

# Photocatalytic production of hydrogen from binary mixtures of C-3 alcohols on Pt/TiO<sub>2</sub>: influence of alcohol structure

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## **Abstract**

The effect of alcohol structure on photocatalytic production of H<sub>2</sub> from C-3 alcohols was studied on 0.5% Pt/TiO<sub>2</sub>. A C-2 alcohol (ethanol) was also included for comparative purposes. For individual reactions from 10% v/v aqueous solutions of alcohols, hydrogen production followed the order ethanol  $\approx$  propan-2-ol > propan-1-ol > propane-1,2,3-triol > propane-1,2-diol > propane-1,3-diol. The process was found to be quite sensitive to the presence of additional alcohols in the reaction medium, as evidenced by competitive reactions. Therefore, propan-2-ol conversion was retarded in the presence of traces of the other alcohols, this effect being particularly significant for vicinal diols. Additional experiments showed that adsorption of alcohols on Pt/TiO<sub>2</sub> followed the order propane-1,2,3-triol > propane-1,2-diol > propane-1,3-diol > propan-1-ol > ethanol > propan-2-ol. Adsorption studies (DRIFT) and monitoring of reaction products showed that the main photocatalyzed process for propan-2-ol and propan-1-ol transformation is dehydrogenation to the corresponding carbonyl compound (especially for propan-2-ol both in the liquid and the gas phase). In the case of liquid-phase transformation of propan-1-ol, ethane was also detected which is indicative of the dissociative mechanism to lead to the corresponding C-1 alkane. All in all, competitive reactions proved to be very useful for mechanistic studies.

**Keywords:** hydrogen photocatalytic production; photoreforming; dehydrogenation; Pt/TiO<sub>2</sub>; competitive reactions of alcohols

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## 1. Introduction

The photocatalytic production of hydrogen has been shown as a green and promising technology for hydrogen generation since Fujishima and Honda produced hydrogen from water using  $\text{TiO}_2$  as a photocatalyst [1]. Many investigations have been carried out in order to improve the efficiency of this process. The addition of a sacrificial organic reagent leads to an improvement in hydrogen production through a photo-reforming process mainly, in which the sacrificial reagent reacts irreversibly with the hole thus preventing electron-hole recombination [2].

Several alcohols have been studied in the hydrogen photoproduction, such as methanol ethanol, propane-1,2,3-triol (glycerol) or sugars [3-5].  $\text{TiO}_2$  is the most studied catalyst and the modification with noble metals one of the most efficient ways found to improve its activity due to the metal nanoparticles trapping electrons and thus extending the electron-hole pair lifetime [5].

There are many factors influencing hydrogen photocatalytic production from alcohols, some of them being as follows:

- i) *Titania phase composition and morphology* [6, 7]. Cargnello et al [7], for instance, improved hydrogen production from alcohols through reduction of electron-hole recombination by tuning the structure of nanorods in the brookite phase. The phase composition of titania can also influence the morphology of the metal co-catalyst [8].
- ii) *The metal of choice* (nature, loading, particle size, morphology etc) [9-10]. In a previous work [10] on hydrogen photocatalytic production from propane-1,2,3-triol and propan-2-ol on  $\text{M/TiO}_2$  systems ( $\text{M}=\text{Au}, \text{Pt}, \text{Pd}$ ), we found that under our experimental conditions both processes were structure-sensitive with higher TOF

values obtained for bigger metal particle sizes (in all cases in the 2-5 nm range). Moreover, for propan-2-ol dehydrogenation TOF values followed the work function order (Pt>Pd>Au).

- iii) *The substrate*. Idriss et al [11] found a correlation between alcohol polarity (or oxidation potential) and hydrogen production. Moreover, it is also generally accepted that the presence of hydrogen atoms in alpha position with respect to hydroxyl groups favors photoreforming [5, 12]. An additional point to take into account is the possibility of byproducts being generated as the reaction proceeds. Carbon monoxide, for instance, is known to poison metals which would be detrimental to activity [13]. Sola et al [14] studied photocatalytic production of hydrogen from ethanol aqueous solutions. The authors ascribed the decrease in the hydrogen production rate as the reaction proceeded to the presence of some intermediate products (e.g. acetaldehyde, acetic acid, butane-2,3-diol).
- iv) *Other factors* affecting hydrogen production include the reactor configuration or light intensity, just to cite some of them [15].

There are several studies applying methods such as factorial design of experiments [15] or artificial neural networks [16] to estimate the extent to which the different factors influence hydrogen production and to optimize reaction parameters.

The motivation of the present piece of research is the study of hydrogen generation from binary mixtures of alcohols. There are two main reasons for that: a) it is interesting from the mechanistic point of view and can cast further light on some features such as adsorption of substrates; b) it means working on “more real” conditions. Most of the studies on hydrogen photoproduction from alcohols are usually carried out using neat alcohols or aqueous solutions whereas initial streams, especially if one tries to valorize biomass, will be rarely so pure. Ribao et al, for

instance [17], have recently compared hydrogen production from glycerol on titania modified with Pt deposited on graphene oxide. The authors found that hydrogen production dropped from 71 mmol·g<sup>-1</sup>·h<sup>-1</sup> down to 13 mmol·g<sup>-1</sup>·h<sup>-1</sup> when crude propane-1,2,3-triol (glycerol) rather than 20% glycerol in water was used, despite the catalyst concentration being doubled for experiments with crude glycerol.

## **2. Experimental**

### **2.1. Materials**

Ethanol (Art Nr. 51976), propan-1-ol (ref. 402893), propan-2-ol (Art. Nr. 190764), propane-1,2-diol (ref. G9012), propane-1,3-diol (ref. 82280) and propane-1,2,3-triol (glycerol, Ref. P5,040-4) were purchased from Sigma Aldrich. Milli-Q water was used for preparation of solutions.

The catalyst used in the present paper consists in Pt (0.5% by weight) deposited on TiO<sub>2</sub> (Degussa-Evonik P25) through the deposition-precipitation method whose synthesis is described elsewhere [10]. In short, TiO<sub>2</sub> was dispersed in distilled water at 60°C, stirring rate fixed at 150 rpm and pH set at 6.8 which was maintained throughout the whole process using an aqueous solution of 0.2M K<sub>2</sub>CO<sub>3</sub> (Merck Art. 4928). Then, 2g·L<sup>-1</sup> platinum aqueous solution (prepared from H<sub>2</sub>PtCl<sub>6</sub>·H<sub>2</sub>O, Re. 262587 from Sigma-Aldrich) were added, the mixture being aged for 1h. The solid was filtered, washed with distilled water until negative chlorine test (AgNO<sub>3</sub>), dried overnight (110°C) and calcined at 4h for 2h.

### **2.2. Characterization of the solid**

Platinum content was studied both by elemental analysis, ICP-MS, and EDX measurements. For ICP-MS, measurements were made on a Perkin-Elmer ELAN DRC-e instrument following dissolution of the sample. In the case of EDX, a JEOL JSM-6300

scanning electron microscope (SEM) equipped with an energy-dispersive X-Ray (EDX) detector was used. It was operated at an acceleration voltage of 20keV with a resolution of 65 eV.

