

## Review Article

# Hydrogen Production by Photoreforming of Renewable Substrates

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This paper focuses on the application of photocatalysis to hydrogen production from organic substrates. This process, usually called photoreforming, makes use of semiconductors to promote redox reactions, namely, the oxidation of organic molecules and the reduction of  $H^+$  to  $H_2$ . This may be an interesting and fully sustainable way to produce this interesting fuel, provided that materials efficiency becomes sufficient and solar light can be effectively harvested. After a first introduction to the key features of the photoreforming process, the attention will be directed to the needs for materials development correlated to the existing knowledge on reaction mechanisms. Examples are then given on the photoreforming of alcohols, the most studied topic, especially in the case of methanol and carbohydrates. Finally, some examples of more complex but more interesting substrates, such as waste solutions, are proposed.

## 1. Introduction

$H_2$  production through water splitting (WS) is thermodynamically limited by the high Gibbs-free energy (237 kJ/mol, 1.23 eV), representing a typical uphill reaction. Nevertheless, solar energy storage as  $H_2$  by photocatalysis is an intriguing topic, but very low efficiency is reported for direct photocatalytic WS [1–3]. In order to reduce protons and oxidize oxygen ions, a semiconductor should possess a band gap energy higher than the required energy for such reaction. Moreover, the energy levels of the valence and conduction bands should be compatible with those of the species to be reduced or oxidized. Indeed, the electron, promoted somehow in the conduction band, should have much negative potential than the redox couple  $H^+/H_2$ , and the hole left in the valence band should possess higher positive potential than  $O_2/H_2O$  (Figure 1). The band gap energies of many common oxides and sulphides have been recently recalled in [1], together with their performance in direct WS.

Since the first report of WS on  $TiO_2$  [5], various photocatalysts were developed [1], but the efficiency for WS remains very low [6–8]. Sacrificial reagents, such as methanol or EDTA, can improve hydrogen productivity, but they are

nonrenewable [9]. Compared to thermochemical processes, photocatalytic reforming (PR) is a valid approach to produce  $H_2$  under ambient conditions and using sunlight, the cheapest energy source available on earth. PR is also thermodynamically more feasible than WS [10]. After a pioneering study in 1980 [11], the attention was more recently focused mostly on the PR of methanol, the simplest molecule, and a few examples of PR of compounds really obtainable from biomass can be found, for example, ethanol, glycerol [12–14], glucose, sucrose [14], starch and wood [11], and sewage sludge [15]. Glucose and cellulose were also processed with homogeneous catalytic processes [16]. Interestingly, biomass-derived substrates, such as alcohols or carbohydrates, may be used for hydrogen production particularly in the case of waste materials (sewage from food, wine, or paper industry) [17], simultaneously helping to clean wastes (without disposal costs) and to produce a highly valued fuel [18]. On the other hand, technology is mature for the conversion of lignocellulosic biomass, not competing with the food and feed chain, into elementary alcohols and carbohydrates.

PR offers a route to  $H_2$  that, unlikely thermal reforming or gasification, may be exploited under ambient conditions and, using sunlight, it is particularly attractive for areas of

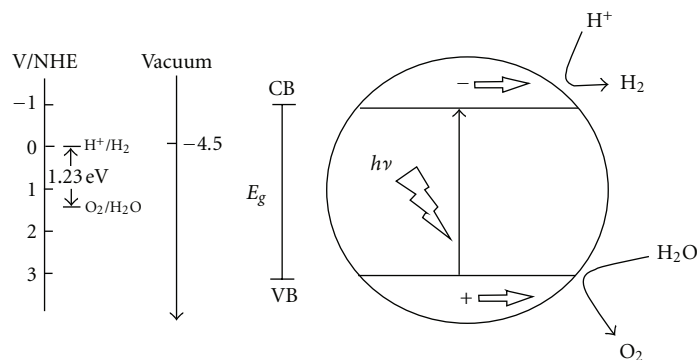


FIGURE 1: Basic mechanism of photocatalytic WS over semiconductors with proper band gap.

the world where high biomass supply coincides with high sunlight intensity. Furthermore, it is a relatively low tech method and therefore particularly useful for small production facilities and developing countries.

Various reviews have been published till now on WS (see e.g., [1, 19–25]), whereas much more limited records can be found relative to PR. In this latter case the attention was predominantly focused on methanol as sacrificial agent and on the development of materials and mechanisms. In this work, besides recalling some of such points, the central topic will be the evaluation of  $H_2$  productivity of different materials and substrates to assess process feasibility and to critically compare various solutions.

## 2. Materials and Mechanisms

The mechanism of PR in aqueous medium is based on photon absorption by a semiconductor, which causes the photopromotion of an electron to the conduction band, with formation of positively charged holes in the valence band. The bandgap energy extension of the semiconductor has to fit the above mentioned requirements on coupling with the redox potential of the hydrogen reduction and oxygen oxidation half reactions. Therefore, it should be in general higher than 1.23 eV. However, if it overcomes 3 eV solar light harvesting becomes minimal. Low efficiency is usually due to light scattering/reflection, poor absorption, and quick electron/hole recombination in the bulk or on the surface of catalyst particles [19] and fast back reaction of  $O_2$  and  $H_2$  during WS. The addition of small quantities of metals limit charge recombination [26], since excited electrons are captured by the metal and reduced protons. Metals should better have low overpotential for  $H_2$ . Strong metal support interaction also improves the efficiency of the metal as electron scavenger helping in the decrease of electron/hole recombination in semiconductors photocatalysis [17, 27, 28]. However, the recombination rate increases at high metal loading because the distance between trapping sites in a particle decreases with the amount of metal, so that an optimum exists [29]. It is also worth mentioning the importance of the spill-over effect in the surface process for hydrogen production [17].

On the other hand, holes migrate to the surface where they oxidize the adsorbed organic molecules, so, another key

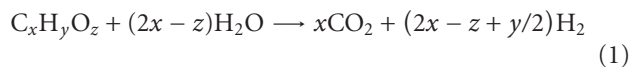
factor to decrease the electron/hole recombination rate is the ability of the organic substrate as hole scavenger, in turn related with geometry and electronic structure upon adsorption [1–3].

The time scale of the different reaction steps is very different. The photoinduced generation of an electron-hole couple occurs in femtoseconds, their recombination in 10–100 ns. Reduction mediated by electrons needs a much longer time, in the order of ms, whereas the oxidative reaction carried out by holes takes *ca.* 100 ns, a comparable time scale with respect to recombination. Therefore, electrons need to be preserved for longer time by trapping them into a metal where they can migrate, or by making holes react with a suitable hole scavenger [30, 31]. When a metal (with proper work function) is deposited on a semiconductor, excited electrons from the semiconductor migrate to the metal until the two Fermi levels are aligned. The Schottky barrier [10, 32] formed at the metal and semiconductor interface can serve as an efficient electron trap to prevent photogenerated electron-hole recombination, greatly enhancing the efficiency of the photocatalytic reaction. The metal also serves as an active site for  $H_2$  production, in which the trapped photogenerated electrons are transferred to protons to produce  $H_2$ .

