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Comparison of hydrothermal and photocatalytic conversion of glucose with commercial TiO₂: Superficial properties-activities relationships

Insaf Abdouli, Marion Eternot, Frederic Dappozze, Chantal Guillard*, Nadine Essayem*

Institut De Recherche Sur La Catalyse Et L'Environnement De Lyon (IRCELYON), CNRS, University Lyon 1, 2 Avenue Albert Einstein, 69626, Villeurbanne, France

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ABSTRACT

Recently, the photocatalytic conversion of glucose appeared as an environmentally friendly route to produce valuable molecules. However, the potential of this new route in comparison with the usual hydrothermal catalytic process remained questionable. In this paper, we compared the two routes using three commercial TiO₂ as catalysts in the same reactor. The TiO₂ superficial acidity and basicity were determined by calorimetry and FTIR of CO₂, NH₃ and pyridine adsorption. Relationships between the acid-base properties, the TiO₂ glucose adsorption capacities measured in water and their photocatalytic or hydrothermal performances were proposed: while the photocatalytic performances could be linked to the catalysts' Lewis acid sites density and their glucose adsorption capacities, the hydrothermal performances were dependent of the catalysts' basic/acid sites balance. We highlighted that the conversion of glucose over TiO₂ was as efficient with the photocatalytic process at ambient temperature as with the hydrothermal process at 120 °C. This underlines the potential of the photocatalytic route at the lab scale as regards to the milder experimental conditions involved.

1. Introduction

Photocatalysis is an ecofriendly and energy-saving technology, efficient at ambient temperature, largely used for water/air decontamination through the mineralization of organic compounds into CO₂ or for hydrogen production [1]. Different semiconductors have been designed to fit with photocatalysis requirements: light absorption and charges separation. Titanium dioxide, despite its large band gap near to 3.2 eV limiting its light absorption to UV light (< 390 nm), is one of the most used semiconductor. This is explained by its efficiency combined to its easy synthesis and large commercialization in different crystalline structures (anatase, rutile and mixture of anatase and rutile) and with different properties (specific surface area, porosity, surface hydroxylation...).

The photocatalytic conversion of glucose was investigated as a soft method for hydrogen production. In such case, TiO₂ with noble metals (Pt, Au, Pd, Rh, Ag...) is used under anaerobic conditions [2,3]. The use of a noble metal dispersed on TiO₂ is mandatory for the production of H₂ to avoid the recombination of electron-holes pairs generated by the photons absorption. In the earliest studies, the liquid phase composition wasn't investigated in parallel to hydrogen formation [4,5]. Anatase TiO₂ was reported to be more efficient than rutile TiO₂ for hydrogen production [5]. The co-formation of valuable products in the liquid

phase together with hydrogen released in the gas phase during the photocatalytic reforming of glucose has been reported in 2014 [6]. After 120 h of reaction, arabinose, erythrose and formic acid were the main products analyzed in the liquid phase with a total arabinose and erythrose yield as high as 60 %. Glyceraldehyde and gluconic acid were also detected in lower amounts. A pathway with successive C1-C2 α-scissions was proposed to explain the formation of C₅, C₄ sugars [6,7]. In this case, Ru/rutile TiO₂ was more efficient than anatase TiO₂ or P25 for the production of value added products in the liquid phase [6].

Photo-oxidation of glucose, conducted under aerobic conditions, appeared also as an efficient method leading to the formation of value added products in the liquid phase [8]. One can note the formation of similar chemicals under the aerobic than under anaerobic conditions: gluconic acid, arabinose and formic acid in addition to xylitol and deeper oxidized compounds such as glucaric acid and CO₂ [9–14]. It was shown that the selectivity of the glucose photo-oxidation could be controlled by the use of organic solvent mixture such as water/acetonitrile [9–12] and/or by the use of a metal loaded catalyst i.e. Ag-TiO₂ or Au-TiO₂ [11–13]. The combined use of a metal loaded on TiO₂ and soluble basic promoters such as NaOH [13], Na₂CO₃ [11], led to more efficient photo-oxidation of glucose into gluconic acid. Generally, anatase TiO₂ is reported to be more efficient than other TiO₂

* Corresponding authors.

E-mail addresses: chantal.guillard@ircelyon.univ-lyon1.fr (C. Guillard), nadine.essayem@ircelyon.univ-lyon1.fr (N. Essayem).

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polymorphs to produce chemicals in aerobic conditions [10,11].

Interestingly, Bellardita et al. have investigated the photocatalytic glucose conversion under aerobic/anaerobic conditions using bare TiO_2 or Pt/TiO_2 [15]. They reported the same liquid products formation i.e. arabinose, erythrose, formic acid, fructose and gluconic acid, whatever the conditions. However as expected, hydrogen was produced only over Pt-TiO_2 in anaerobic conditions. Tentative correlations between the nature of the TiO_2 phases, the hydroxylation degree of the TiO_2 surface and the photocatalytic performances were proposed [15].

Besides, glucose catalytic oxidation under more severe conditions (hydrothermal conditions: high temperature and pressure) has been widely investigated in the absence of light activation of the metallic catalysts. This route was studied under different conditions: air, O_2 , or H_2O_2 used as oxidant, mono-bimetallic (Pt, Pd, Au) catalysts supported on water tolerant supports (carbons, ZrO_2 , TiO_2). Such conditions lead to the formation of a variety of carboxylic acids such as gluconic acid, glucaric acids, glycolic acid, acetic acid, oxalic acid... [16]. Moreover, to be efficient, the catalytic glucose oxidation is generally performed in the presence of soluble bases to produce carboxylic acids in high yields, which is a serious drawback. Despite the general agreement regarding the crucial need of soluble bases, their role at the mechanism level is still not well established [17,18,16]. Recently, few studies have reported the feasibility of catalytic glucose oxidation, in base free conditions using Au based catalysts supported on TiO_2 [19–21]. In the same way, the role of each function of the catalytic system Au(M)/TiO_2 , remains controversial.

