The origins of photocatalysis

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Abstract The study of photocatalytic reactions was initiated in 1970's. The definitions of photocatalysis, photosynthesis and photodegradation (photo-ageing) are given. For photocatalysis the wavelength of UV irradiation and the nature of the photocatalyst are discussed. The experimental conditions and the mechanism of the photo-partial-oxidation of alkanes and olefinic hydrocarbons into aldehydes and ketones, at R.T., are presented. Conditions for the "photosplitting" of water are discussed.

Keywords Photocatalysis · Photodehydration · Photodissociation · Photo-splitting · Photodehydrogenation · Spillover · Titania · Hydrocarbons · Alkohols · Olefins · Water · Sacrificial compounds

It is interesting to recall when and how the discipline of photocatalysis was born and how the first photocatalytic reactions were carried out in Lyon at the Institute of Research on the Catalysis and University Claude Bernard. Indeed, today photocatalysis has become a major branch of catalysis and it is the basis for many scientific papers. In Lyon, various photocatalytic reactions continue to be studied, particularly in environmental catalysis (Central School and University Claude Bernard) [1]. Catalytic processes for purification of polluted water are commercial and utilize either UV produced by lamps or sunlight [1]. (This reference won the award for the Top 10 most cited articles in Catalysis Today in 1999). The concept and the term

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"heterogeneous photocatalysis" (photocatalyse hétérogène) were introduced and developed in Lyon in 1970 to describe the partial oxidation (not total) of alkanes and olefinic hydrocarbons [2]. The reactions took place at ambient temperature in the presence of titanium dioxide (TiO_2, anatase) under UV irradiation. The "heterogeneous" adjective specifies the nature of the reaction medium which is not homogeneous but comprises at least two phases: the solid (catalyst) and a fluid reagent (gas or liquid).

The term "photocatalysis" can be applied only to the reactions occurring with a reduction in the free energy ($\Delta G < 0$). The speed of these reactions is increased thanks to a particular reaction pathway involving photocreated species. This pathway differs from the usual thermal reaction sequence (without irradiation) and leads to reaction product selectivities different from those for the thermal reactions.

For thermodynamically unfavorable reactions ($\Delta G > 0$), the energy of UV irradiation is converted into chemical energy and the term "photosynthesis" (with or without catalytic steps) applies.

These two processes, photocatalysis and photosynthesis, are entirely different and should not be confused. The second has been known since a long time and one of the best examples is chlorophyll photosynthesis. Reactions of photodegradation ($\Delta G < 0$) can be qualified as photocatalytic only when one catalyst (heterogeneous or homogeneous) is clearly highlighted. If not they are recognized as "photoageing", a common phenomenon where the energy of the irradiation compensates for the potential barrier (activation energy). An example taken from modern life illustrates this case: a food plastic sheet undergoes degradation by the sun over many years (photo-ageing). But when

particles of TiO_2 (catalyst) are built into the sheet, degradation is significantly accelerated(catalytic photodegradation). A misunderstanding of the difference between photocatalysis ($\Delta G < 0$) and photosynthesis ($\Delta G > 0$) was exhibited as recently as 1996 at the 11th International Congress of Catalysis in Baltimore.

The studies in Lyon were induced by the initial observation of the behavior of TiO_2 under irradiation UV at ambient temperature. Indeed, when this oxide is simultaneously evacuated (10^{-6} torr) and subject to UV irradiation, it becomes blue by losing a fraction of its surface oxygen. When the sample is again exposed to oxygen, its stoichiometry is restored along with its initial color (white). Simultaneously, a small quantity of oxygen was photoadsorbed [3]. These phenomena are expressed in the chemical equations shown below.

Titanium dioxide is not a typical hydrocarbon oxidation catalyst, in contrast with oxides of Cu, Ni, Co, Cr, Mo, or V. One needs a temperature higher than 300°C to observe hydrocarbon oxidation in the presence of TiO_2. CO_2 and H_2O (total oxidation) are the only products for TiO_2 catalyzed hydrocarbon oxidation above 300°C. The discovery at ambient temperature and under UV of photoformed species, mentioned above, encouraged the Lyon group to study photooxidation reactions of light hydrocarbons (C3–C6) in the gas phase with TiO_2, a heterogeneous system [2]. Formation of peroxide free-radical species and their transport to the fluid phase would not be favorable under these (athermal) conditions. Indeed these species lead to the total oxidation of hydrocarbons when the temperature becomes high.

