Emeline, A.V.; Litter, M.I.; Palmisano, L.; Parmon, V.N.; Serpone, N. Glossary of terms used in photocatalysis and radiation catalysis (IUPAC recommendations 2011). *Pure Appl. Chem.* **2011**, *83*, 931–1014. [\[CrossRef\]](#)
- Kubacka, A.; Barba-Nieto, I.; Caudillo-Flores, U.; Fernández-García, M. Interpreting quantum efficiency for energy and environmental applications of photo-catalytic materials. *Curr. Opin. Chem. Eng.* **2021**, *33*, 100712. [\[CrossRef\]](#)
- Muñoz-Batista, M.J.; Kubacka, A.; Hungria, A.B.; Fernández-García, M. Heterogeneous photocatalysis: Light-matter interaction and chemical effects in quantum efficiency calculations. *J. Catal.* **2015**, *330*, 154–166. [\[CrossRef\]](#)
- Muñoz-Batista, M.J.; Caudillo-Flores, U.; Ung-Medina, F.; Chávez-Parga, M.d.C.; Cortés, J.A.; Kubacka, A.; Fernández-García, M. Gas phase 2-propanol degradation using titania photocatalysts: Study of the quantum efficiency. *Appl. Catal. B Environ.* **2017**, *201*, 400–410. [\[CrossRef\]](#)
- Fontelles-Carceller, O.; Muñoz-Batista, M.J.; Rodríguez-Castellón, E.; Conesa, J.C.; Fernández-García, M.; Kubacka, A. Measuring and interpreting quantum efficiency for hydrogen photo-production using Pt-titania catalysts. *J. Catal.* **2017**, *347*, 157–169. [\[CrossRef\]](#)
- Caudillo-Flores, U.; Muñoz-Batista, M.J.; Cortés, J.A.; Fernández-García, M.; Kubacka, A. UV and visible light driven H₂ photo-production using Nb-doped TiO₂: Comparing Pt and Pd co-catalysts. *Mol. Catal.* **2017**, *437*, 1–10. [\[CrossRef\]](#)
- Caudillo-Flores, U.; Muñoz-Batista, M.J.; Hungria, A.B.; Haro, M.L.; Fernández-García, M.; Kubacka, A. Toluene and styrene photo-oxidation quantum efficiency: Comparison between doped and composite tungsten-containing anatase-based catalysts. *Appl. Catal. B Environ.* **2019**, *245*, 49–61. [\[CrossRef\]](#)
- Caudillo-Flores, U.; Avilés-García, O.; Alonso-Núñez, G.; Kubacka, A.; Fernández-García, M. Assessing quantitatively charge carrier fate in 4-chlorophenol photocatalytic degradation using globular titania catalysts: Implications in quantum efficiency calculation. *J. Environ. Chem. Eng.* **2021**, *9*, 106074. [\[CrossRef\]](#)
- Fontelles-Carceller, O.; Muñoz-Batista, M.J.; Conesa, J.C.; Fernández-García, M.; Kubacka, A. UV and visible hydrogen photo-production using Pt promoted Nb-doped TiO₂ photo-catalysts: Interpreting quantum efficiency. *Appl. Catal. B Environ.* **2017**, *216*, 133–145. [\[CrossRef\]](#)

14. Guayaquil-Sosa, J.F.; Serrano-Rosales, B.; Valadés-Pelayo, P.J.; Lasa, H.d. Photocatalytic hydrogen production using mesoporous TiO₂ doped with Pt. *Appl. Catal. B Environ.* **2017**, *211*, 337–348. [\[CrossRef\]](#)
15. Kumaravel, V.; Imam, M.; Badreldin, A.; Chava, R.; Do, J.; Kang, M.; Abdel-Wahab, A. Photocatalytic Hydrogen Production: Role of Sacrificial Reagents on the Activity of Oxide, Carbon, and Sulfide Catalysts. *Catalysts* **2019**, *9*, 276. [\[CrossRef\]](#)
16. Chiarello, G.L.; Ferri, D.; Selli, E. Effect of the CH₃OH/H₂O ratio on the mechanism of the gas-phase photocatalytic reforming of methanol on noble metal-modified TiO₂. *J. Catal.* **2011**, *280*, 168–177. [\[CrossRef\]](#)