Furthermore, under anaerobic-hydrothermal conditions, bare or modified TiO_2 , has been also used as acid-base catalyst to promote glucose transformation. In that case, different valuable products have been reported such as fructose, 5-hydroxymethylfurfural (5-HMF), lactic, levulinic and acetic acids [22–24]. It is generally accepted that, in hydrothermal conditions, the formation of these chemicals from glucose is controlled by the catalysts' acid-base properties: glucose isomerization into fructose is catalyzed by Lewis acid sites [25] or basic sites [26,27] whereas the dehydration reaction leading to 5-HMF [28] as well as its rehydration into levulinic and formic acids [29] are catalyzed only by Brønsted acids sites. Again, in the literature, discrepancies exist between the nature of the superficial acid-base properties of the TiO_2 polymorphs and their abilities to promote one of the above-mentioned elementary steps. For instance, bare anatase TiO_2 was reported to be unable to produce 5-HMF from glucose by contrast to H_3PO_4 modified anatase TiO_2 , ascribed to its water tolerance Lewis-acidity [23]. On the other hand, the efficiency of anatase TiO_2 to produce 5-HMF derivatives was explained by in situ sulfation of the synthesized TiO_2 nano-particles due to the synthesis procedure, while S free TiO_2 was unable to produce 5-HMF derivatives [24]. Earlier studies of Watanabe et al., in 2005, have highlighted that anatase and rutile TiO_2 showed different catalytic activities in the conversion of glucose in hot pressurized water [22]. The superior performances of anatase TiO_2 compared to rutile TiO_2 was correlated to the bifunctional acid-base properties of anatase TiO_2 allowing first glucose-fructose isomerization over the basic sites and further dehydration into 5-HMF over the acid ones. Rutile TiO_2 would not present this required bi-functionality. Note the acid/base ratio were determined by CO_2 and NH_3 TPD and that the commercial TiO_2 had specific surfaces area lower than $6\text{ m}^2\text{ g}^{-1}$ [22,30].

As recalled above, the two possible routes of glucose valorization into platform molecules via catalytic hydrothermal conversion or photocatalysis have already been well investigated. However, their comparison is almost impossible because they have been studied under quite different conditions: temperature, pressure, substrate concentrations, substrate/catalyst ratio, TiO_2 phases, light irradiations, reactors and stirring... In fact, the hydrothermal processes are performed in autoclaves that handle high pressure and high temperatures, while photocatalysis that operates at low temperature and atmospheric pressure is studied in Pyrex reactors that allow irradiation transmission.

Accordingly, from the literature data, it is not possible to compare the two routes in order to evaluate whether or not the photocatalytic way is competitive to the catalytic hydrothermal route. Moreover, the crucial characterization of the acid-base properties of the different TiO_2 crystalline phases are rarely provided in the same paper that prevents any reliable structure/superficial properties/activities correlation in the hydrothermal or photocatalytic route.

Thus, in this work, the photocatalytic conversion of glucose and the catalytic hydrothermal glucose conversion at mild conditions were studied with commercial anatase/rutile titanium dioxide to compare the potential and the reaction pathways of the two routes to produce valuable platform molecules. The two processes were performed in the same reactor suited to handle light irradiation as well as high temperature and pressure. They were performed under the same conditions of atmosphere, pressure, volume, stirring, glucose and catalyst concentrations but under temperature below or above $100\text{ }^\circ\text{C}$ for photocatalysis or hydrothermal treatment, respectively. Moreover, the catalysts' acid-base properties were investigated in a systematic way by mean of gaseous probe molecules adsorption monitored by calorimetry and Fourier transform infrared spectroscopy in addition to glucose adsorption isotherms in water, searching for potential relationships between the superficial properties of TiO_2 phases with their catalytic activities with or without light irradiation.

2. Experimental section

2.1. Materials

Three commercial titanium dioxide catalysts (TiO_2) were chosen in order to compare one pure TiO_2 anatase phase (UV100) and one pure rutile phase (Rut160) with the reference P25 made of an anatase/rutile mixture. Hereafter, they were referred to by their commercial names as follows: UV100, Rut160 and P25.

P25 was from Evonik, Hombikat. UV100 was from Sachtleben Chemie, and Rut160 was from Nanostructured and Amorphous Materials Incorporation. The latter TiO_2 sample was pretreated for 20 h at $400\text{ }^\circ\text{C}$ before use in order to remove carbon pollution. It contained Si (5 wt %). Glucose was purchased from Merck and all the chemicals used for the calibration with HPLC were purchased from Aldrich.

2.2. TiO_2 physicochemical properties

2.2.1. X-Ray diffraction (XRD)

The catalysts' crystalline structures and the sizes of their crystallites were analyzed by XRD using a Bruker D8 Advance diffractometer A25 equipped with a copper anode. Powdered samples were analyzed within a 2θ range of $4\text{--}80\text{ }^\circ$ at 0.02 ° per step and with an acquisition time of 96 s per step. The diffractograms were collected by the IRCEL-YON's XRD Service.

2.2.2. Brunauer-Emmett-Teller surface area (S_{BET}) analysis and pores size distribution

The catalysts' structures were characterized using nitrogen adsorption/desorption isotherm at $-196\text{ }^\circ\text{C}$ in a Micromeritics ASAP 2020 device. Before the analysis, the catalysts were degassed at $300\text{ }^\circ\text{C}$ (heating rate $5\text{ }^\circ\text{C/min}$) during 2 h.