Thus, a new reaction pathway (channel) would be available under UV irradiation at ambient temperature. The new photoformed species could facilitate selectivity other than total oxidation.

The experimental conditions for the subsequent studies of the photo-partial-oxidation of alkanes and olefinic hydrocarbons to aldehydes and ketones were thus determined. These included an understanding of the following influences [4]:

1. The wavelength of UV irradiation
2. The nature of the catalyst (TiO_2 and some other oxides, like ZnO)
3. The quantum yields and the selectivities in the partial oxidation

These results lead to suggest possible photocatalytic solutions to several environmental problems in the presence of TiO_2 in 1972 (related to pollutants such as CO, SO_2 and NO) [5].

The Lyon school presented their results for partial photo-oxydation of various paraffins to aldehydes and ketones in the presence of TiO_2 in 1972 at the 5th International Congress on Catalysis held in Palm Beach (Florida) [6]. This was the first and the only contribution on photocatalysis at an international meeting. The number of communications on this topic has increased significantly in each subsequent meeting.

In 1974, the Lyon team presented a rather exhaustive study of the reactivity of various carbon atoms for photooxydation reactions [7]. This reactivity follows the sequence Ctert > Cquat > Csec > Cprim. In addition, the average product selectivity for partial hydrocarbon oxidation (into aldehydes and ketones) is 76% for N-alkanes, 80% for Iso-alkanes and 57% for néo-alkanes. Compared with the 100% selectivity to CO_2 for thermal oxidation, these results seemed completely exceptional. They made it possible to propose a mechanism of photocatalytic oxidation of hydrocarbons that is different from that of catalytic thermal oxidation. It is necessary to briefly describe this mechanism because it is the basis for all subsequent photocatalytic oxidation mechanisms.

The reaction of the primary, secondary and tertiary carbon atoms with photoadsorbed oxygen (for the moment designated as $O_{(ads)}$) proceeds with the formation of an alcoholic intermediate. Peroxydic or hydroperoxydic intermediates are not formed, as found in thermal oxidation:

$$R–H + O_{(ads)} \Rightarrow R–OH$$

This alcoholic intermediate can subsequently be oxidized to an aldehyde or ketone but for secondary and tertiary carbon atoms it can also be photodehydrated to an olefinic hydrocarbon which, finally, is oxidized to an aldehyde or ketone.

The variation of the potential of the thermoelectronic work function of the titanium dioxide in the presence of isobutene was studied. This showed that this hydrocarbon is not chemically adsorbed at ambient temperature by TiO_2 with or without UV irradiation. It reacts as a physically absorbed species with the other partner, oxygen [8]. The essential problem thus consists in defining the nature of active oxygen.

An electron e^- and positive hole h^+ pair is formed in the solid catalyst when the wavelength of irradiation UV corresponds to the absorption transition of the solid catalyst (width of the forbidden band, 3.2 eV for TiO_2):

$$h\nu(3.2 \text{ eV}) + TiO_2 \Rightarrow h^+ + e^-$$

Oxygen is then photoadsorbed:

$$O_{2(g)} + e^- \Rightarrow O_{2(ads)}^- \tag{A}$$

The species $O_{2(ads)}^-$ is not directly active in this process; otherwise, one would observe the formation of peroxides or hydroperoxides. The active species is formed by the recombination of the preceding species with the positive hole:

$$O_{2(ads)}^- + h^+ \Rightarrow 2\,O_{(ads)}^* \tag{B}$$

It is this last species which is added to the hydrocarbon to yield the alcohol, as mentioned above:

$$O_{(ads)}^* + R\text{–}H \Rightarrow R\text{–}OH$$
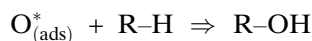
It, indeed, was shown that the hydrocarbons give alcohols by interaction with the atomic oxygen formed by dissociation of N_2O. As it was shown previously, alcohol is not stable and can be photodehydrated to an olefinic hydrocarbon which subsequently can be photo-oxydized to an aldehyde or ketone. This last part of the mechanism of oxidation is likely to involve a photo-redox step, either, from gas oxygen or from the TiO_2 surface. It was mentioned above that titanium dioxide is likely to lose its surface lattice oxygen $O_{(r)}^=$ under irradiation UV in vacuum (or under the reducing conditions), becoming blue:
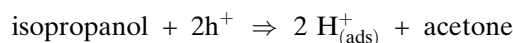
$$2\,h\nu + TiO_2 \Rightarrow 2\,h^+ + 2\,e^- \tag{C}$$