Platinum average particle size were determined from Transmission electron microscopy (TEM) images obtained using a JEOL JEM 1400 microscope by counting 100 particles. Sample was mounted on 3 mm holey carbon copper grids.

Surface area was determined from nitrogen adsorption–desorption isotherms obtained at liquid nitrogen temperature on a Micromeritics ASAP-2010 instrument, using the Brunnauer–Emmett–Teller (BET) method. The sample was degassed to 0.1 Pa at 120°C prior to measurement.

Band gap value was obtained from diffuse reflectance UV–vis spectrum performed on a Cary 1E (Varian) instrument, using polytetraethylene (density = 1 g cm<sup>-3</sup> and thickness = 6 mm) as reference material.

X-ray photoelectron spectroscopy (XPS) data was recorded on 4 mm × 4 mm pellets 0.5 mm thick that were obtained by gently pressing the powdered materials following outgassing to a pressure below about  $2 \times 10^{-8}$  Torr at 150°C in the instrument pre-chamber to remove chemisorbed volatile species. The main chamber of the Leibold–Heraeus LHS10 spectrometer used, capable of operating down to less than  $2 \times 10^{-9}$  Torr, was equipped with an EA-200MCD hemispherical electron analyser with a dual X-ray source using AlK $\alpha$  (h $\nu$ = 1486.6 eV) at 120 W, at 30 mA, with C (1s) as energy reference (284.6 eV).

### ***2.3. Liquid-phase photocatalytic reactions***

The liquid-phase photocatalytic reactions were performed in a 30 mL double mouthed heart-shaped reactor under UV light irradiation (UV Spotlight source Lightningcure™ L8022, Hamamatsu, maximum emission at 365 nm), which was

focalized on the sample compartment through an optic fiber (radiant flux  $0.25\text{W}\cdot\text{cm}^{-2}$ ). In a typical process 10mg of catalyst was dispersed into 10 mL of alcohol solution and an Ar flow was bubbled through the suspension ( $20\text{ mL min}^{-1}$ ) for removing the  $\text{O}_2$  from solution and atmosphere, that Ar flow being kept during photocatalytic experiments. Catalyst suspension was continuously stirred (800 rpm) and the reactor was thermostated at  $10^\circ\text{C}$ . Outlet gas composition passed through a cold trap and was on-line analyzed by mass spectrometry,  $\text{H}_2$  ( $m/z = 2$ ) and  $\text{CO}_2$  ( $m/z = 44$ ) being calibrated using 10%  $\text{H}_2$  and 5%  $\text{CO}_2$  in Ar cylinders; when required those reference gas flows were diluted in Ar. Moreover,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  were monitored when ethanol, propan-1-ol and propane-1,2-diol were used as the sacrificial agents. Additionally, liquid phase composition was analyzed by GC-FID (Agilent Technologies 7890 chromatograph using a Supelco 25357 Nukol capillary column 30 m long, 0.53 mm ID and 1  $\mu\text{m}$  film thickness. The monitored chemicals were the alcohols used as the sacrificial reagents and the main intermediate products such as acetone (in the case of propan-2-ol transformation), acetaldehyde (for ethanol), propanaldehyde (for n-propanol) or acetol (for propane-1,2-diol). In the case of propane-1,3-diol, a peak with  $m/z=74$  was also detected, which could correspond to 3-hydroxypropanal.

Adsorption studies of propan-2-ol, propan-1-ol and reaction products on the catalyst were carried out by DRIFT on an ABB Bomen MB 3000 Series IR spectrophotometer equipped with a SpectraTech P/N 0030-100 environmental chamber including a diffuse reflectance device capable of performing 256 scan at  $8\text{ cm}^{-1}$  resolution at an adjustable temperature. The same sample holder was used both in the photocatalytic reactor and in the DRIFT system. In a typical experiment, the catalyst was submitted to reaction conditions in the dark for 30 min. The sample holder was then transferred carefully to the DRIFT system and cleaned with a  $\text{N}_2$  flow ( $30\text{mLmin}^{-1}$ ) for 30 min and the spectrum of adsorbed species registered, taking the spectrum of the fresh catalyst as the reference.

Afterwards, the solid was submitted to UV irradiation (UV Spotlight source Lightningcure™ L8022, Hamamatsu, maximum emission at 365 nm) for 30 minutes and then transferred to the DRIFT equipment. Again, the fresh catalyst was used as the reference.

#### ***2.4. Gas-phase photocatalytic reactions***

Gas-phase experiments using the most volatile C-3 alcohols, i.e. propan-2-ol and propan-1-ol, were carried out on an experimental device described elsewhere [18]. He (10 mL·min<sup>-1</sup>) was used as the carrier gas. For individual reactions alcohols were present in the gas phase at a concentration of 0.4% v/v (ca. 1.5 μmol·min<sup>-1</sup>) whereas two additional experiments for competitive reactions were conducted at a concentration of 0.4% v/v each or 0.4% v/v propan-2-ol and 0.04% v/v propan-1-ol. The gas flow was allowed into the photocatalytic reactor, in which 30 mg of catalyst had been placed. The fix bed of the catalyst was in contact with the gas flow. The lamp was the same used for experiments in the liquid phase. Therefore, UV light (UV Spotlight source Lightningcure™ L8022, Hamamatsu, maximum emission at 365 nm) was focalized on the sample compartment through an optic fiber. Radiant flux in the catalyst compartment was measured to be 0.25W·cm<sup>-2</sup> (Newport UV-meter 818P-015-19 Model). Reactor was on-line connected to a HP6890 chromatograph equipped with a six-way valve, a HP-PLOTU column (30 m long, 0.53 mm ID, 20 mm film thickness) and a Ni methanator (Agilent Part Number G2747A) which allowed us to determine propan-2-ol, propan-1-ol, propanal, acetone and the percentage of CO<sub>2</sub> resulting from mineralization. Temperature at the photoreactor was controlled by water thermostated at 10 °C.

### **3. Results and discussion**

### ***3.1. The catalyst***

The catalyst used in the present manuscript was fully characterized in a previous paper [10]. Basically, surface area is  $52 \text{ m}^2 \cdot \text{g}^{-1}$ , the Pt content is ca. 0.35% by weight (ICP-MS and EDAX), platinum particle size is ca. 2.0 nm and the band gap 3.04 eV. XPS studies of as-synthesized solid showed that platinum is in the  $\text{Pt}^{2+}$  oxidation state. Nevertheless, prior to the photocatalytic experiments, the catalyst was not submitted to any pre-reduction treatment since platinum was found to be in situ reduced within a few minutes (confirmed by XPS and consistent with results found by Bahruji et al [13]).