17. Caudillo-Flores, U.; Muñoz-Batista, M.J.; Fernández-García, M.; Kubacka, A. Bimetallic Pt-Pd co-catalyst Nb-doped TiO₂ materials for H₂ photo-production under UV and Visible light illumination. *Appl. Catal. B Environ.* **2018**, *238*, 533–545. [\[CrossRef\]](#)
18. Xie, S.; Shen, Z.; Deng, J.; Guo, P.; Zhang, Q.; Zhang, H.; Ma, C.; Jiang, Z.; Cheng, J.; Deng, D.; et al. Visible light-driven C–H activation and C–C coupling of methanol into ethylene glycol. *Nat. Commun.* **2018**, *9*, 1181. [\[CrossRef\]](#)
19. Zhang, H.; Xie, S.; Hu, J.; Wu, X.; Zhang, Q.; Cheng, J.; Wang, Y. C–H activations of methanol and ethanol and C–C couplings into diols by zinc–indium–sulfide under visible light. *Chem. Commun.* **2020**, *56*, 1776–1779. [\[CrossRef\]](#)
20. Rusinque, B.; Escobedo, S.; Lasa, H.d. Hydrogen Production via Pd-TiO₂ Photocatalytic Water Splitting under Near-UV and Visible Light: Analysis of the Reaction Mechanism. *Catalysts* **2021**, *11*, 405. [\[CrossRef\]](#)
21. Barba-Nieto, I.; Christoforidis, K.C.; Fernández-García, M.; Kubacka, A. Promoting H₂ photoproduction of TiO₂-based materials by surface decoration with Pt nanoparticles and SnS₂ nanoplatelets. *Appl. Catal. B Environ.* **2020**, *277*, 119246. [\[CrossRef\]](#)
22. Satuf, M.L.; Brandi, R.J.; Cassano, A.E.; Alfano, O.M. Experimental method to evaluate the optical properties of aqueous titanium dioxide suspensions. *Ind. Eng. Chem. Res.* **2005**, *44*, 6643–6649. [\[CrossRef\]](#)
23. Du, Y.; Liu, M.; Guo, L. Numerical investigation on the optical properties of TiO₂ photocatalyst suspension by light scattering model of particulate aggregates. *J. Photonics Energy* **2021**, *11*, 016501. [\[CrossRef\]](#)
24. Song, D.; Hatami, M.; Wang, Y.; Jing, D.; Yang, Y. Prediction of hydrodynamic and optical properties of TiO₂/water suspension considering particle size distribution. *Int. J. Heat Mass Transf.* **2016**, *92*, 864–876. [\[CrossRef\]](#)
25. Muñoz-Batista, M.J.; Ballari, M.M.; Kubacka, A.; Alfano, O.M.; Fernández-García, M. Braiding kinetics and spectroscopy in photo-catalysis: The spectro-kinetic approach. *Chem. Soc. Rev.* **2019**, *48*, 637–682. [\[CrossRef\]](#)
26. Platero, F.; López-Martín, A.; Caballero, A.; Colón, G. Mechanistic Considerations on the H₂ Production by Methanol Thermal-assisted Photocatalytic Reforming over Cu/TiO₂ Catalyst. *ChemCatChem* **2021**, *13*, 3878–3888. [\[CrossRef\]](#)
27. Berto, T.F.; Sanwald, K.E.; Eisenreich, W.; Gutiérrez, O.Y.; Lercher, J.A. Photoreforming of ethylene glycol over Rh/TiO₂ and Rh/GaN:ZnO. *J. Catal.* **2016**, *338*, 68–81. [\[CrossRef\]](#)
28. Ouyang, W.; Muñoz-Batista, M.J.; Kubacka, A.; Luque, R.; Fernández-García, M. Enhancing photocatalytic performance of TiO₂ in H₂ evolution via Ru co-catalyst deposition. *Appl. Catal. B Environ.* **2018**, *238*, 434–443. [\[CrossRef\]](#)
29. Yamakata, A.; Ishibashi, T.; Onishi, H. Electron- and Hole-Capture Reactions on Pt/TiO₂ Photocatalyst Exposed to Methanol Vapor Studied with Time-Resolved Infrared Absorption Spectroscopy. *J. Phys. Chem. B* **2002**, *106*, 9122–9125. [\[CrossRef\]](#)