2.3. TiO_2 acid-base properties

2.3.1. Pyridine adsorption followed by Fourier Transform Infrared Spectroscopy (FTIR)

The nature of the acid sites present on the catalysts (Lewis and/or Brønsted) were identified by the adsorption of pyridine followed by FTIR. FTIR spectra were recorded with a Bruker Vector 22 spectrometer in absorption mode with a resolution of 2 cm^{-1} . Catalysts' powder were pressed into self-supported pellets. The pellets were

placed in an IR glass cell equipped with CaF_2 windows and connected to a first vacuum equipment allowing thermal treatments first and then, to another vacuum equipment to perform pyridine adsorption and desorption. All the samples were first treated under flowing air (2 L.h^{-1}) for one hour at 150°C and then under vacuum while cooling down the catalyst pellets for one hour to eliminate pollutants adsorbed on the surface without deeper dihydroxylation. Then, pyridine was adsorbed under saturation vapor pressure at ambient temperature for 15 min, secondly the pyridine was desorbed for one hour at ambient temperature, finally at 150°C for one hour to remove the physisorbed species from the catalyst surface.

2.3.2. Ammonia adsorption monitored by calorimetry

The number and strength of acid sites of the catalysts were measured by ammonia adsorption at 80°C monitored by calorimetry using a Tian-Calvet calorimeter coupled with a volumetric equipment. This technique allows to measure the differential heats of adsorption evolved when successive small known amounts of ammonia molecules are adsorbed on the catalyst surface. This energy depends on the acid strength of the acid sites of the catalyst surface. First, 30 mg of each catalyst was placed in a glass cell and pretreated at 150°C ($2^\circ\text{C}/\text{min}$) for 5 h under secondary vacuum. The cell was then placed in a Tian-Calvet calorimeter coupled to a volumetric equipment up to the temperature stabilization at 80°C under secondary vacuum during one night. Finally, successive small doses of ammonia were brought into contact with the catalyst while the differential heats of NH_3 adsorption were recorded. More details about the technic can be found elsewhere [31].

2.3.3. Carbon dioxide adsorption monitored by calorimetry

The number and strength of the basic sites of the catalysts were measured by the same technique reported above for the acid sites quantification, but using carbon dioxide as a probe and the adsorption was done at 30°C . The catalysts (50 mg) were treated using the same procedure as for the acid sites quantification.

2.4. Glucose adsorption isotherm in aqueous phase

The adsorption of glucose on P25, UV100 and Rut160 was carried out using closed glass flasks shacked at 100 rpm and maintained at 30°C for 24 h and in the presence of 1.24 g of catalyst in 50 mL of glucose aqueous solution. The glucose concentration was varied between 0.2 and 10.8 g/L.

2.5. Glucose photocatalytic conversion

The photocatalytic conversion of glucose was carried in a stainless steel autoclave equipped with a glass window in its bottom allowing to work under irradiation. The reaction was done using 50 mL of an aqueous solution of glucose of 0.5 g/L, with a weight ratio Glucose/Catalyst of 1, under air or Ar (5 bar) and under ambient temperature. Once the glucose solution and the catalysts were filled into the autoclave, a leaks test was done using air or Ar (5 bar). The mixture was mechanically stirred at 500 rpm. Before the UV light irradiation, the glucose solution was stirred in the presence of the TiO_2 catalyst, in the autoclave, for 1 h, according to the usual photocatalytic experiment procedure in order to favor the glucose adsorption on the TiO_2 surface. The reactor was then illuminated with a PLL-lamp (18 W, 365 nm and $6.2 \text{ mW}/\text{cm}^2$). The reaction time zero corresponds to the start of irradiation. The relative error obtained by reproducing three times the same experiment is around $\pm 20\%$.

2.6. Glucose hydrothermal conversion

The hydrothermal conversion of glucose was carried in the same stainless steel autoclave used for the photocatalytic conversion of

glucose. The reaction was done using the same total volume of an aqueous solution of glucose, 50 mL of 0.5 g/L of glucose, with a ratio Glucose/Catalyst of 1, under air or Ar (5 bar) and under different temperature: 90, 120 and 150°C . To avoid uncontrolled glucose conversion during the temperature increase, first 48 mL of deionized water were filled into the autoclave at ambient temperature. Then, the leaks test was done using pressurized air or Ar (5 bar). A 2 mL of glucose aqueous solution was added once the temperature was stabilized. The reaction time zero corresponds to the introduction of glucose in the reaction media at high temperature. The relative error obtained by reproducing three times the same experiment is around $\pm 20\%$.

2.7. Liquid phase analysis

2.7.1. High-Performance liquid chromatography (HPLC)

During the reactions, the substrate (glucose) and the products in liquid phase were quantified by HPLC Shimadzu Prominence system equipped with a refractive index detector (RID), a photometric diode array detector (PDAD) and the products separation was done with a COREGEL 107H column. The RID was used to detect the monosaccharides, the aldehydes and the acetones. While the PDAD was used to detect the carboxylic acids and furanic compounds at 210 nm.

The glucose conversion and the products yields (%C) are calculated as follows:

$$\text{Conversion (\%)} = 100 \times (\text{Glucose consumed}) / (\text{initial Glucose})$$

$$\text{Yield(\%C)} = 100 \times (\text{Product's molar concentration}) / (\text{Glucose initial molar concentration}) \times (\text{Product's carbon number}) / 6$$

2.7.2. Total organic carbon (TOC)

To determine the carbon balance (C balance) in liquid phase at the end of the reaction, a Shimadzu TOC-VSCH total organic carbon (TOC) was used to quantify the total mass of carbon in the liquid phase (residual glucose and products). It consisted in the mineralization of the organic compounds at 720°C catalyzed by $\text{Pt}/\text{Al}_2\text{O}_3$ into CO_2 that was then quantified by IR detector. The C balance was then calculated by dividing the TOC by 200 mg/L which was the initial mass of carbon of the glucose solution before reaction.

$$\text{C balance (\%)} = \text{TOC} / 200 \times 100$$

2.8. Gas phase analysis

The products in gas phase were analyzed by gas chromatography using a GC Clarus 590 (Perkin Elmer). The gas is first separated with a PoraPlot Q column ($25 \text{ m} \times 0.53 \text{ mm} \times 20 \mu\text{m}$ df - Agilent J&W Technologies). The gas outlet is then divided into two parts: one part is directed to Polyarc (R) system (Activated Research Company) coupled to a Flame Ionization Detector (FID) and the second part is separated by RT-Msieve5A column ($30 \text{ m} \times 0.32 \text{ mm} \times 30 \mu\text{m}$ df - Restek) coupled to a Pulsed Discharge Helium Ionization Detector (VICI).