### ***3.2. Reactions in the liquid -phase***

Firstly, individual reactions were conducted on alcohol:water solutions (10% v/v). Results obtained in terms of hydrogen production after 6 hours are represented in Figure 1A. From that figure, it is evident that the greatest hydrogen production corresponded to monoalcohols, especially propan-2-ol and ethanol (940 and 960  $\mu\text{mol H}_2$ , respectively) whereas hydrogen production from polyalcohols is much lower (ca. 200  $\mu\text{mol H}_2$  for propane-1,2-diol or propane-1,2,3-triol and 120  $\mu\text{mol H}_2$  for propane-1,3-diol). With regards  $\text{H}_2/\text{CO}_2$  ratios (not represented) the values range from ca. 250 (propan-2-ol which is mainly converted to acetone) to 5 in the case of propane-1,2,3-triol. In any case,  $\text{H}_2/\text{CO}_2$  ratios are higher than those corresponding to pure photoreforming, which is indicative of the presence of some intermediates. The main reaction products detected were acetone (transformation of propan-2-ol), propanaldehyde (propan-1-ol), acetaldehyde (ethanol) and acetol (propane-1,2-diol). In the case of propane-1,3-diol, a peak with  $m/z=74$  was detected, which was tentatively associated to 3-hydroxypropanal. Moreover, alkanes were also detected for propan-1-ol (ethane) and ethanol (methane).



Competitive reactions were then conducted on binary mixtures of alcohols using propan-2-ol as the reference (10% v/v) and adding trace amounts (0.033% v/v) of any of the other alcohols. Results are depicted in Figure 1B. For comparative purposes results obtained for individual reactions of alcohols (10% v/v in water) are also represented. From that figure, it is evident that propan-2-ol transformation is inhibited in the presence of polyols, especially vicinal ones. Figure 2 shows the results obtained for competitive reactions in terms of propan-2-ol conversion (Figure 2A) or competitive alcohol disappearance (Figure 2B) (analysis of the liquid phase by GC-FID). These results confirm those obtained through H<sub>2</sub> monitoring by MS. Therefore, the presence of small amounts of alcohols in solution decreased propan-2-ol conversion, the extent of the decrease being different depending on the alcohol structure: the drop in propan-2-ol conversion is more significant in the presence of vicinal polyalcohols as compared to non-vicinal polyols or monoalcohols. Figure 2A also allows us to observe that inhibition effect of other alcohols on propan-2-ol conversion can vary as the reaction proceeds, as a consequence of the change in propan-2-ol/other alcohol relative ratios and that there is probably a minimum concentration for each alcohol for which inhibition effect is evident. Therefore, for instance, up to 6h of reaction propan-2-ol conversion is negligible in the presence of both propane-1,2,3-triol and propane-1,2-diol (Fig. 2A). Nevertheless, propan-2-ol conversions of 1.5 and 6.5% are found with propane-1,2,3-triol and propane-1,2-diol, respectively, after 20h. At that time, propan-2-ol/other alcohol v/v ratio has passed from 300 (initial value) to ca. 58,500 and 33,000 for reactions with propane-1,2,3-triol and propane-1,2-diol, respectively.

Inhibition effect can be explained in terms of the adsorption strength which seems to follow the sequence triol > vicinal diol > non-vicinal diol > monoalcohol.

The study was then extended to competitive reactions of alcohols starting from mixtures of them at equal concentrations (5% v/v each), the results being represented in Figure 3. Data are given as relative activity percentages, i.e. conversion of the alcohols in competitive reactions as compared to the value obtained when they are alone (5% v/v). 100% would mean that conversion of a certain alcohol is the same as in individual reaction (i.e. it is not affected by the presence of another alcohol). On the contrary, 0% relative activity means complete inhibition. As can be observed, at equal concentrations (5% v/v), ethanol and especially propan-1-ol had a remarkable inhibition effect on propan-2-ol transformation much more significant than the one observed when they were added as traces (Figure 2A).

Furthermore, results depicted in Figure 3 confirms the adsorption order triol>vicinal diol>non-vicinal diol and allow us to comment on the influence of the carbon chain (ethanol vs propan-1-ol) and the alcohol group position (propan-2-ol vs propan-1-ol) (Figure 3B). Therefore, under our experimental conditions, if all three substrates are compared, their adsorption order is propan-1-ol > ethanol > propan-2-ol that is, the primary alcohols adsorb stronger than secondary ones and the C-3 primary alcohol stronger than C-2.

### ***3.3. Reaction in the gas-phase***

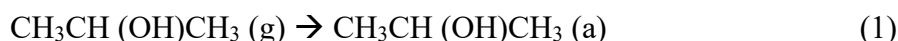
Once the relative adsorption strength of the different C-3 alcohols have been studied through competitive reactions of binary mixtures in the liquid-phase, the question is whether those results will be the same for reactions in the gas-phase. The boiling points of the C-3 substrates are as follows: propan-1-ol (97°C), propan-2-ol (82.6°C), propane-1,2-diol (188.2°C), propane-1,3-diol (213°C), propane-1,2,3-triol (290°C). Therefore, due to operational limitations, experiments in the gas-phase were just carried out on the most volatile compounds (propan-2-ol and propan-1-ol).

Figure 4 shows the results obtained for photocatalytic transformation of an equimolecular mixture of propan-1-ol and propan-2-ol (0.4% v/v in He each, Figure 4A) or 0.4 % v/v propan-2-ol and 0.04% v/v propan-1-ol (Figure 4B). As commented for Figure 3A, results are expressed as relative activity and confirm the greater adsorption of propan-1-ol as compared to propan-2-ol. In fact, inhibitory effect of the presence of propan-1-ol on propan-2-ol adsorption is even more pronounced than in the liquid phase. Therefore, propan-2-ol conversion in the presence of an equimolecular amount of propan-1-ol drops to 3% the value achieved when it is alone whereas propan-1-ol transformation is hardly affected by the presence of propan-2-ol (relative activity of 95%, Figure 4A). In the case of the reaction performed on binary mixtures containing 0.4% v/v propan-2-ol and 0.04 % propan-1-ol (Figure 4B), relative activities of both substrates were 27.3 and 56%, respectively. Selectivity to acetone and propanal is ca. 95% thus indicating that the alcohol dehydrogenation is the main photocatalyzed process in the gas-phase under our experimental conditions. Even though the experimental device used for gas-phase experiments does not allow direct determination of hydrogen, considering reaction stoichiometry and acetone and propanal yield, hydrogen production can be estimated. Therefore, H<sub>2</sub> production is ca. ca. 64.5 μmol and 18.1 μmol after 3h, for experiments from propan-2-ol and propan-1-ol, respectively. In the case of competitive reactions, hydrogen production is ca. 17.2 and 28.1 μmol after 3 hours for reactions containing 0.4% or 0.04% of propan-1-ol, respectively.