Methanol and other organic compounds may act as sacrificial agents and hole scavengers in photocatalysis, being able to combine with photogenerated valence-band holes more efficiently than water. For instance, glucose is an efficient hole scavenger for titania [10, 33–35]. Theoretical studies on glucose adsorption over titania showed distinct intragap states; this explains its hole trapping role in  $TiO_2$  [34]. Possible mechanisms for the whole PR process have been proposed, but this complex mechanism still needs validation. In aqueous solution other powerful oxidizing agents may be formed from surface adsorbed water, such as hydroxyl radicals and superoxide anions ( $O_2^-$ ) which are able to oxidize and mineralize almost all organic pollutants yielding  $CO_2$ . As a matter of fact, PR is a much less explored route for obtaining  $H_2$  from oxygenates, such as alcohols, or from biomass extracts and wastes [13, 36, 37].

The feasibility of PR of different biomass-derived compounds has been proved [38] with alcohols, organic acids, and different carbohydrates, such as ribose, arabinose, glucose, galactose, fructose, and mannose. In all cases, the amounts

of excess  $H_2$  with respect to simple WS and  $CO_2$  produced are in accordance with the stoichiometry of the following reaction:



The rate of  $H_2$  production depends strongly on the nature and concentration of the organic substrate and, to a lesser extent, on pH and temperature. For instance,  $H_2$  productivity under solar light irradiation as high as *ca.* 3.75 mol  $H_2$ /h kg of photocatalyst (0.5% Pt/TiO<sub>2</sub>). The heat content of  $H_2$  produced was higher than that of the substrate, demonstrating efficient storage of solar energy.

Among the photocatalysts, TiO<sub>2</sub> is a cheap, widely available and chemically stable, wide bandgap energy semiconductor, hence, the most studied material [39, 40]. Its main properties and photocatalytic application issues have been extensively reviewed recently [41]. However, its main drawback is the scarce harvesting of sunlight, TiO<sub>2</sub> absorbing in the UV region, which constitutes not more than 5% of the solar spectrum. The crystalline phase of TiO<sub>2</sub> is also believed to be a pivotal factor for  $H_2$  production [10, 42, 43]. However, there is not univocal interpretation on the activity of the different crystal phases. Anatase is often considered the most active single phase photocatalyst, though its coupling with rutile may lead to the most interesting results [44]. Indeed, the photogenerated electrons in the anatase crystals may transfer to the conduction band of the rutile crystal and contribute to the reduction of  $H^+$ . The valence bands of both phases have similar energy and thus contribute to the photooxidation of methanol in the same way. Furthermore, the anatase structure is usually more defective than the rutile one, but oxygen defects are alternatively believed as efficient electron traps, enhancing charge separation [45], or undesired recombination sites [46].

Other materials, such as La doped NaTaO<sub>3</sub> [47], Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> [48], Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> [48], La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [49], K<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> [50] have been also proposed for WS, but they share with TiO<sub>2</sub> the drawback of absorption only in the UV region, thus limiting solar light harvesting. Another very active photocatalyst is NaTaO<sub>3</sub>, with NiO as cocatalyst, which however keeps the limitation of absorption in the UV range only [51]. A recent review focused on various materials for photocatalytic applications, where some suggestions on photocatalyst properties are proposed [52].

The effect of crystal or particle size is not univocal, since on one hand quantum confinement of photogenerated charges, revealing for nanometric systems, should enhance activity. Furthermore, increased available surface sites concentration usually improves catalyst activity [53–55]. Nevertheless, surface recombination of electron and holes may prevail, thus limiting the overall activity of the sample [56]. Also porosity may be important since holes may migrate to the surface of micro- or mesopores to oxidize an organic substrate, provided that it is able to diffuse inside the pores. The complementary  $H^+$  reduction reaction may occur on the external surface, where some metal nanoparticles may be present, drawing the photogenerated electrons. This physical

separation of the reaction sites may help to avoid charge recombination, more likely if both species, electrons, and holes, should else migrate towards the external surface [57].

Besides offering a high catalytic activity [58], nano-materials can provide enhanced performances thanks to a suppression of ohmic losses, usually occurring in bulk semiconductors [59, 60]. In addition, the band gap energy may be in principle tuned with particle size, in order to increase light absorption in the solar spectrum [61]. However, size effects sometimes induce an upward/downward shift of the CB/VB edges, complicating the prediction of the exact band positions [62].

Finally, morphology also showed important, especially when 1D nanostructures have been developed, such as nanotubes and nanowires [63–66]. The higher photocatalytic activity of such systems is usually attributed to the high surface area combined with the short diffusion path of the photoexcited species across the bulk to reach the surface, where the reactants are adsorbed [66]. The effect of structure and morphology of semiconductors active for WS has been also recently reviewed [67].

The role of metal ions or oxides as cocatalysts has been enunciated since long time. For instance, bare TiO<sub>2</sub> was almost inactive for both WS and PR of alcohols, whereas 1.0 wt% loading of various noble metals, such as Pt, Pd, Au, Rh, Ag, and Ru, improved  $H_2$  evolution. The activity scale (better results with Pd and Pt) was correlated with the workfunction of the metal. TiO<sub>2</sub> has a large overpotential for  $H_2$  evolution. Since the work functions of the noble metals are larger than that of TiO<sub>2</sub> [68–70], a Schottky barrier can be formed at the metal-TiO<sub>2</sub> interface, as introduced above. The presence of such barrier can decrease the recombination of photogenerated electron-hole pairs and prolong their lifetime, so greatly enhancing the photocatalytic activity [71]. Among nonnoble metals NiO was also effective [72–75]. Complex activation procedures are however reported for NiO cocatalysts, such as combined redox treatments in order to obtain a Ni/NiO system, able to trap electrons while inhibiting the backward electron transfer [76, 77].

The role of metal loading is not univocal.  $H_2$  productivity during WS increased with increasing Pt content up to 1 wt% [10, 78]. When the metal loading was too high, the TiO<sub>2</sub> surface was excessively covered, so decreasing light absorption. Furthermore, excessive metal sites may act as recombination centers. Furthermore, the presence of O<sub>2</sub> strongly inhibits hydrogen production due to back reaction to H<sub>2</sub>O. In addition, dissolved oxygen can quickly consume electrons of TiO<sub>2</sub> due to its stronger ability to trap electrons compared to  $H^+$ .