3. Results and discussion

3.1. TiO_2 physicochemical properties

TiO_2 physico-chemical characteristics are shown in the Table 1. Their XRD analysis confirmed the nature of the TiO_2 phases (S1 in Supplementary informations): presence of a mixture of anatase and rutile phase for P25 and pure TiO_2 phases for UV100 (anatase) and Rut160 (rutile). Regarding the particles sizes deduced from the XRD patterns, the pure TiO_2 phases, UV100 and Rut160 are characterized by nano-sized TiO_2 particles while P25 has larger TiO_2 particles of 18 nm. This probably accounts for different methods of synthesis. Accordingly, a smaller BET surface area was measured over P25, $55 \text{ m}^2 \text{ g}^{-1}$, while

Table 1

Main physico-chemical features of UV100, Rut160 and P25.

Catalyst	Crystalline Phase	Particles size ¹ (nm)	S _{BET} ² (m ² g ⁻¹)
P 25	Anatase + Rutile	18	55
UV 100	Anatase	7.5	300
Rut160	Rutile	8.5	175

¹from XRD patterns.²pretreatment: 2 h at 300 °C (Temperature ramp: 5 °C.mn⁻¹).

higher values were obtained for UV100 and Rut160, 300 and 175 m² g⁻¹ respectively. The N₂ isotherms revealed the presence of hysteresis loops at high relative partial pressures on all the TiO₂ samples, indicating the presence of large mesopores (S2 in supplementary informations). Besides, the high N₂ uptake at low partial pressure observed on the UV100 and Rut160 isotherms indicated the presence of significant amounts of micropores on these two nano-sized TiO₂.

3.2. TiO₂ acidity and basicity

3.2.1. Nature of the TiO₂ acid sites

The type of catalysts' acid sites (Lewis vs Brønsted) was first probed by the adsorption of pyridine followed by FTIR. Fig. 1 shows the FTIR spectra of pyridine chemisorbed on dehydrated TiO₂ samples. All the catalysts exhibited absorption bands at 1445 and 1610 cm⁻¹ ascribed to the vibration of the pyridine coordinated to the catalysts' Lewis acid sites. The spectra show also a band at 1575 cm⁻¹ ascribed to the vibration of pyridine molecules retained to the catalyst surface by hydrogen bonds [32]. The band at 1490 cm⁻¹ is common to the vibrations of pyridine coordinated to the catalysts' Lewis acid sites and to pyridinium ions. However, the catalysts did not exhibit the 19b₁CC vibration at 1545 cm⁻¹ nor the one at 1638 cm⁻¹ (8a₁CC), both characteristic of the vibration of the pyridinium ions which could be formed on Brønsted acid sites [32]. Thus, one can conclude that the three commercial TiO₂ (anatase and/or rutile) have only Lewis acid sites.

3.2.2. Strength and number of TiO₂'s acid sites

The total amount of acid sites and the distribution of acid strength were determined by ammonia adsorption monitored by calorimetry coupled to a static volumetric equipment. The total amounts of acid sites and the amount of strong acid sites as well as their density (acid sites amount divided by the catalysts surface area) were determined from the isotherms and calorimetric curves of ammonia adsorption

Fig. 1. FTIR spectra of pyridine retained on TiO₂ catalysts after desorption at 150 °C.

Conditions: 1) TiO₂ self-supported pellets vacuum treated for 1 h at 150 °C (reference spectra).

2) Saturation with pyridine vapor at ambient temperature 3) Difference spectra recorded after desorption under vacuum for 1 h at 150 °C to remove physisorbed pyridine.

shown in Fig. 2 and are summarized in Table 2. UV100 (anatase) has, by far, the highest amount of acid sites (900 μmol.g⁻¹) but an intermediate acid site density (3 μmol.m⁻²). P25 (anatase and rutile) has the lowest amount of acid sites (200 μmol.g⁻¹) but the highest acid density (3.64 μmol.m⁻²). And Rut160 (rutile) has an intermediate acid sites amount (240 μmol.g⁻¹) and the lowest acid sites density (1.37 μmol.m⁻²).

From the calorimetric curves of ammonia adsorption shown in Fig. 2, one can see that the anatase TiO₂ catalysts, UV100 and P25, have a homogeneous surface acidity characterized by an extended plateau around 140 kJ.mol⁻¹ for UV100 and a shorter one for P25 around 120 kJ.mol⁻¹. By contrast, rutile TiO₂, Rut160, has a heterogeneous surface acidity characterized by a progressive decrease of the heat of ammonia adsorption with the ammonia coverage. This surface heterogeneity in terms of acid strength cannot be easily explained. It could be due to the presence of 5 % Si (determined by XPS) in the catalyst [33] or other remaining organic impurities on the catalyst's surface could be possible reasons. This could also be a feature of the Rutile TiO₂ phase and/or its low crystallinity with a wide variability of the Lewis acid site (Ti⁴⁺) local environments. The calorimetric curves show also that UV100 has the highest amount of strong acid sites (with Q_{diff} > 150 kJ.mol⁻¹), 150 μmol.g⁻¹ while Rut160 and P25 have only 25 and 10 μmol/g, respectively.