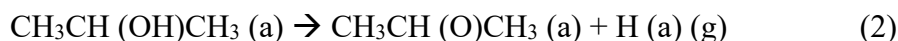
Experiments in the gas-phase were supplemented with some DRIFT studies. Figure 5 depicts the spectra obtained for individual reactions of propan-2-ol and propan-1-ol as well as competitive reactions with an equimolecular mixture (0.4% v/v each). In all cases, the spectrum of the catalyst was taken as the reference. A first conclusion from that figure is

that the adsorption of the alcohols results in the appearance of some positive bands just below  $3000\text{ cm}^{-1}$  due to C-H stretching in the alcohols [19], and some negative bands in the  $3500\text{-}3750\text{ cm}^{-1}$  region, which are indicative of the adsorption of the substrates on the surface hydroxyl groups of the catalyst [20]. Furthermore, bands at ca.  $1100\text{ cm}^{-1}$  could be ascribed to the interaction of the alcohol and the surface (adsorption as alkoxides [21]). Some other bands identified are the asymmetric methyl and *gem*-dimethyl bends centered at ca.  $1460$  and  $1370\text{ cm}^{-1}$ , respectively, characteristic of gaseous propan-2-ol and C-H bends of propan-1-ol at  $1455$  and  $1380\text{ cm}^{-1}$  [19]. A zoom of C-H stretching region for individual substrates and the equimolecular mixture can be seen in Figure 6 and seems to confirm the greater adsorption of propan-1-ol as compared to propan-2-ol (see relative intensities of bands at ca.  $2934$  and  $2848\text{ cm}^{-1}$  in all three spectra). Finally, it is interesting to point out that C=O signal at ca.  $1700\text{ cm}^{-1}$  is not seen in the DRIFT spectra of propan-1-ol or propan-2-ol which seems to indicate that once produced the corresponding carbonyl compound is rapidly desorbed which would account for the high propanal and propanone selectivity values (over 95%). According to Bahruji et al. [22], once adsorbed on the catalyst as the corresponding alkoxide (evidenced by DRIFT) alcohols can either dehydrogenate via beta-hydride elimination or dissociate. In the former case the corresponding carbonyl compound would be formed whereas the latter would result in a C-1 alkane. Under our experimental conditions, the high selectivity observed to acetone (>95%) both in the liquid and gas phase seems to suggest that its photocatalytic transformation proceeds via beta-hydride elimination mainly according to:

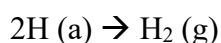
Adsorption of propan-2-ol



Dehydrogenation of propan-2-ol



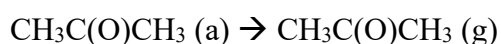
Recombinative desorption of hydrogen (3)



Dehydrogenation via beta-hydride elimination (4)



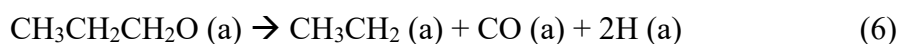
Fast desorption of acetone (5)



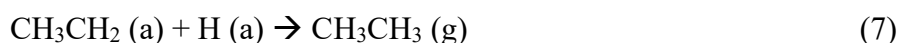
In the case of propan-1-ol, detection of ethane for reactions in the liquid-phase is also supportive of the dissociative route whereas beta-hydride elimination is more important in the gas-phase (selectivity over 95% to propanone).

Formation of ethane would proceed as follows:

Dissociation of alkoxide



Formation of alkane



#### 4. Conclusions

Competitive reactions have been shown as a powerful tool to study reaction mechanisms, in particular to examine different adsorption strengths of substrates. In this piece of research, hydrogen production from C-3 alcohol solutions was studied on a Pt/TiO<sub>2</sub> system. Ethanol (C-2 alcohol) was also used for comparative purposes. In individual reactions, hydrogen evolution followed the sequence ethanol  $\approx$  propan-2-ol > propan-1-ol > propane-1,2,3-triol > propane-1,3-diol > propane-1,2-diol. Competitive reactions of binary mixtures of alcohols containing propan-2-ol and traces of other alcohol evidenced the retardation of propan-2-ol transformation, inhibition effect being more significant in the presence of

vicinal diols.

Competitive reactions of binary mixtures of alcohols at the same volume percentage (5% v/v each) allowed us to obtain a relative adsorption order which follows the sequence propane-1,2,3-triol > propane-1,2-diol > propan-1,3-diol > propan-1-ol > ethanol > propan-2-ol.

Competitive reactions in the gas-phase on propan-2-ol/propan-1-ol binary mixtures monitored by DRIFT confirmed the greater adsorption of propan-1-ol as compared to propan-2-ol.

Once adsorbed on the catalyst, alkoxide can undergo dehydrogenation via beta-hydride elimination, thus yielding the corresponding carbonyl compound or dissociate to form a C-1 alkane. Under our experimental conditions, the former mechanism seems to predominate, especially for propan-2-ol, whereas the latter is more important for the other substrates in particular in the liquid phase.

All in all, this study highlights the importance of working with real solutions which rarely consist in aqueous solutions of pure compounds. In this sense, the presence of some other chemicals even at trace levels can significantly affect hydrogen photoproduction.

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### **Caption to figures**

Fig. 1. Hydrogen photocatalytic production after 6h for reactions in the liquid phase. A) Individual reactions (10% v/v alcohols in water). B) Competitive reactions on binary water mixtures of alcohols.

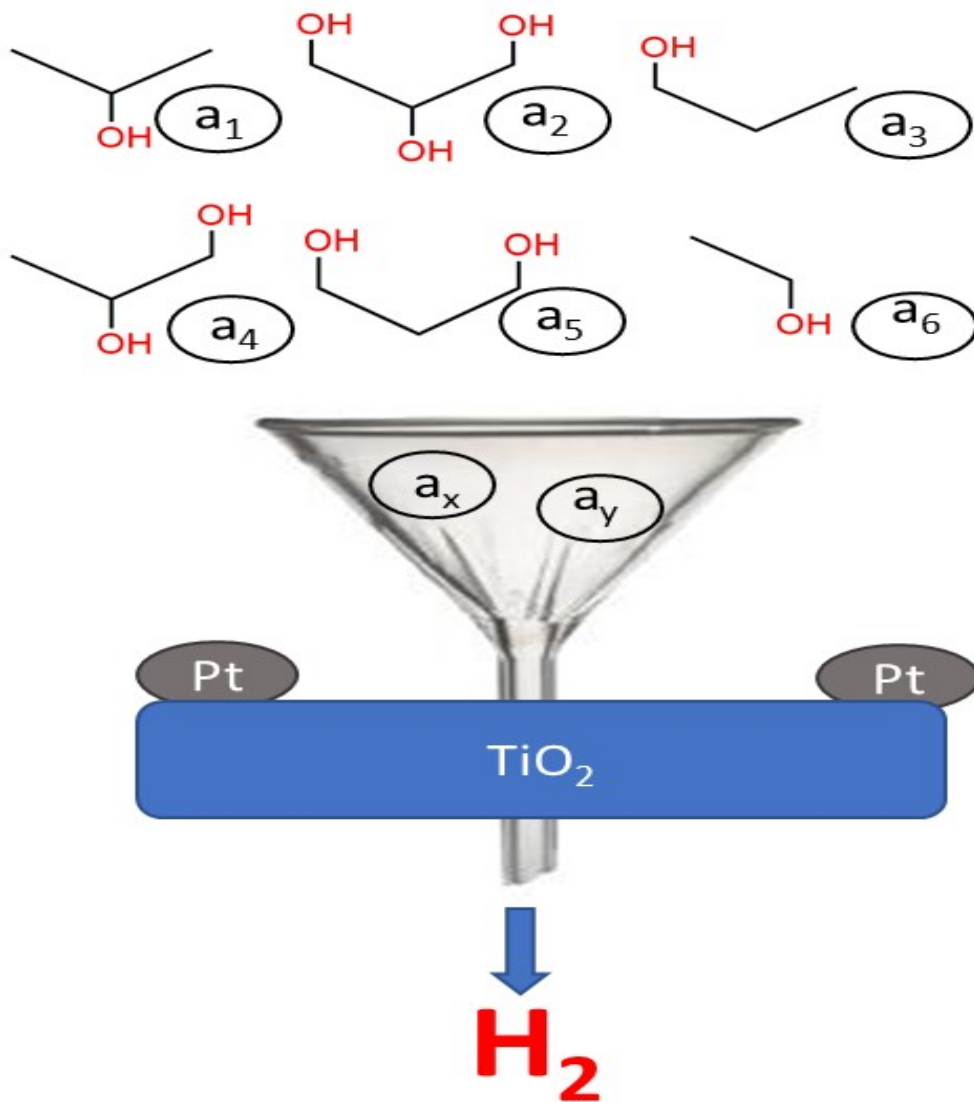
Fig. 2. Competitive reactions of propan-2-ol (10% v/v in water) and traces of other alcohols (0.033% v/v). A) propan-2-ol conversion and B) evolution of the other alcohols.