PR reaction mechanism has been proposed for Pt/TiO<sub>2</sub> catalysts (Figure 2) [10]. Alternative reaction paths have been proposed for Pd/TiO<sub>2</sub> catalysts, where the metal is the main responsible for activity, while photoactivation plays a somehow limited role, leading to activated oxygen species on titania, which may contribute to further oxidation of CO, strongly chemisorbed over Pd particles (Figure 3) [79, 80]. However, the true process must be more complex and relies on the determination of intermediates [10].

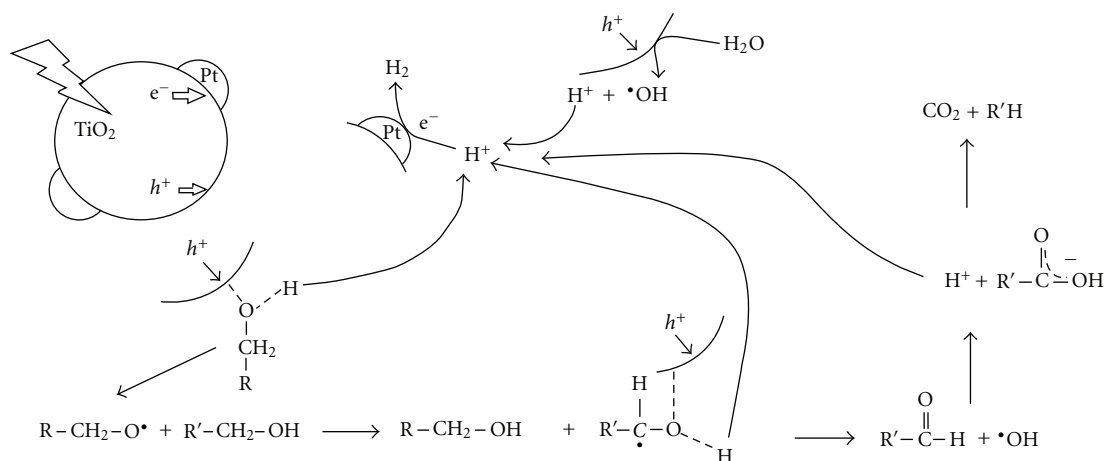


FIGURE 2: Proposed alcohols PR mechanism over Pt/TiO<sub>2</sub> photocatalysts.

One of the key points to develop a reliable catalyst for the PR of biomass derived substrates is its ability to harvest solar light, which is only in part constituted by UV radiation, mostly of IR and visible light (*ca.* 43%). Keeping in mind the requirement on minimum bandgap energy and its coupling with the redox potential of the reactants, different strategies have been considered, such as metal and nonmetal ions doping to narrow bandgap energy, dye-sensitization, development of new photocatalysts through bandgap engineering.

Metals have been sometimes added to improve response of the semiconductor (mainly TiO<sub>2</sub> and SrTiO<sub>3</sub>) [53, 81–84] under visible light irradiation. Indeed, transition metal ions may add unoccupied orbitals allowing electron transfer with much lower energy absorption than the undoped compound, as confirmed by the theoretical evaluation of density of states [85].

Different transition metals were proposed to improve visible light absorption and to generate effective charge separation [86, 87]. Doping ions may trap electrons or holes making them available for the reaction but acting as recombination inhibitors, though this point has been not univocally accepted. Attempts to dope TiO<sub>2</sub> to improve absorption in the visible region have been also reported [18]. Doping with V, Mn, and Cr effectively decreased the TiO<sub>2</sub> bandgap energy from 3.2 to 2.2–2.8 eV. By contrast, addition of Au imparted a pink-violet color due to surface plasmon resonance [88]. It has been demonstrated recently that plasmonic nanostructures of noble metals (mainly Ag and Au) induced interesting applications for photocatalysis, in particular for plasmon-enhanced WS on composite photocatalysts containing semiconductor and plasmonic-metal systems [89].

More exotic catalyst formulation (Bi<sub>x</sub>Y<sub>1-x</sub>VO<sub>4</sub>) showed activity for the PR of glucose under visible light, especially at high Bi loading [90]. Sulphides were also used [1, 91], but they showed much less stability than oxides.

Doping has been proposed with anions, which more likely shift the valence band to higher energy (reducing in any case the bandgap energy) [53, 92]. Some examples of anions doping led however to very limited red-shift [14, 18].

Dye-sensitization, thoroughly explored for solar cells, has some limitations for the present application. In principle a dye, able to absorb visible light, promotes an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied one (LUMO) upon photon absorption. The LUMO has higher energy than the conduction band of the semiconductor, so the net effect may be that an electron is pumped in the CB, able to reduce H<sup>+</sup> to H<sub>2</sub> (Figure 4). On the other hand, the situation is complicated by the need of additional redox couples to oxidize water or any other substrate and to recover the original electronic state of the dye molecule (Figure 5). Furthermore, due to their direct participation in the reaction, many concerns are raised by the stability of the dye molecule for repeated reaction cycles.

Finally, the coupling of different semiconductors has been proposed to improve visible light absorption, provided that the band gap energy of one of them is sufficiently small to efficiently harvest solar radiation and that the electron promoted in its conduction band may actually migrate into the conduction band of the other semiconductor [93, 94]. The same concept has been extended to visible light absorbing semiconductors embedded into a lamellar [95] or tubular [96, 97] structures, able to withdraw the photogenerated separated charges (Figure 6).

Bioinspired approaches have been also attempted, as recently reviewed [98]. During the photosynthetic process, light is absorbed over a wide range of energy and charge recombination is effectively prevented by electron transfer. In particular, two proteins, called Photosystem I and II, are involved in these key steps, coadjuvated by other enzymes. By looking at the active sites of such natural catalysts, many researchers took inspiration to prepare metal complexes able to carry out some interesting reactions. For instance, the enzyme hydrogenase, responsible of H<sup>+</sup> reduction to H<sub>2</sub>, has been immobilized over different materials. TiO<sub>2</sub> has been functionalized with both hydrogenase and a Ru-based complex acting as sensitizer. The latter indeed absorbs visible light, transferring one electron into the conduction band of TiO<sub>2</sub>, which is further transferred to the enzyme for