3.2.3. Strength and number of TiO₂'s basic sites

The TiO₂ catalysts' basicity was probed by the adsorption of CO₂ monitored by calorimetry. The amounts of basic sites and their density (basic sites amount divided by the catalysts surface area) and the total basic to acid sites ratios were determined from the isotherms of CO₂ adsorption shown in Fig. 3 and are summarized in Table 2. UV100 (anatase) has the highest amount and density of basic sites (120 μmol.g⁻¹ and 0.4 μmol.m⁻², respectively). Rut160 (rutile) has 40 μmol.g⁻¹ of basic sites with a density of 0.23 μmol.m⁻² and P25 (anatase/rutile mixture) has the lowest amount and density of basic sites, equals to 10 μmol.g⁻¹ and 0.18 μmol.m⁻², respectively. The calorimetric curves (Fig. 3) confirm that the surface of P25 has almost no basicity with a rapid fall off the differential heat of CO₂ adsorption. By contrast, the pure rutile and anatase TiO₂ phases have significant basic surface with distinct features. Pure anatase TiO₂, UV100, presents the most homogenous basic surface in terms of basic strength distribution with a pseudo plateau observed around 105 kJ.mol⁻¹. The pure rutile TiO₂, Rut160, is characterized by a very heterogeneous surface as regards to the basic sites' strength. This is evidenced by the continuous decrease of the differential heat of CO₂ adsorption with the CO₂ coverage. It may be concluded that each of the studied pure rutile and pure anatase TiO₂ have a bi-functional acid-base surface by contrast to the reference P25 which exhibited only a mono-functional acidic surface. Moreover, the calorimetric measurements have underlined that the studied rutile TiO₂ was characterized by heterogeneous superficial acid-base properties whereas the studied anatase TiO₂ presented, by far, a more homogeneous acid-base surface. To strengthen this assumed correlation between the acid-base properties and the nature of the TiO₂ phase, complementary investigations are in progress.

3.3. Aqueous phase glucose adsorption capacities of TiO₂

The adsorption of the substrate on the photocatalysts has been reported as a key factor in photocatalytic conversion [33]. Therefore, the adsorption of glucose in water on P25, UV100 and Rut160 was studied in water. As shown in Fig. 4, the more the catalyst had a high acid sites density, the more it adsorbed glucose suggesting that the Lewis acid sites would act as adsorption sites. P25 that has the highest Lewis acid sites density (3.64 μmol.m⁻²) adsorbed the most glucose (1.2 μmol.m⁻²) and Rut160 that has the lowest Lewis acid sites density (1.37 μmol.m⁻²) adsorbed the least glucose (0.3 μmol.m⁻²). This difference could be explained by the fact that glucose could necessitate 3

Fig. 2. Ammonia adsorption on TiO₂ (anatase and/or rutile): isotherms and calorimetric curves.

Conditions: TiO₂ samples pre-treated at 150 °C to secondary vacuum for 5 h, NH₃ adsorption performed at 80 °C.

Table 2

Acid and basic sites amounts of TiO₂ determined by calorimetry of NH₃ and CO₂ adsorption.

Catalyst	¹ Acid sites amount (μmol g ⁻¹)	¹ Acid sites density (μmol m ⁻²)	¹ Amount of strong acid sites (μmol g ⁻¹)	¹ Basic sites amount (μmol g ⁻¹)	¹ Basic sites density (μmol m ⁻²)	¹ Basic/Acid sites ratio	² Glucose adsorption capacities (μmol.m ⁻²)
P25	200	3.64	10	10	0.18	0.05	1.2
UV100	900	3	150	120	0.4	0.13	0.7
Rut160	240	1.37	25	40	0.23	0.17	0.3

Conditions: ¹TiO₂ samples pretreated at 150 °C to secondary vacuum for 5 h, NH₃ adsorption performed at 80 °C, CO₂ adsorption performed at 30 °C. ² Glucose adsorption isotherms performed at 30 °C in aqueous phase.

near acid sites for its optimal adsorption on the catalyst forming a polydentate complex. In this regard, an earlier study had already suggested the possible formation of a bidentate complex [31].

3.4. Glucose (photo)catalytic conversion over TiO₂ catalysts

To validate whether or not the photocatalytic conversion of glucose into valuable chemicals could compete with the usual heterogeneously catalyzed glucose hydrothermal conversion, the two transformations were carried out in the same reactor that enable to keep equals the main experimental parameters except the temperature and the irradiation (Table 3).

3.4.1. Glucose photocatalytic conversion over anatase and/or rutile TiO₂ catalysts

3.4.1.1. Influence of the atmosphere, Ar vs air, investigated over the reference P25. First, the influence of the atmosphere, Ar vs Air, was studied over the reference P25 TiO₂. Not surprisingly, the glucose transformation was rapidly stopped in absence of oxygen resulting in a glucose conversion of only 20 % after 4 h of irradiation. In the presence of oxygen, the glucose conversion achieved 38 % after 4 h. However, whatever be the atmosphere or the reaction progress, the same products are formed: gluconic acid (C₆ carboxylic acid), arabinose and erythrose (respectively C₅ and C₄ sugars) and formic acid. This would suggest that a similar glucose transformation pathway proceeds whatever be the atmosphere. As expected, the role of oxygen would be to limit electron-

Fig. 4. Glucose adsorption isotherms in aqueous phase performed at 30 °C.

holes recombination. Therefore, in the subsequent steps on the investigation, only air was used (aerobic conditions).