Fig. 3. A) Competitive reactions of binary mixtures of alcohols (5% v/v in water each) expressed as relative activity (i.e. comparative conversion alone or in the presence of the other alcohol). B) Suggested adsorption strength order.

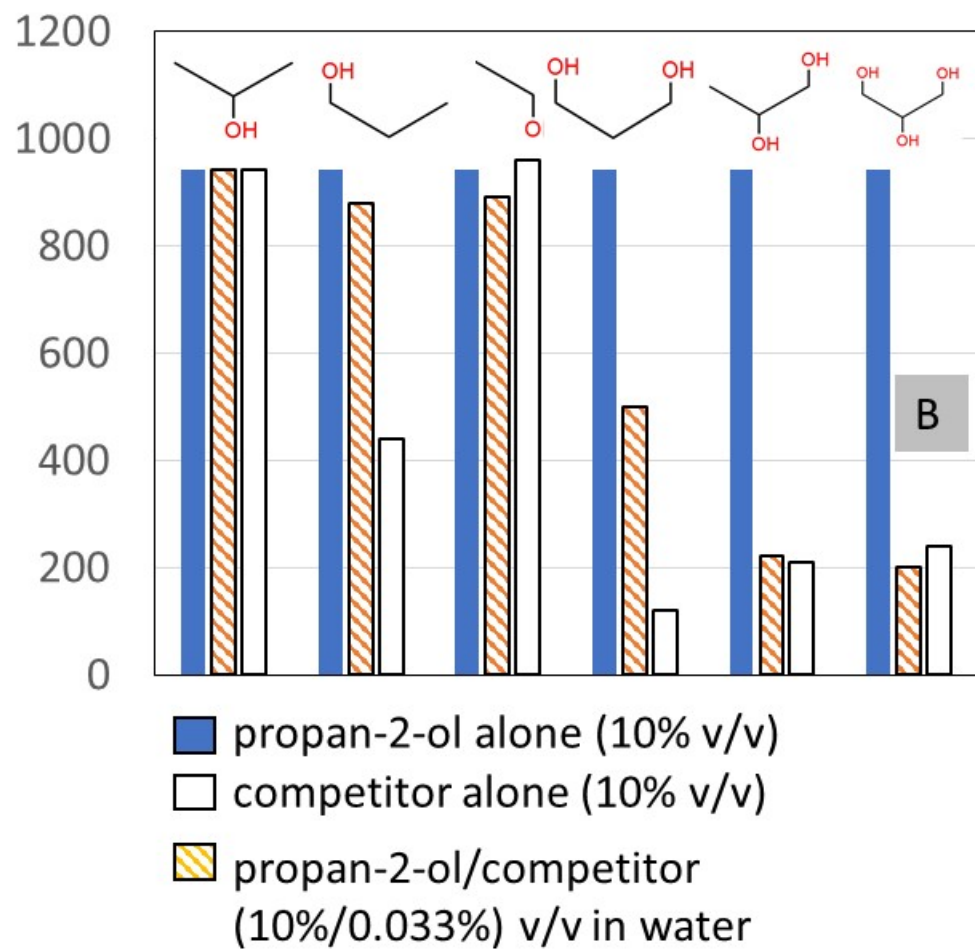
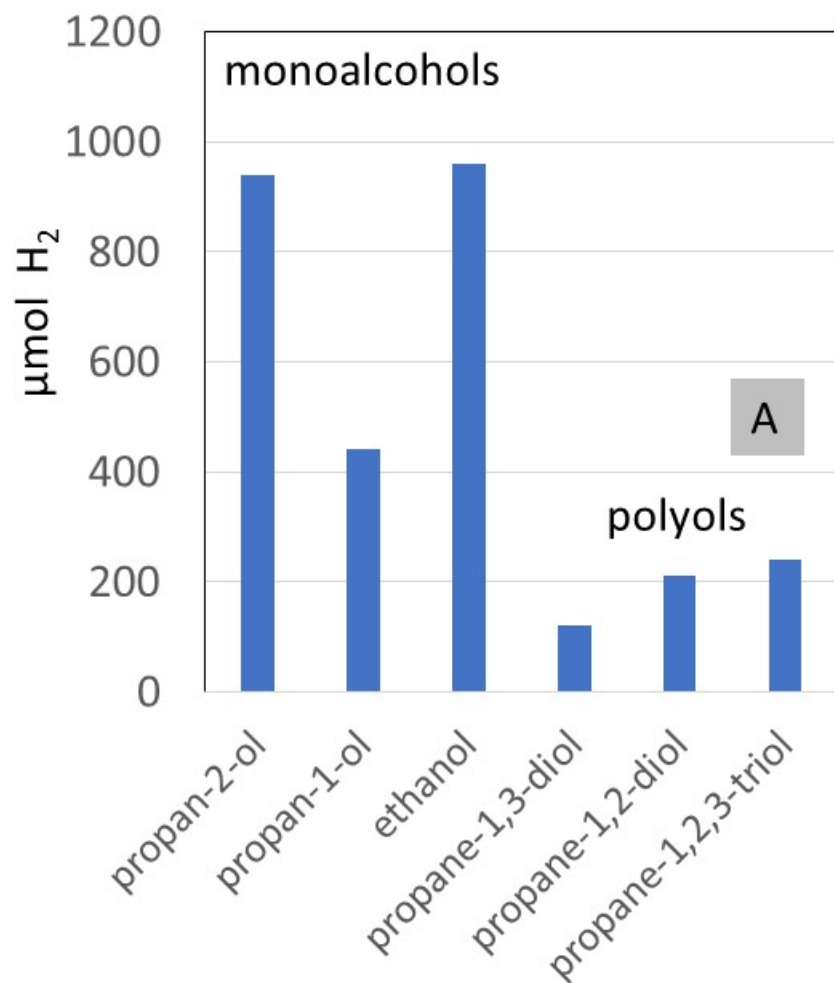
Fig. 4. Competitive reactions of propan-2-ol and propan-1-ol in the gas-phase expressed as relative activity (i.e. comparative conversion alone or in the presence of the other alcohol). A) 0.4% v/v in He each. B) 0.4% v/v propan-2-ol and 0.04% v/v propan-1-ol.