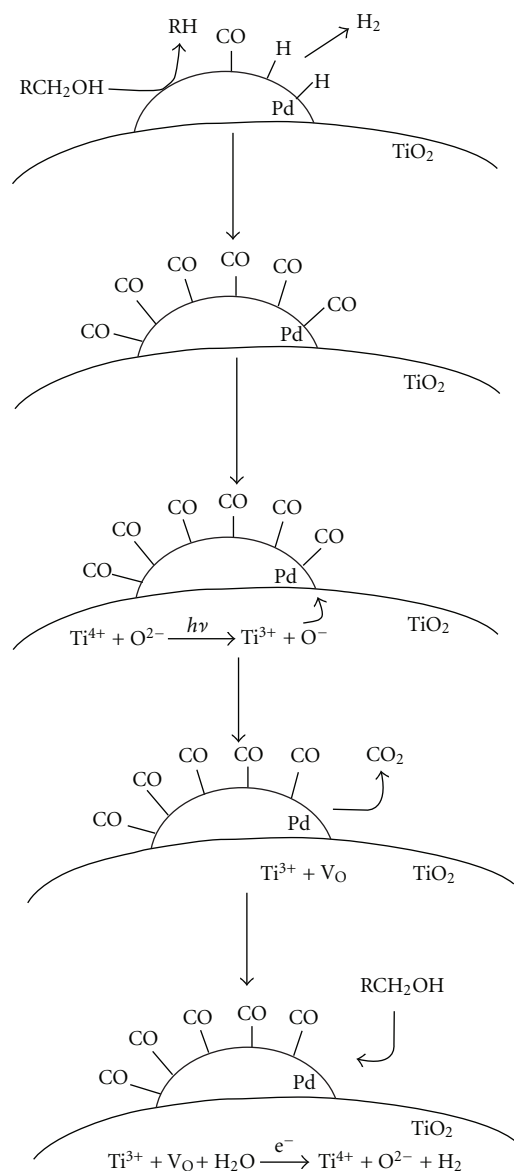


FIGURE 3: Proposed PR mechanism over Pd/TiO<sub>2</sub> samples. V<sub>O</sub> represents an oxygen vacancy.

H<sub>2</sub> production. Of course the cycle should be closed by oxidation of an electron donor species at the Ru complex side [99, 100]. Different ligands have been proposed for Ru, the most common ones being polypyridyl or mixed pyridyl-CO complexes. Other metals have been also proposed, such as Re, Pt, and Ir, showing very high photoactivity for H<sub>2</sub> evolution [101–103]. Unfortunately most of these systems did not prove stable under irradiation [104] and leaching of the dye was often observed. Interesting complexes have been also reported for Co, active for both water reduction and oxidation [3].

Unfortunately, for most of the catalytic systems proposed poor attention is paid to deactivation phenomena. Due to mild temperature conditions sintering is usually ruled out,

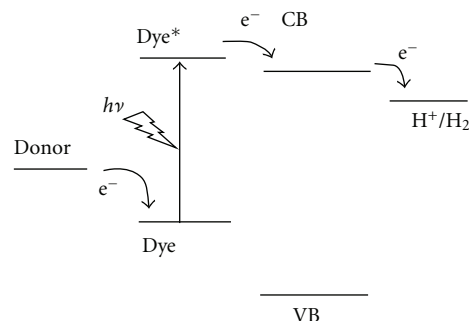


FIGURE 4: Dye-sensitized photocatalytic H<sub>2</sub> production.

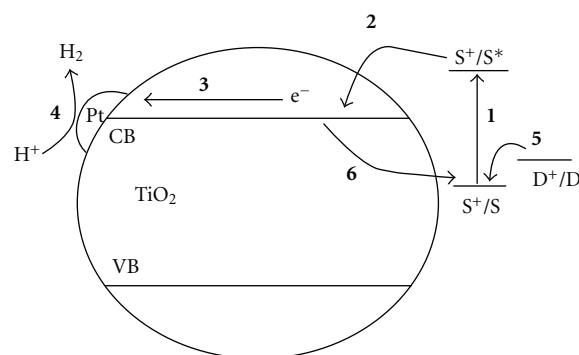


FIGURE 5: Electron transfer paths in dye-sensitized TiO<sub>2</sub>. 1: dye (S) excitation; 2: electron injection from the excited dye to TiO<sub>2</sub> conduction band (CB); 3: electron entrapment into Pt particles; 4: H<sup>+</sup> reduction and H<sub>2</sub> evolution over the metallic site; 5: regeneration of the oxidized dye by an electron donor (D); 6: electron recombination in the oxidized dye. Readapted from [1].

but poisoning, often by reaction intermediates, and leaching are very critical points [105].

Details on the different catalyst formulations and their features will be discussed in the next sections.

### 3. Photoreforming of Alcohols

A possible mechanism for the PR of alcohols on TiO<sub>2</sub> involves the oxidation of water molecules by photoinduced holes in the semiconductor. This produces hydroxyl radicals, which abstract an alpha-hydrogen to create a  $\cdot\text{RCH}_2\text{OH}$  radical. The radical is further oxidised to an aldehyde [106–108].

The effect of different metals and their loading on the reactivity of titania-based catalysts for the PR of methanol has been investigated [109]. The highest catalytic activity was achieved with Pd and Pt, though significant improvement of the photocatalytic activity has been observed also with Ir and Au. High activity has been ascribed to noble metals due to their hard oxidability, and they are likely involved in the first dehydrogenation step of the reaction. In particular, the metal should be reduced by methanol or in general by the organic substrate [2]. An optimal loading exists for Pd, at *ca.* 0.5 wt%, and even two optimal loadings (two activity maxima) for Au. This has been correlated to the reaction mechanism,



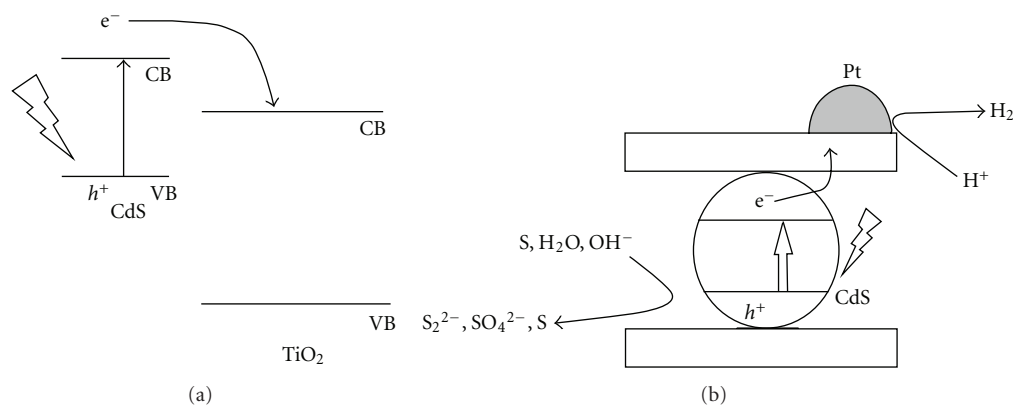


FIGURE 6: Mechanism of charge separation in CdS-TiO<sub>2</sub> composite semiconductors (a). Mechanism of photocatalytic H<sub>2</sub> evolution on CdS-intercalated layered composites loaded with Pt. Photogenerated electrons in CdS are quickly transferred to host layers through the nanostructure, preventing charge recombination. Readapted from [1].

studied in detail over Pd/TiO<sub>2</sub> catalysts. The metal active sites should be exposed on the surface of the metallic particle, and it should be connected with photoactive sites on titania [2, 109, 110].