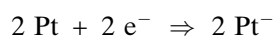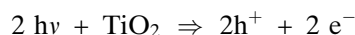$$2\,h^+ + 2\,O_{(r)}^= \Rightarrow O_{2(g)} + [\,2e^-\,]_{(r)} \tag{D}$$
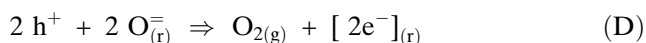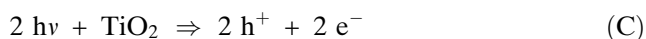
Where $[2e^-]_{(r)}$ is the anion vacancy, having trapped two electrons.

It is not yet completely clear which active oxygen species participates in the transformation of olefinic hydrocarbons into aldehydes and ketones i.e., the species formed starting from adsorbed oxygen gas (Eqs. A and B), or that formed from lattice oxygen (redox mechanism, Eqs. C and D). It is reasonable to assign the activity for more complete oxidation to lattice oxygen, by analogy with the redox mechanism for thermal oxidations, and to photoadsorbed oxygen for partial oxidation.

Another point still remains to be elucidated. It was shown above that TiO_2 is active for the photo-dehydration of alcohols. This is the only reaction that occurs in the absence of oxygen. However, it is possible to prevent the dehydration of alcohols and to induce these compounds to dehydrogenate and not to dehydrate. The resultant products would be aldehydes and ketones. To this end, it is necessary to associate titanium dioxide with a metal such as Pt (or Pd, Ru, Ni, but not Cu), which collects the hydrogen formed at the expense of the corresponding alcohol. It was thus shown that the a Pt/TiO_2 photocatalyzes the dehydrogenation of isopropanol to acetone under UV irradiation at ambient temperature [9]. The Pt particles present on TiO_2 facilitate recombination and desorption of the atomic hydrogen formed by dehydrogenation of the alcohol. This phenomenon bears the name of reverse spillover and was studied extensively by the Lyons school [10].

$$2\,h\nu + TiO_2 \Rightarrow 2h^+ + 2\,e^-$$

$$2\,Pt + 2\,e^- \Rightarrow 2\,Pt^-$$

$$isopropanol + 2h^+ \Rightarrow 2\,H_{(ads)}^+ + acetone$$

The migration of the H^+ protons towards the Pt particles leads to the formation of the hydrogen gas and is the slow step of the process:

$$2\,H_{(ads)}^+ + 2\,Pt^- \Rightarrow 2\,Pt + H_{2(g)}$$
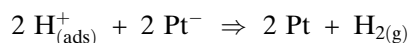
The presence of the steam increases the speed of this reverse spillover. Also, a fundamental question arises in this discussion: could one photodissociate water vapour and not an alcohol to H_2 and O_2 in the presence of Pt/TiO_2? Such a reaction would be very beneficial to mankind, employing natural water resources and solar energy. Unfortunately, the reaction of steam dissociation does not seem feasible because hydrogen does not desorb even in the presence of "sacrificial" reagents (such as alcohols or CO), which would have allowed the capture of the oxygen, possibly formed at the expense of the steam.

The preceding reactions all were conducted in the gas phase. However, it is important to know if the photodissociation of water is possible in the liquid phase. It was thus found [9] that a Pt/TiO_2 catalyst allows the very limited formation of H_2 and CO_2 (but not O_2) in the presence of pure liquid water at ambient temperature and under U.V irradiation. This reaction does not result from the photodissociation of water. Hydrogen comes from the photolysis of surface hydroxyls (OH) on the Pt/TiO_2 catalyst. Pure TiO_2

and Pt/Al_2O_3 are inactive. Oxygen formed thus remains on the surface of the solid in the form of peroxydic species and the reaction stops quickly. But in the presence of organic compounds dissolved in water ("sacrificial compounds") the peroxydic species are consumed yielding CO_2. The rehydration of the surface of TiO_2 in water allows the continuous formation of H_2 and of CO_2 until the exhaustion of the sacrificial compound.

These very first studies of the heterogeneous photocatalysis in Lyon were extensively extended to environmental and pollution applications by P.Pichat and J.M.Herrmann, the successors in Lyon. These investigators were initially at the Institute of Research on the Catalysis, then at the Central School of Lyon and are currently at the University Claude Bernard (L.A.C.E.).

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