3.4.1.2. Influence of the TiO₂ phases investigated in aerobic conditions. Table 4 summaries the glucose conversion in the presence of P25, UV100 and Rut160 after 4 h of irradiation at ambient

Fig. 3. CO₂ adsorption on TiO₂: isotherms and calorimetric curves.

Conditions: TiO₂ samples pre-treated at 150 °C to secondary vacuum for 5 h, CO₂ adsorption at 30 °C.

Table 3

Experimental parameters of glucose photocatalytic and catalytic hydrothermal conversions.

Glucose conversion	Photocatalytic	Hydrothermal
Temperature (°C)	24-29	120
Light irradiation	UV	without
Pressure (bars)	5	
Water (mL)	50	
[TiO ₂] (g.L ⁻¹)	0.5	
[Glucose] (g.L ⁻¹)	0.5	
Atmosphere	Air vs Argon	

Table 4

Glucose conversion and carbon balance after 4 h of irradiation with P25, UV100 and Rut160.

Catalyst	Glucose conversion (%)	C Balance (%) (TOC)
P25	38	88 ± 5
UV100	31	100 ± 5
Rut160	29	100 ± 5

Conditions: T = 20 °C, Pair = 5 bars, V_{water} = 50 mL, [glucose] = 0.5 g.L⁻¹, [TiO₂] = 0.5 g.L⁻¹, UV irradiation.

temperature in aerobic conditions (S3 in Supplementary informations shows glucose conversions with time course). P25, the catalyst with the highest Lewis acid sites density and the highest glucose adsorption capacity, converted the most the glucose. In fact, the more the catalyst adsorbs substrate the faster the substrate is oxidized by the holes generated by the photons absorption. The less active catalyst was the pure rutile (Rut 160) showing the lowest Lewis acid sites density and the lowest glucose adsorption capacities. The pure anatase TiO₂, UV100 exhibited an intermediate photocatalytic activity, well correlated with its Lewis acid sites density and its glucose adsorption capacity.

Fig. 5 shows the time course of the main products yields, gluconic and formic acids, fructose, arabinose and erythrose. Other minor products are also detected such as lactic and glycolic acids, in total yield lower than 1 C %. Note that after 4 h, the sums of the carbon yields of products analyzed by HPLC are in the order of magnitude of the glucose conversion for UV100 and Rut160, in good agreement with the liquefied carbon balance deduced from TOC analyses. For P25, the most active photocatalyst, the sum of the carbon yields of the products analyzed by HPLC represents roughly 75 % of glucose conversion. This agrees with the lowest liquefied carbon balance measured over P25, ~ 88 %. This indicates the formation of products, not detected by HPLC, which might be solid or gaseous products.

Among the main products detected by HPLC, gluconic acid was first produced with the three commercial TiO₂. It resulted from the oxidation of the glucose aldehyde function into carboxylic acid function. It was then converted by decarboxylation into arabinose which was one of the major products with the formic acid in the presence of the three commercial TiO₂. The arabinose was then probably oxidized into

erythrose most likely through intermediate formation of arabinoic acid (not detected). This is in agreement with the previous works in this field [6,10,15]. By contrast to P25, Rut 160 and UV100 allowed significant fructose yield after 2 h of reaction. It is known that fructose is produced by glucose isomerization, catalyzed as well by Lewis acid sites as by basic sites [25–27]. After two hours of irradiation, fructose was more produced with UV100 and Rut160 reaching yields around 4 % than with P25 having a yield of only 0.4 %. This difference could be related to the higher basic/acid sites ratio that characterizes the UV100 and Rut160 (Table 2). Indeed, the glucose isomerization into fructose which is catalyzed by both Lewis acid and basic sites appears to be facilitated by the basic sites in agreement with previous findings [36].

It is worth noting that the evolution of the products during the reaction period didn't show significant differences between anatase and/or rutile TiO₂ phases suggesting that, most likely, the same reaction mechanism prevailed whatever be the TiO₂ phase. The proposed reaction pathway is illustrated in Scheme 1.

The carbon balance in liquid phase after 4 h of irradiation was around 88 % in the presence of P25 (Table 4). The missing carbons could have been transformed into products in gas phase as suggested above by mineralization into CO₂. This has been observed along the irradiation duration not only with P25 but also with UV100 and Rut160 (Fig. 6). The analysis of the gas phase composition strengthened the proposed mechanism in Scheme 1. Less CO₂ was detected over Rut160, in agreement with the higher amount of products analyzed by HPLC.

3.4.2. Glucose hydrothermal conversion over TiO₂

3.4.2.1. Influence of the temperature investigated over the reference P25 under air. The hydrothermal conversion of glucose was first studied at different temperatures (90, 120 and 150 °C) with P25. Fig. 7 shows that rising the temperature from 90 °C to 150 °C, as expected, increased the glucose conversion. First, one can see that for T ≤ 120 °C and with or without catalysts, the kinetic curves show a rapid slowdown of the rate of glucose consumption with time which could be ascribed to the occurrence of fast glucose-fructose isomerization, an equilibrated reaction. Additionally, a blank experiment, done at 120 °C in absence of TiO₂ P25, lead to a maximum glucose conversion of 12 %, quite equivalent to the value achieved at 90 °C with P25. This is ascribed to the contribution of homogeneously catalyzed transformations promoted by hot water self-protolysis [35]. Thus, to achieve a significant contribution of the TiO₂ P25, the temperature should be at least 120 °C. In fact, compared to the blank experiment at this temperature, the presence of the solid catalyst P25 improved the initial rate of glucose consumption and its conversion after 4 h of reaction by a factor of 3 to reach 30 % after 4 h. Such a value was in the range of magnitude of glucose conversion achieved in the photocatalytic process carried out exactly in the same experimental conditions but at ambient temperature and with UV activation (Table 4).