The H<sub>2</sub> production rate showed dependent on methanol concentration only for diluted solutions, that is, up to the formation of a monolayer of chemisorbed methanol on the catalyst surface. This suggests that the reaction rate follows a Langmuir-type mechanism. Due to instability of methanol adsorbed over Pd, the authors proposed its decomposition and oxidation to form CO, which is strongly chemisorbed over Pd particles and limits the kinetics of the reaction [111, 112]. This part of the reaction is suggested to occur also without irradiation, but in the dark Pd poisoning by CO would stop any further reactive event. Once the catalyst is irradiated with suitable wavelength to promote an electron from the valence band to the conduction band of TiO<sub>2</sub>, it may form strongly oxidizing species such as O<sup>-</sup>, which induce further CO oxidation to CO<sub>2</sub>, finally released making a metal site free for further methanol adsorption (new reaction cycle). Of course this implies a bifunctional catalyst where the metal active site and the oxidising one on the titania surface are adjacent. In this view, H<sub>2</sub> production occurs only when H<sub>2</sub>O reoxidises the reduced titania site (Figure 3). Metals with dehydrogenating activity may form acetaldehyde, which is weakly adsorbed, and it may desorb in gas phase [2].

At least for TiO<sub>2</sub>, the main oxidising species are reported to be free or trapped holes, OH<sup>•</sup> radicals, O<sub>2</sub><sup>•-</sup>, <sup>1</sup>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and O<sub>2</sub> [30, 113]. In most cases direct oxidation by holes is simply hypothesised, in others the process is reported to be mediated by other highly oxidizing species, for example, OH<sup>•</sup> radicals, derived by the reaction of photogenerated holes with water molecules [114]. Several studies highlight the presence of both shallowly and deeply trapped holes on the photocatalyst surface [115, 116]. Shallowly trapped holes show reactivity and mobility comparable to free ones, reacting thus very rapidly with chemisorbed species. In this case, oxidation processes might even be competitive with ultrafast charge-trapping events. On the other hand, deeply trapped

holes, which exhibit lower oxidizing potentials, preferentially react with more mobile physisorbed substances, and the corresponding reaction rates are lower [105, 117].

The reaction mechanism of methanol PR over Au/TiO<sub>2</sub> catalysts likely follows a different mechanism [4]. At first, two maxima for reaction rate were observed when varying metal loading up to 5 wt%. Slow rates at low and high loading were interpreted on the same basis above reported for Pd catalysts, that is, unavailable perimeter of metal particles leading to too scarce interphase between the photoactive species (TiO<sub>2</sub>) and the metal. The two maxima are located at 0.5 and 2.0 wt% Au, likely corresponding, in the view of the authors, to different morphologies of the metal particles. The proposed reaction mechanism is slightly different than that above outlined for Pd. Indeed methanol dissociatively adsorbs on a free metal site forming an adsorbed methoxy species, which seems stable at room temperature. Then, this species is further oxidized by photogeneration of strongly oxidizing agents (e.g., O<sup>-</sup>) on the surface of titania upon absorption of a photon of sufficient energy (>3.2 eV). The oxidant migrates to the interface of the metal promoting the oxidation of the methoxy group to CO<sub>2</sub>, which is finally desorbed. This liberates 2 moles of H<sub>2</sub> per mol of methanol. Finally, the catalyst is regenerated by water, which acts as an oxidant, refilling titania with its oxygen and making another H<sub>2</sub> molecule available (Figure 7). The effect of phase composition and textural properties for Au/TiO<sub>2</sub> catalysts has been also investigated [118].

Similar results for methanol PR over Au/TiO<sub>2</sub> have been reported by Wu et al. [119], particularly focusing on low CO selectivity. The reaction rate was dependent on methanol concentration up to a certain value, after which the reaction order with respect to the reactant was *ca.* zero, and the rate dependence was of Langmuir type. Thus, methanol adsorption on catalyst surface showed a pivotal role. This in turn partly explained the effect of pH, since adsorption (of reactant and intermediates) depends on surface charge of the semiconductor. The role of Au particle size was central most of all to address CO selectivity problems, since full CO oxidation may occur at the interface between the metal