Fig. 5. DRIFT spectra for competitive reactions of propan-2-ol and propan-1-ol in the gas-phase (0.4% v/v in He each). For the sake of comparison, results obtained for individual reactions (0.4% v/v in He) as well as spectrum of acetone are also included.

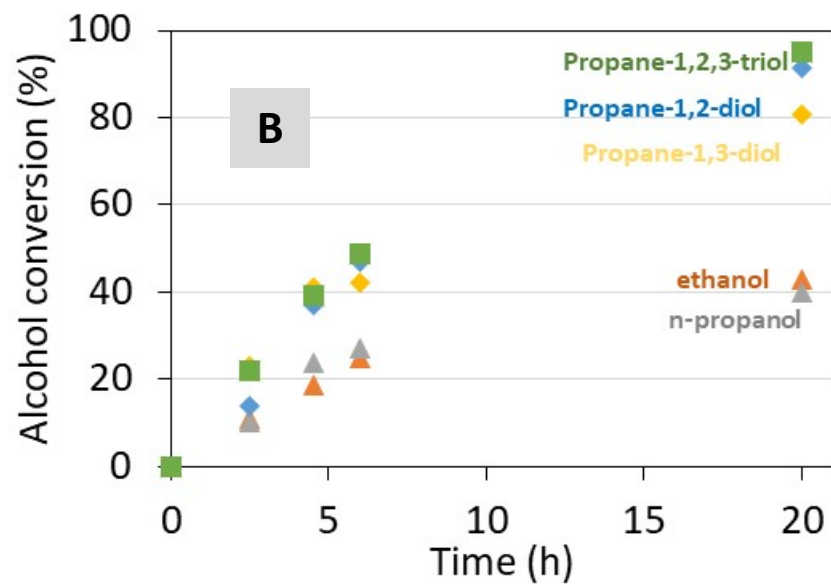
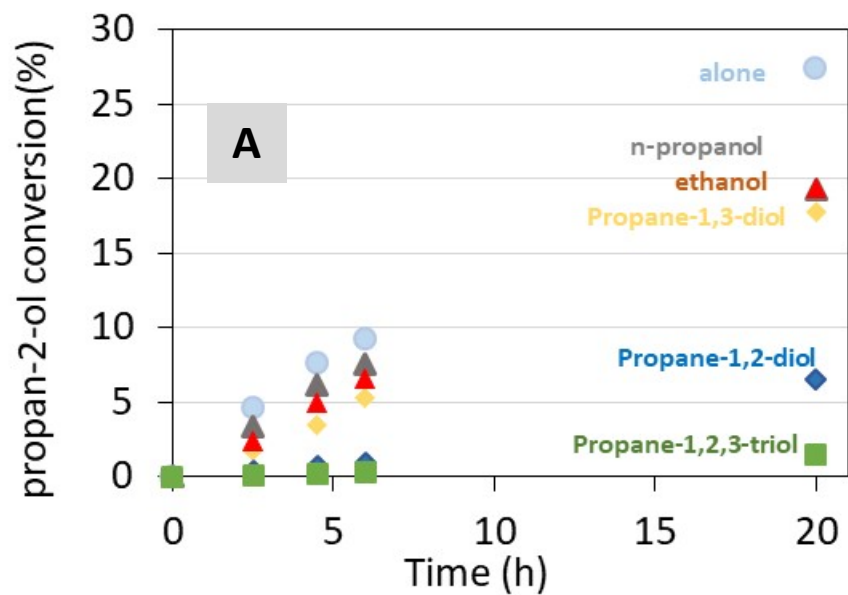
Fig. 6. DRIFT spectra of propan-2-ol, propan-1-ol and propan-2-ol+ propan-1-ol (0.4% v/v each) adsorbed on the catalyst.