This comparison of glucose photocatalytic transformation with its hydrothermal catalytic transformation, both carried out for the first time in the same reactor and with the same TiO₂ catalyst, proves that

Fig. 5. Glucose photocatalytic conversion: evolution of the products yields (%C) over P25, UV100 and Rut160.

Conditions: T = 24–29 °C, Pair = 5 bars, V_{water} = 50 mL, [glucose] = 0.5 g.L⁻¹, [TiO₂] = 0.5 g.L⁻¹, UV irradiation.

Scheme 1. Proposed glucose photocatalytic pathway prevailing over TiO_2 .

Fig. 6. Time course of CO_2 produced by glucose photocatalytic conversion over UV100 (anatase), Rut160 (rutile) and P25 (anatase/rutile). Conditions: $T = 20^\circ\text{C}$, $P = 5$ bars, $V_{\text{water}} = 50$ mL, $[\text{glucose}] = 0.5$ g.L $^{-1}$, $[\text{TiO}_2] = 0.5$ g.L $^{-1}$, UV irradiation.

Fig. 7. Effect of temperature on glucose hydrothermal conversion catalyzed by P25. Conditions: $P = 5$ bars, $V_{\text{water}} = 50$ mL, $[\text{glucose}] = 0.5$ g.L $^{-1}$, $[\text{TiO}_2] = 0.5$ g.L $^{-1}$, without UV irradiation.

the photocatalytic valorization of sugars is a competitive and a less energy demanding route compared to their usual catalytic valorization in hot water.

Fig. 8. Hydrothermal glucose conversion catalyzed by P25, UV100, Rut160 at 120°C .

Conditions: $P = 5$ bars, $V_{\text{water}} = 50$ mL, $[\text{glucose}] = 0.5$ g.L $^{-1}$, $[\text{TiO}_2] = 0.5$ g.L $^{-1}$, without UV irradiation.

3.4.2.2. Influence of the TiO_2 phases. The three commercial TiO_2 catalysts converted glucose into chemicals at 120°C more than without their addition (Fig. 8). Additionally, a general slowdown of the glucose consumption was observed after 0.5 h, partly due to the glucose-fructose equilibrium. Indeed fructose was always one of the main primary products and the formation of the other products generally increased with the reaction progress (Fig. 10). However, it is worth noting that for short reaction time, the sums of the carbon yields of the products (Fig. 10) are far below the glucose conversions for the two most active catalysts, UV100 and Rut160 and represent roughly 40 % and 25 % of the converted glucose after 1 h of reaction. This indicates that the fast disappearance of glucose in the presence of UV100 and Rut160 might lead to the initial formation of products not analyzed by HPLC such solid/gaseous products or most likely soluble oligomers. After 4 h of reaction, the sums of the carbon yields of products detected by HPLC increase and represent 75 % and 45 % of the glucose conversion for UV100 and Rut160, respectively. Besides, the liquefied carbon balance drawn from TOC analyses are respectively equal to 70 % and 87 % for UV100 and Rut160. One can conclude from the agreement between the sum of carbon yields of the products analyzed by HPLC and the TOC analyses over UV100 that the missing products might be solid products or gaseous products. Note that CO_2

Fig. 9. Relationship between the initial rate of glucose conversion and the Basic/Acid sites balance.

formation was continuously detected over UV100. By contrast, the marked difference between the sum of carbon yields of the products detected by HPLC and the TOC analyses over Rut160 is rather ascribed to an important contribution of soluble oligomers formation, not detected by HPLC.

It is worth noting that the ranking of the three catalysts with regards to their effects on hydrothermal glucose conversion (Rut160 > UV100 > P25) did not match their ranking observed in the photocatalytic process: (P25 > UV100 > Rut160) which corresponded to their glucose adsorption capacities and Lewis acid sites density ranking. Of all evidences, this indicates that neither the glucose adsorption, nor the Lewis acid sites densities were the main driving forces of the TiO₂ catalysts functionalities in hydrothermal conditions. However, the TiO₂ basicity and more precisely their Basic/Acid sites balance would be correlated to their catalytic glucose conversion efficiency. The dependence between the initial rate of glucose consumption and the TiO₂ basic/acid sites ratio is shown in Fig. 9.

A variety of products was analyzed by HPLC in liquid phase in the presence of all the TiO₂ catalysts: fructose, gluconic acid, formic acid, arabinose, erythrose, glycolic acid, lactic acid, dihydroxyacetone, acetic acid, levulinic acid and 5-HMF. Fig. 10 shows the evolution with time of the products yields for the two more active catalysts, Rut160 and UV100. Fructose and gluconic acid were the main products detected in the presence of the three catalysts and they had the behavior of primary products. With the exception of acetic acid, levulinic acid and 5-HMF which apparently were secondary products, most of the other products were also formed in the photocatalytic conversion of glucose at atmospheric temperature.

According to the clear relationship between TiO₂ catalytic

performance to convert glucose and their basic/acid sites balance, it was expected to observe fructose among the main products. Indeed fructose formation from glucose was found as a tracer of the catalyst superficial basicity workable in water [26,27]. Maximum fructose yields of 20 % were achieved with Rut160 and only 10 % with UV100 having basic/acid site ratios of 0.17 and 0.13, respectively. These results strengthened our previous remark concerning the superior activity of the basic sites over the Lewis acid sites on glucose isomerization to fructose.