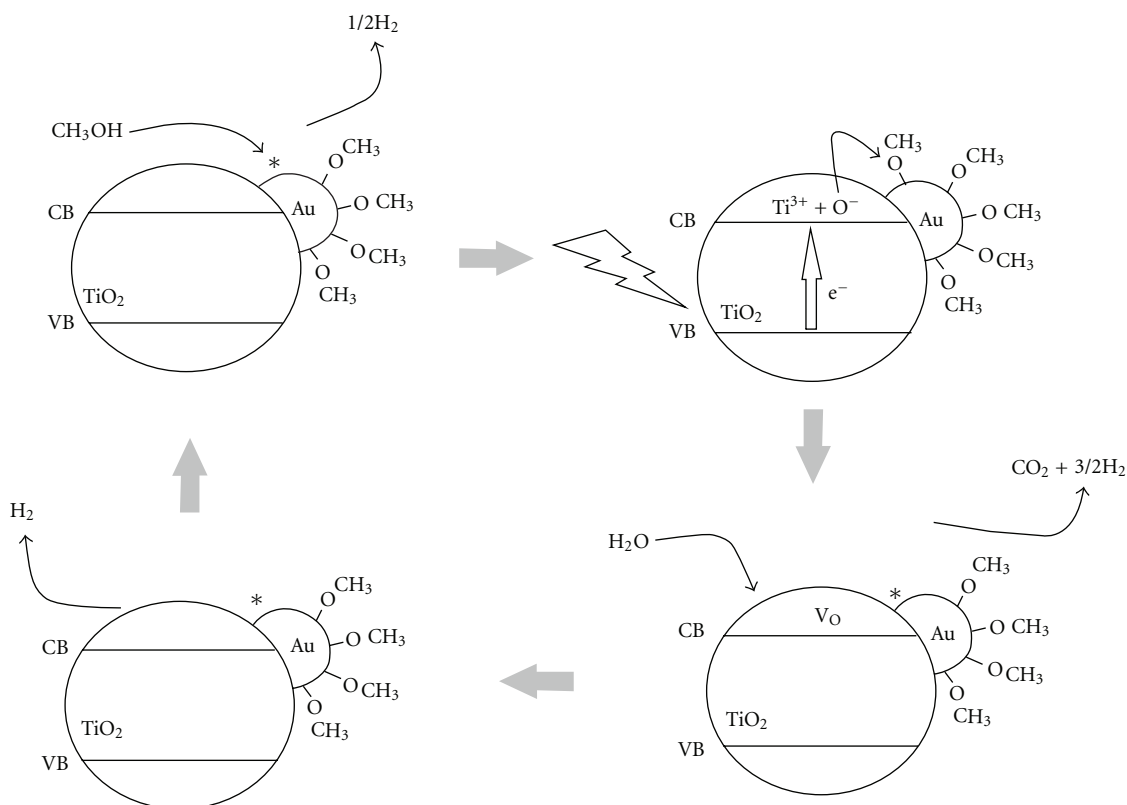


FIGURE 7: Proposed mechanism for methanol PR over Au/TiO<sub>2</sub> catalysts. Readapted from [4].

and the semiconductor. Thus, Au nanoparticles may expose higher contact perimeter for CO conversion. A parallel investigation on CO suppression has been carried out over Pt/TiO<sub>2</sub> samples [120]. The effect of Pt loading was considered together with the addition of small amounts of inorganic anions. Focusing on the main route bringing to CO formation, for example, the dehydrogenation of a formic acid intermediate, Pt showed to adsorb on defective sites of TiO<sub>2</sub>, which act both as recombination sites, decreasing photocatalytic efficiency, and as active sites for CO formation. Similarly, anions were competing for adsorption with formic acid.

In this model the rate determining step is the rate of CO removal [2, 80]. The attribution of the nature of the active oxygen species that removes CO<sub>2</sub> from the Pd surface is still uncertain: OH• radicals have been observed by electron spin resonance [121]. On the other hand, H<sub>2</sub>O<sub>2</sub> has been observed over Pt/TiO<sub>2</sub> catalysts, maybe formed through the dimerization of hydroxyl radicals [122].

In this view, a detailed investigation on the effect of Pd loading over titania has been carried out, evidencing the highest reaction rate for methanol PR 0.5 wt% metal loading [110]. The effect of metal loading has been often interpreted in view of the availability of surface metal sites (increasing with loading) and surface titania exposure, the semiconductor surface being shadowed at too high metal coverage. However, Bowker and coworkers proposed a different explanation, based on the rate determining step of the reaction.

As stated above, the latter should be something happening at the interface between the Pd particle and TiO<sub>2</sub>, if the bifunctional mechanism proposed by this research group is valid. Therefore, for reactions with rate dependence on the active sites located at the interphase, the extension of the metal particle perimeter is the predominant factor influencing activity. A calculation of the dependence of the particle perimeter with respect to its volume (radius) is proposed and correlated to initial reaction rate for methanol PR [110]. The model fits the data as for the curve trend with metal loading, though some refinements are needed to provide accurate numerical fitting.

The mechanism of PR of different alcohols has been also investigated on Pd/TiO<sub>2</sub> [79]. The reaction byproducts were widely variable depending on the substrate structure. For instance, methanol gave only H<sub>2</sub> and CO<sub>2</sub>, ethanol and 2-propanol produced also methane as the only major by-product, 1-propanol produced ethane, 1-Butanol and 2-butanol produce propane and ethane, respectively. D-glucose, sucrose and glycerol also showed very good reactivity. The presence of hydrogen atoms in the molecule at the alpha carbon position seems a necessary condition for the reaction. The amount of H<sub>2</sub> produced can be estimated by the number of alpha-hydrogen atoms present. In methanol and glycerol reforming all the carbon atoms possess alpha-hydrogen; thus, complete dehydrogenation occurs on Pd, leaving absorbed CO on the surface, and converting all the hydrogen atoms into H<sub>2</sub> with a rate for glycerol PR *ca.* twice

than for methanol [13]. As mentioned above [109], the semiconductor plays an active role in the further oxidation of CO to CO<sub>2</sub>, thus regenerating an active site. Therefore, CO actually acts as hole scavenger according to this mechanism [79].

A general rule has been derived to predict the PR products of a general alcohol [80]:

- (a) a hydrogen atom in alpha position to the alcoholic function must be present (tertiary alcohols show very poor H<sub>2</sub> productivity);
- (b) alkyl groups attached to alcohols yield the corresponding alkanes;
- (c) methylene groups are fully oxidised to CO<sub>2</sub>.

K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> showed the highest activity for H<sub>2</sub> evolution from an aqueous methanol solution, with *ca.* 50% quantum yield at 330 nm [123–125]. The addition of various cocatalysts, such as NiO, Au, Pt, and Cs [126–131] improved H<sub>2</sub> productivity even from pure water.

H<sub>2</sub> production with only 10 ppm CO was observed with methanol PR over Pt-TiO<sub>2</sub> catalysts with adsorbed sulfate/phosphate ions [120, 132]. Furthermore, a significant H<sub>2</sub> production efficiency (120 μmol/min) was obtained with very low methanol concentration without any significant deactivation even after long irradiation time [118].

Ag-doped TiO<sub>2</sub> was studied for various applications like sucrose mineralization [133], photocatalytic decomposition of O-cresol [134], degradation of salicylic acid [135], E-coli bacteria degradation [136], and selective NO reduction to N<sub>2</sub> and N<sub>2</sub>O [137]. Ag and AgO were differently added to TiO<sub>2</sub> for use in the PR of methanol [138]. A broadband around 450–550 nm was observed corresponding to the surface plasmon resonance of silver particles, and the appearance of this band confirms the presence of metallic silver [139]. The highest H<sub>2</sub> productivity was reached with 1 wt% metal loading and activity increased with substrate concentration up to 5%. At lower concentration mass transfer limitations prevailed, whereas when methanol was too abundant the surface was saturated and the reactions at the interface dominated the whole process [140]. When Ag<sub>2</sub>O/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> catalysts are irradiated by UV light, titania absorbs the photons and the generated electron-hole pairs are separated by both the metal and the metal oxide. Under solar light the mechanism is different. Silver ions interacting with the surface layers of TiO<sub>2</sub> expanding the poor visible response of the latter (bandgap energy 2.88 eV).