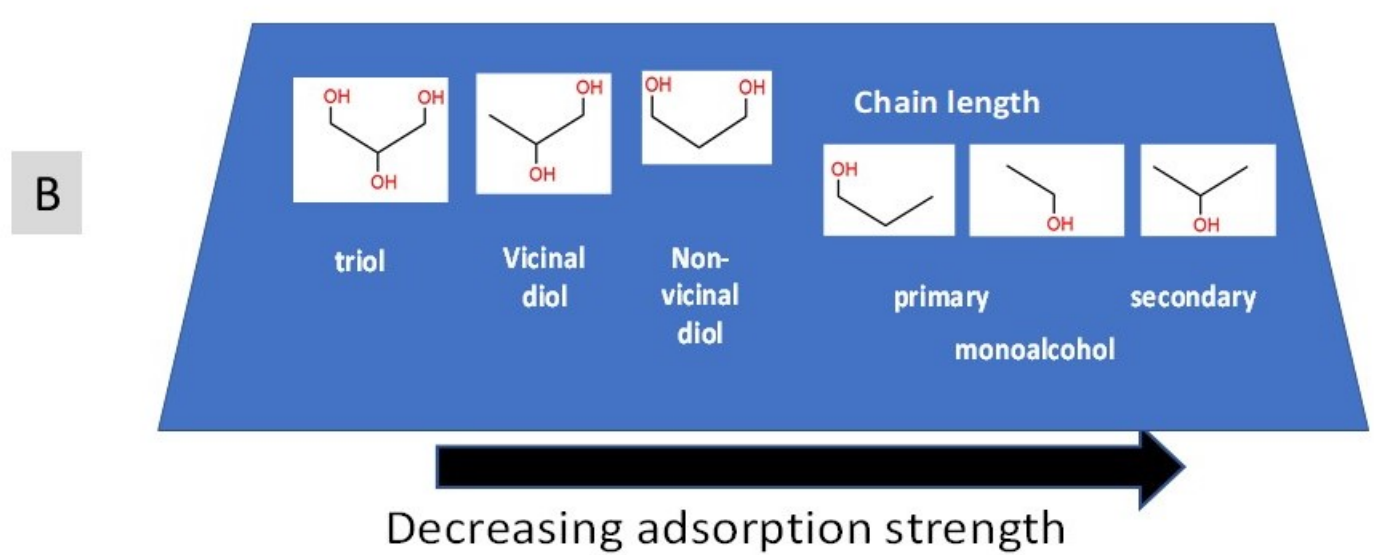
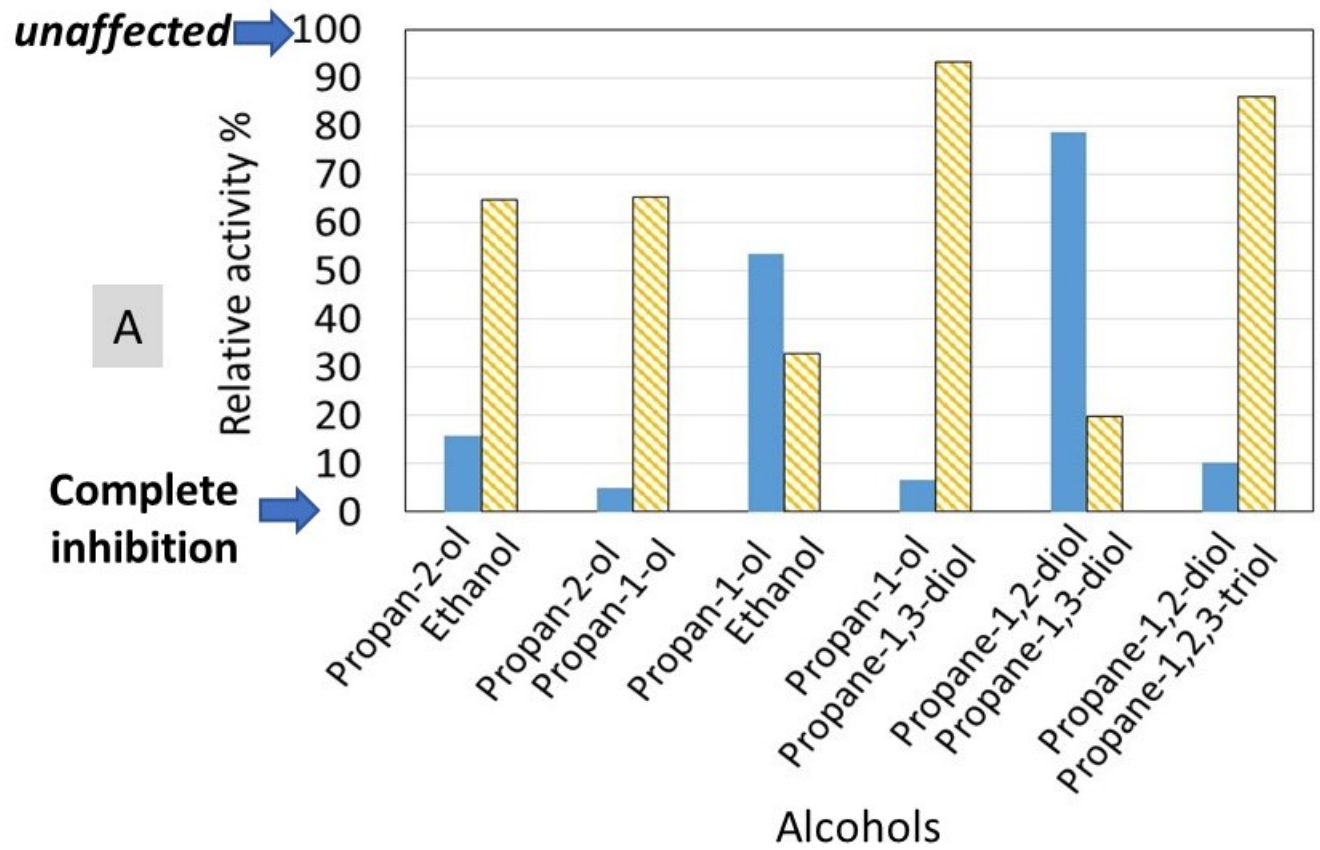
Graphical abstract



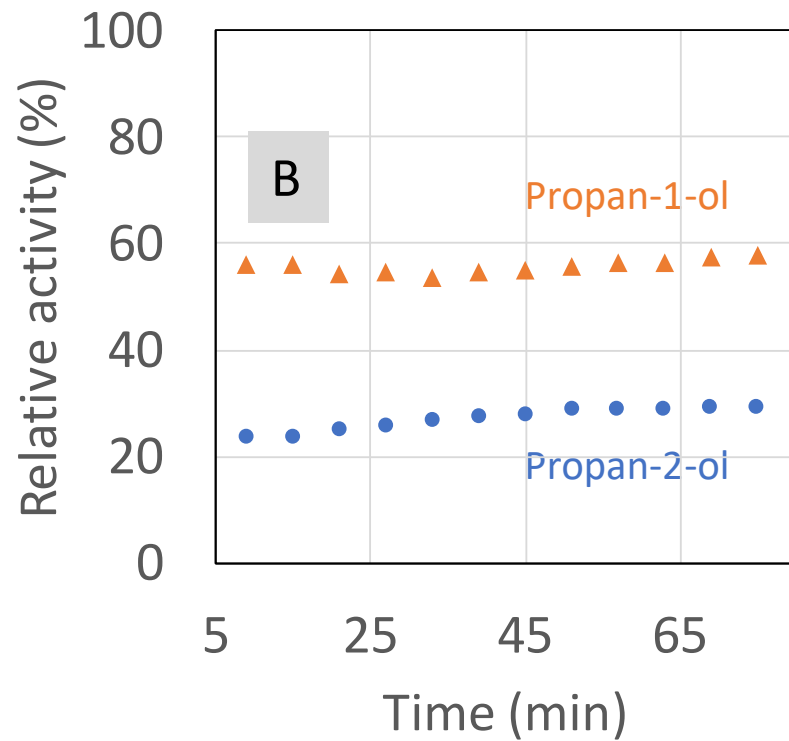
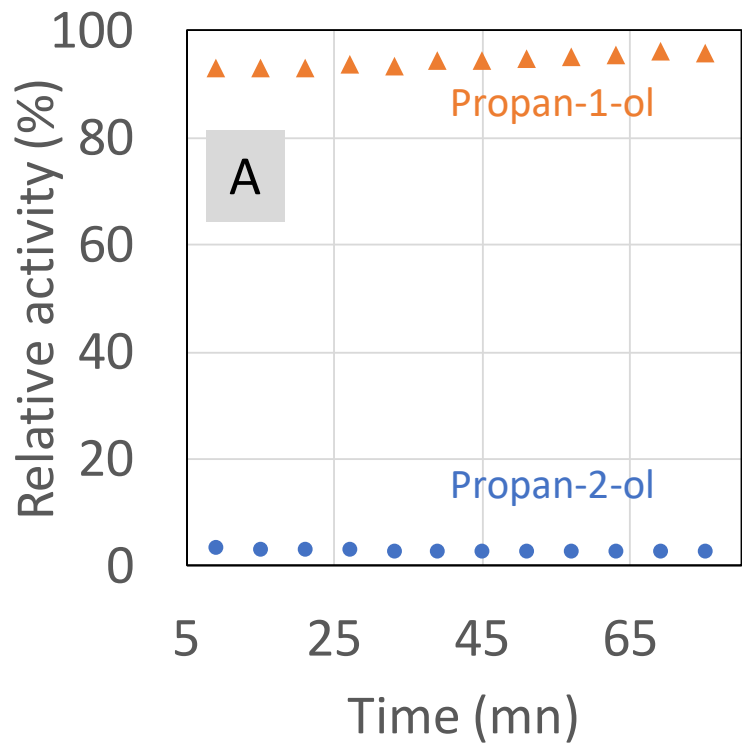
**Figure 1**