Gluconic acid was one of the main product (Fig. 10). Additionally, it was not deeper oxidized into glucaric acid. A gluconic acid yield as high as 14 % was obtained with UV100 without metal promotion. It was also produced significantly with Rut160 but only in trace amount with P25 (S4 in supplementary information). It is known that the oxidation of glucose catalyzed by supported metal catalysts gives gluconic acid which can be oxidized into glucaric acid [21–26] and that the presence of a soluble bases is crucial for efficient glucose oxidation into chemical [21–23]. Moreover, one can note that Au-M/TiO₂ were recently reported as efficient catalytic system for the glucose oxidation in base free conditions [24,22–26]. So, metal free TiO₂ are disclosed as efficient catalysts for the oxidation of glucose into gluconic acid in soluble base free conditions and under low pressure of air. Since UV100 and Rut160 have more basic sites (120 and 40 μmol/g, respectively) than P25 (10 μmol/g), one might propose that the oxidation of glucose into gluconic acid would require basic sites. But also, Lewis acid sites could intervene in the overall pathway since the more efficient catalysts for gluconic acid formation is UV100 which is characterized by a more balanced basic/acid sites ratios among the three studied TiO₂ catalysts (Table 2).

Levulinic acid and 5-HMF, that are unexpected products in the absence of Brønsted acid were observed. Discrepancies exist in the literature as regards to the abilities of TiO₂ catalysts to produce 5-HMF as a function of the nature of the TiO₂ phase and/or its assumed acid-base properties not investigated in a systematic way [28–30,35]. It has been clearly demonstrated that the dehydration of fructose into 5-HMF is a Brønsted acid catalyzed step and that soluble carboxylic acids are more efficient than their solid homologues [28,36]. Therefore, since the used TiO₂ catalysts didn't exhibit Brønsted acid sites as deduced from our FTIR of pyridine adsorption study, it is logical to propose that levulinic acid and 5-HMF production could be catalyzed by the homogeneous carboxylic acids formed in the reaction medium, such as gluconic acid and formic acid. Accordingly, levulinic acid is favored over UV100 (anatase). When the total yield in gluconic and formic acid achieved 14 % after 2 h, levulinic acid is detected and increased gradually up to a yield of 4 % after 4 h.

Many other products with lower carbon numbers are formed such as dihydroxyacetone, pyruvaldehyde, lactic acid but also shorter aldoses such as erythrose and arabinose. The formation of the three former

Fig. 10. Products yields of glucose hydrothermal conversion over UV100 (anatase) and Rut160 (rutile): Evolution of the products yields with time at 120 °C. Conditions: Pair = 5 bars, V_{water} = 50 mL, [glucose] = 0.5 g.L⁻¹, [TiO₂] = 0.5 g.L⁻¹, without UV irradiation.

Scheme 2. Proposed TiO_2 superficial Lewis acid, basic sites and neutral hydroxyl groups.

products were previously explained by C-C cleavages catalyzed by basic sites (retro-aldol reaction) [37] as well as by Lewis acid sites which promotes also hydrides or hydroxides transfers [34,38].

It is worth noting that erythrose was also detected as a product. It could have been formed by retroaldolisation of glucose catalyzed by basic sites [30] or the oxidation of gluconic acid through the same pathway described in photocatalysis. Indeed, some CO_2 and arabinose were produced under hydrothermal conditions (120 °C and 5 bar) in the presence of TiO_2 . This suggests the occurrence of a pathway, under hydrothermal conditions conditions having, most likely, some similarities with the photocatalytic one.

Based on presented results and the above discussion, a general mechanism is proposed to account for the detected products where all the elementary steps are catalyzed by Lewis acid or basic sites as the catalytic functions present on the TiO_2 surface or by the homogeneous

Bronsted acidity brought by the produced carboxylic acids. One can reasonably assume that the Lewis acid sites are coordinatively unsaturated Ti^{4+} ions and Lewis basic sites are O^{2-} ligands, close to superficial neutral hydroxyl groups, as presented in the Scheme 2. A proposed general mechanism is shown in Scheme 3.

4. Conclusion

To conclude, the surface properties of the three commercial titanium dioxide catalysts (P25: mixture of anatase and rutile, UV100: anatase and Rut160: rutile) have been first characterized. All these catalysts have Lewis acid sites with different amounts and densities but no Brønsted acid sites. They showed also differences in term of basicity (amount and density). Moreover, the adsorption of glucose in water on the TiO_2 samples was evaluated and was correlated to the Lewis acid sites density (adsorption sites). Besides, the glucose photoconversion and hydrothermal conversion have been compared in the same reactor. The photocatalytic performances of the three commercial titanium dioxide catalysts could be correlated to their Lewis acid sites density and hence to their glucose adsorption capacities. Glucose was valorized to higher value added chemicals: gluconic acid, arabinose and erythrose. Glucose hydrothermal conversion was rather related to the TiO_2 base/acid sites ratio and fructose, gluconic, formic and levulinic acids were the main products of interest. Among the used catalysts, UV100, was seen as an efficient metal free catalyst for the glucose oxidation into gluconic acid. Moreover, the hydrothermal glucose isomerization into fructose was facilitated by the more basic TiO_2 surfaces. Furthermore, the gluconic and formic acids formed in-situ acted as homogeneous catalysts for dehydration and hydration reactions giving 5-HMF from fructose and levulinic acid from 5-HMF, respectively. Finally, the glucose oxidation by photocatalysis and hydrothermal treatment, studied in the same reactor and the same conditions, gave the same platform chemicals gluconic and formic acid, with total yields in the same order of magnitude. Our results demonstrate the photocatalytic process potential as regards to the catalytic hydrothermal process due to the milder experimental conditions involved. However, it is clear that the scaling-up perspectives of the photocatalytic processes will be more complex and would require to solve known limitations such as the substrate and catalysts concentrations as well as the reactor design.

CRediT authorship contribution statement

Insaf Abdouli: Investigation, Validation, Writing - original draft. **Marion Eternot:** Methodology, Formal analysis, Resources. **Frederic Dappozze:** Methodology, Formal analysis, Resources. **Chantal Guillard:** Supervision, Validation, Writing - review & editing. **Nadine Essayem:** Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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