A laser-based method for the PR of methanol over WO<sub>3</sub> photocatalyst has been proposed. Hydrogen, carbon monoxide, and methane were obtained and no catalyst aging was observed during 15 days [141]. NiO was also tested under the same conditions for the PR of methanol and higher alcohols [142]. It is p-type semiconductor with a bandgap energy of 3.5 eV and the potentials of the valence and conduction band edges at +3.0 and –0.5 V, respectively [143]. Absorption of a photon of suitable energy ( $E > E_g$ ) causes the transfer of an electron from the valence band of oxygen (2p) to the conduction band of Ni (3d) atom and in turn the

reduction of Ni<sup>2+</sup> to Ni<sup>+</sup>. This electron transfer process weakens the Ni–O bond forming an oxygen vacancy. Increasing water concentration with respect to pure methanol allowed to increase the H<sub>2</sub>/CO ratio and to virtually eliminate the byproduct methane.

Copper oxide may also be effective for methanol PR, because the CuO conduction band is located below that of TiO<sub>2</sub>, so electron transfer to the conduction band of CuO is possible [144]. The phenomenon becomes important when a part of incident radiation has wavelength in the UV range. The hole transfer from the valance band of TiO<sub>2</sub> to that of CuO is also possible [145]. Kawai and Sakata [146, 147] have described that the reaction can proceed either stepwise, involving stable intermediates such aldehydes and acids, whereas a single step reaction was proposed by Chen et al. [148]. The overall process can be divided into three steps. At first WS occurs on the surface of TiO<sub>2</sub>, but its rate is limited by accumulation of holes and oxydryl radicals. In the second step, the photogenerated holes oxidise methanol to formaldehyde, then further oxidized by both OH radicals and photogenerated holes to produce formic acid. In the third step, formic acid is decarboxylated by the photo-Kolbe reaction to release CO<sub>2</sub>. H<sup>+</sup> ions deprotonated along all the steps transfer to CuO and reduce to hydrogen by action of the photogenerated electrons [145].

High CuO/TiO<sub>2</sub> activity for methanol PR was reported by Xu and Sun [149]. The active sites for hydrogen generation were likely located at the interface rather than on the isolated CuO or TiO<sub>2</sub> surfaces, since no H<sub>2</sub> production was achieved over both the pure oxides. Activity decreased at high CuO loading, partly for the shrink of available CuO-TiO<sub>2</sub> interface and for depressed light absorption by TiO<sub>2</sub>. Methanol adsorption confirmed a rate limiting step, interpreted according to a Freundlich isotherm. Different causes of catalyst deactivation have been taken into account, with Cu reduction and leaching (under acidic conditions) as main problems. Cu doping for TiO<sub>2</sub> under visible light irradiation for methanol PR was attempted by Yoong et al. [144].

Sonochemical synthesis of Pd, Pt, and Au doped TiO<sub>2</sub> photocatalysts was reported for the PR of ethanol [150]. Pt was the most active catalysts due to its higher dispersion. Noble metal doped samples prepared by flame pyrolysis were also proposed for this reaction [151]. The highest H<sub>2</sub> yield was achieved for 1 wt% Pd/Pt-TiO<sub>2</sub> catalysts, whereas Rh was too prone to oxidation.

Photodeposition of the cocatalyst is a powerful tool to achieve significantly higher dispersion of the metal phase with respect to impregnation and calcination. Indeed, the latter treatment may induce TiO<sub>2</sub> reconstruction over the metallic phase, thus limiting its activity [152].

Flame pyrolysis is a preparation method allowing to obtain single or mixed oxides in nanosized form [153–157]. Titania was also prepared for photocatalytic applications. For instance, Au deposition over titania prepared by flame pyrolysis allowed to improve by *ca.* 30 times the photocatalytic activity for the PR of methanol in liquid phase with respect to the bare titania support and by 50 times with respect to a commercial P25 sample [158]. A gas phase apparatus has been also developed to test the same samples [159]. Methanol



conversion appeared rather low, and a  $\text{CO}_2/\text{H}_2$  production ratio very much lower than that expected from the stoichiometry was achieved. Some attempts to determine possible byproducts have been made, observing the formation of formaldehyde. However, a reliable quantification of intermediates is very hard with such kind of experimental setting, based on recirculation of the reacting mixture through the starting 20 vol% methanol/water solution. Such solution very likely dissolves reaction products (and also  $\text{CO}_2$ ) much more effectively than pure water, preventing their reliable quantification. Other metals were also tested, obtaining the highest  $\text{H}_2$  productivity with 1 wt% Pt/ $\text{TiO}_2$  [160].

Gas phase methanol PR was previously proposed by Bowker and coworkers over Au/ $\text{TiO}_2$  catalysts. They reported *ca.* 135  $\mu\text{L}/\text{g}_{\text{cat}} \text{ min}$   $\text{H}_2$  productivity, more than three times higher value than in liquid phase photoreforming [161].

The effect of  $\text{TiO}_2$  crystalline facets exposition on  $\text{H}_2$  productivity has been taken into account [39, 41, 162, 163]. The most stable form of the anatase polymorph is a tetragonal bipyramidal structure in which {101} facets are exposed, with a small contribution of {001} facets [164], but the use of HF during the synthesis of the semiconductor allows to form truncated bipyramids [165]. Morphological and crystallographic modifications of  $\text{TiO}_2$  nanocrystals have been achieved by modulating F concentration and dosage [166]. Indeed, the use of  $\text{TiF}_4$  as precursor, pure or in mixture, allowed the formation of HF in situ. The latter has been used as a shape directing agent, binding selectively to the {001} facet of anatase and altering the shape of the resulting nanocrystals. The samples were blue colored, due to free conduction band electrons in  $\text{TiO}_2$ . Additional electrons may come from oxygen vacancies or titanium interstitials. In the latter case, irradiation produces conduction band electrons which localize on surface Ti atoms, but this coloration is quickly quenched upon exposure to oxygen or other oxidizers [167, 168], except under extremely high photon flux [169]. A broad Vis-NIR-IR absorption band has been observed for such samples, commonly attributed to the excitation of conduction band electrons in blue  $\text{TiO}_2$  and therefore reflecting the density of states of the conduction band [170]. Fluorine in this case is not substitutionally doped into the  $\text{TiO}_2$  lattice, but it plays an important role in the formation of oxygen vacancies due to stronger Ti–F bond with respect to Ti–O. No hydrogen was evolved in the absence of Pt or photocatalyst or when samples are illuminated with visible light only ( $\lambda > 430 \text{ nm}$ ). An induction period of  $\sim 1 \text{ h}$  was observed, and  $\text{H}_2$  productivity up to  $\sim 2.1 \text{ mmol H}_2 \text{ h}^{-1} \text{ g}^{-1}$  was achieved.