30. Halasi, G.; Schubert, G.; Solymosi, F. Comparative study on the photocatalytic decomposition of methanol on TiO₂ modified by N and promoted by metals. *J. Catal.* **2012**, *294*, 199–206. [\[CrossRef\]](#)
31. Liu, X.; Bao, C.; Zhu, Z.; Zheng, H.; Song, C.; Xu, Q. Thermo-photo synergic effect on methanol steam reforming over mesoporous Cu/TiO₂–CeO₂ catalysts. *Int. J. Hydrogen Energy* **2021**, *46*, 26741–26756. [\[CrossRef\]](#)
32. Walenta, C.A.; Courtois, C.; Kollmannsberger, S.L.; Eder, M.; Tschurl, M.; Heiz, U. Surface Species in Photocatalytic Methanol Reforming on Pt/TiO₂ (110): Learning from Surface Science Experiments for Catalytically Relevant Conditions. *ACS Catal.* **2020**, *10*, 4080–4091. [\[CrossRef\]](#)
33. Al-Azri, Z.H.N.; Chen, W.-T.; Chan, A.; Jovic, V.; Ina, T.; Idriss, H.; Waterhouse, G.I.N. The roles of metal co-catalysts and reaction media in photocatalytic hydrogen production: Performance evaluation of M/TiO₂ photocatalysts (M = Pd, Pt, Au) in different alcohol–water mixtures. *J. Catal.* **2015**, *329*, 355–367. [\[CrossRef\]](#)
34. Zhao, Y.; Li, Y.; Sun, L. Recent advances in photocatalytic decomposition of water and pollutants for sustainable application. *Chemosphere* **2021**, *276*, 130201. [\[CrossRef\]](#)
35. Estahbanati, M.R.K.; Babin, A.; Feilizadeh, M.; Nayernia, Z.; Mahinpey, N.; Iliuta, M.C. Photocatalytic conversion of alcohols to hydrogen and carbon-containing products: A cleaner alcohol valorization approach. *J. Clean. Prod.* **2021**, *318*, 128546. [\[CrossRef\]](#)
36. Zhao, J.; Shi, R.; Li, Z.; Zhou, C.; Zhang, T. How to make use of methanol in green catalytic hydrogen production? *Nano Sel.* **2020**, *1*, 12–29. [\[CrossRef\]](#)
37. Huang, H.; Feng, J.; Zhang, S.; Zhang, H.; Wang, X.; Yu, T.; Chen, C.; Yi, Z.; Ye, J.; Li, Z.; et al. Molecular-level understanding of the deactivation pathways during methanol photo-reforming on Pt-decorated TiO₂. *Appl. Catal. B Environ.* **2020**, *272*, 118980. [\[CrossRef\]](#)
38. Wu, X.; Xie, S.; Zhang, H.; Zhang, Q.; Sels, B.F.; Wang, Y. Metal Sulfide Photocatalysts for Lignocellulose Valorization. *Adv. Mater.* **2021**, *33*, 2007129. [\[CrossRef\]](#)
39. Ismael, M. Latest progress on the key operating parameters affecting the photocatalytic activity of TiO₂-based photocatalysts for hydrogen fuel production: A comprehensive review. *Fuel* **2021**, *303*, 121207. [\[CrossRef\]](#)
40. Siegel, R.; Pinar, M.; Howell, J.R. *Thermal Radiation Heat Transfer*; CRC Press: Boca Raton, FL, USA, 2015; ISBN 978-1466593268.
41. Romero, R.L.; Alfano, O.M.; Cassano, A.E. Cylindrical Photocatalytic Reactors. Radiation Absorption and Scattering Effects Produced by Suspended Fine Particles in an Annular Space. *Ind. Eng. Chem. Res.* **1997**, *36*, 3094–3109. [\[CrossRef\]](#)

-
42. Duderstadt, J.J.; Martin, W.R. *Transport Theory*; Wiley: New York, NY, USA, 1979; ISBN 047104492X/9780471044925.
 43. Marugán, J.; Grieken, R.V.; Cassano, A.; Alfano, O. Intrinsic kinetic modeling with explicit radiation absorption effects of the photocatalytic oxidation of cyanide with TiO₂ and silica-supported TiO₂ suspensions. *Appl. Catal. B Environ.* **2008**, *85*, 48–60. [[CrossRef](#)]