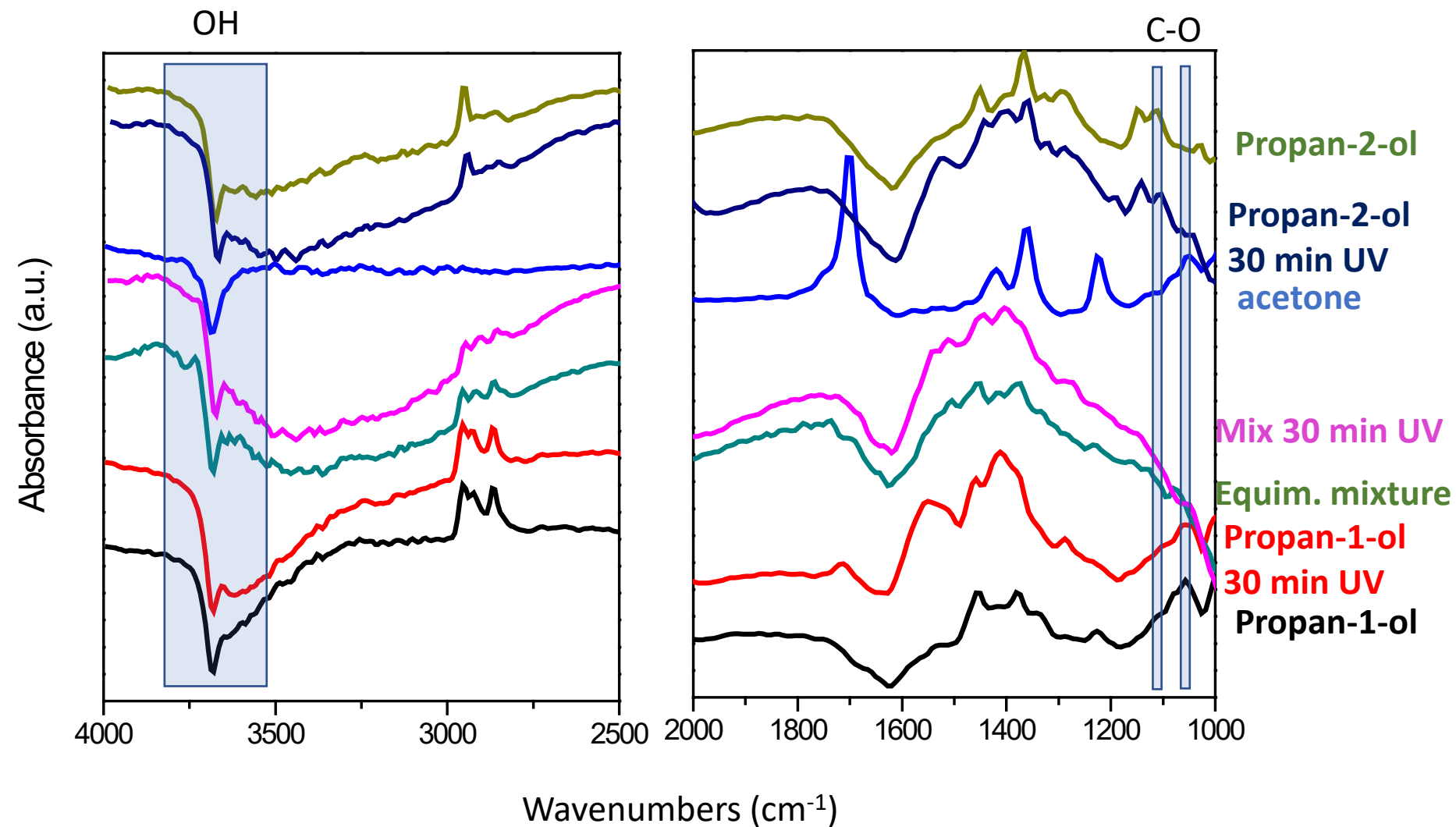
**Figure 2**



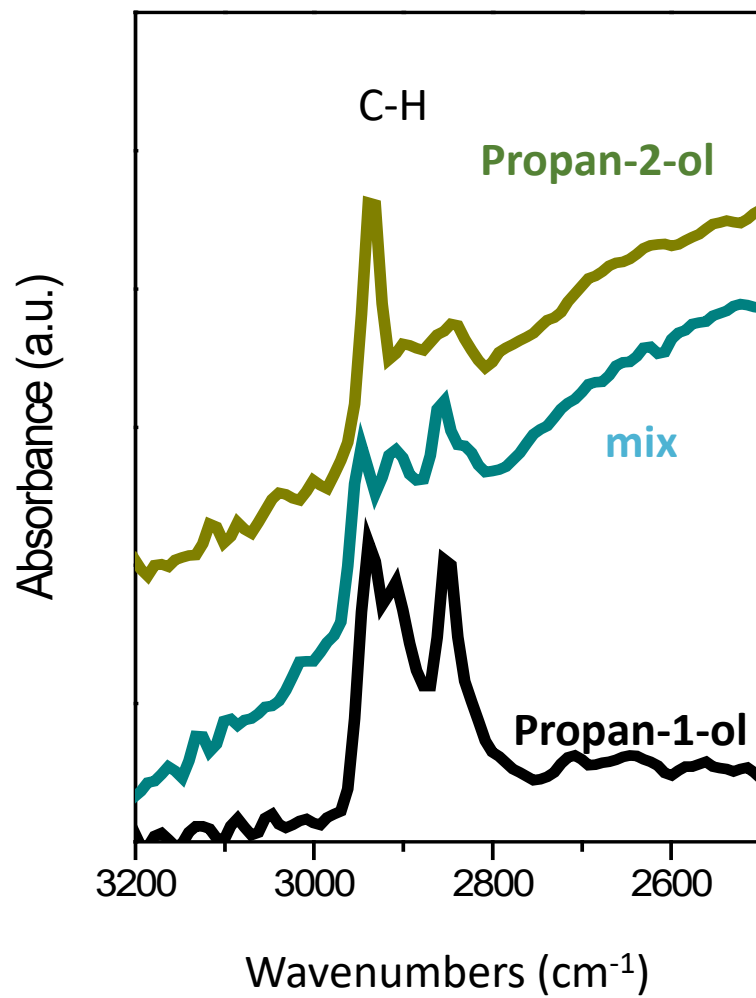
**Figure 3**



**Figure 4**



**Figure 5**



**Figure 6**