Despite the crystal facets exposed, the role of anatase-rutile junctions was investigated by varying calcination temperature of a Degussa P25 sample, originally starting from a 80:20 ratio of the two phases, respectively. Alignment at solid-solid interfaces is one of the most important factors for effective interfacial charge transfer and improved photocatalytic activity. The more numerous the anatase-rutile junctions, the higher the photocatalytic activity for hydrogen production [171]. Indeed, phase boundary suppresses hole-electron recombination and the CO concentration during PR of methanol, glycerol, and glucose was the lowest. The change

of surface acidity/basicity at the interfacial site should be responsible for the suppression of CO in biomass PR.

Metals, especially noble ones, have been extensively investigated as cocatalysts, in spite of their high cost. A much cheaper alternative has been proposed, using graphite silica, a natural mineral as cocatalyst for  $\text{TiO}_2$  for the PR of methanol. The physical mixing of the two solids improved the photocatalytic performance with respect to pure  $\text{TiO}_2$ , though a comparison with a typical Pt/ $\text{TiO}_2$  formulation revealed *ca.* one eighth  $\text{H}_2$  productivity, only [172]. Therefore, graphite silica was added to a Pt +  $\text{TiO}_2$  mixture, obtaining an increase of  $\text{H}_2$  productivity by 150%. However, when adding the mineral to an impregnated Pt/ $\text{TiO}_2$  sample, the  $\text{H}_2$  yield halved [173].

$\text{SrTiO}_3$  has been shown to possess good structural stability as a host for metals [174], and it has been used in photocatalytic WS for hydrogen production with different hole scavengers (alcohols,  $\text{Na}_2\text{SO}_3$ , and D-glucose) [175]. The photocatalytic activity was found in the order:  $\text{MeOH} > \text{EtOH} > \text{D-glucose} > 2\text{-PrOH} > \text{Na}_2\text{SO}_3$ . Mesoporous-assembled  $\text{SrTiO}_3$  nanocrystals exhibited much higher activity than two commercial photocatalysts, that is,  $\text{SrTiO}_3$  and  $\text{TiO}_2$ .

Even if the bandgap energy of ETS-10, a large pore zeotype titanosilicate ( $\text{Na}_2\text{TiSi}_5\text{O}_{11}$ ), is higher than that of  $\text{TiO}_2$  ( $E_g = 3.8 \text{ eV}$  with respect to *ca.* 3.0), its value was cut to 2.25 eV (visible light absorption) by doping with thiourea. This induced C, N, and S ions doping at once, improving the photocatalytic activity for the PR of methanol [176].

The reaction mechanism has been investigated for the PR of ethanol over Pt-based samples. H atoms belonging to adsorbed hydroxyl groups are reduced by electrons cumulating into Pt particles at the Pt- $\text{TiO}_2$  interface, while chemisorbed ethoxide species behave as hole traps [151]. Different indications are furnished about the resistance to deactivation during ethanol PR. Indeed on one hand ethanol is one of the easiest substrate to reform, due to its simple structure and limited amount of byproducts. On the other hand poor resistance to deactivation was reported, with heavy deactivation after 20 h due to the formation of several byproducts, such as acetaldehyde, acetone, and 2-butenal, produced by the partial oxidation and UV decomposition of ethanol [177, 178].

$\text{TiO}_2$  thin films, functionalized with different metals, were used for ethanol PR [140]. Contrarily to most findings, ethanol showed the most efficient hole scavenger, even better than methanol. The importance of optimizing catalyst exposure in form of films has been highlighted and, interestingly, the quantum yield and the energy conversion efficiency have been provided. A stable photoactive layer based on  $\text{TiO}_2$  over a porous polymer membrane has been proposed [179]. The PR of ethanol was investigated under UV light irradiation. The influences of Pt loading, coating, and composition of the  $\text{TiO}_2$  layer and its aging time were determined. Interestingly, the rate of hydrogen production was higher in the liquid-membrane-gas configuration compared to the liquid-membrane-liquid one, opening the way to effective separation of the gaseous products from the reaction environment.

In order to decrease significantly catalyst cost Cu-based catalysts were also developed.  $\text{Cu}_x\text{O-TiO}_2$  ( $x = 1, 2$ ) nanocomposites were tested for ethanol PR [180, 181]. The best performance was achieved with 1 wt% metal loading, due to the main presence of Cu(I) ions, active sites for the transfer of photogenerated electrons, whereas Cu(II) species seem to promote electron-hole recombination. Deactivation was also taken into account [149], due to poisoning by accumulation of intermediates and by reduction to the metallic state.

$\text{VO}_x$  nanorods were also tested for this application, with a bandgap energy of 2.7 eV, with quantum efficiency as high as 40% without addition of noble metals [182]. Pt-doped  $\text{SrTiO}_3$  catalysts proved also active under UV and visible light for the PR of methanol and ethanol [175] and mixed La-Ta oxynitrides were proposed as visible-active photocatalysts for hydrogen production from water/ethanol solutions [183].

Ethanol PR occurs through a progressive oxidation coupled with acetal formation, promoted by the presence of surface acidic sites, and accompanied by dehydration and water gas shift reaction [184].

The PR of aqueous solutions of ethanol and glycerol has been performed over  $\text{CuO}_x/\text{TiO}_2$  catalysts prepared in different ways [181, 185]. The higher dispersion of the metal oxide achieved by embedding CuO via a microemulsion technique allowed superior activity with respect to classical impregnation. The amount and kind of byproducts depends on the type of catalysts and of substrate. During PR of glycerol some deactivation unfortunately occurred over the most active catalyst, leading to *ca.* 10–20% loss of activity. Some metal leaching was observed, limited under irradiation, but by far more pronounced under oxidizing and acidic conditions in the absence of light, up to 25% loss of the cocatalyst.

CuO was also coated by RF-sputtering over ZnO, trying to improve the performance of a powdered composite [186]. The former material has very low bandgap energy, and it absorbs in the visible region, whereas ZnO is characterized by much wider bandgap energy. However, the formation of a p-n heterojunction favors electron-hole separation. CuO has been loaded over ZnO using different RF frequency. The lowest RF-power led to high quality CuO-ZnO interfaces (core-shell structure) improving photogenerated charge carrier separation, but completely covering the underlying ZnO surface. By contrast, the highest RF-power improved CuO particles dispersion. The most promising performances were obtained for the sample prepared with an intermediate RF-power, leading to a sufficient fraction of uncovered ZnO available for reactant adsorption and light absorption, together with a higher active area [187]. These samples were successfully used for  $\text{H}_2$  photogeneration from ethanol/water solutions. However, no complete PR reaction took place, the catalyst mainly produce acetaldehyde through ethanol dehydrogenation, with almost no  $\text{CO}_2$  formation.

$\text{Au/TiO}_2$  catalysts were tested for the PR of ethanol, particularly focusing on the effect of particle size, varying over one order of magnitude [188]. An investigation of intermediates and products has been carried out by mean of infrared spectroscopy and temperature programmed desorption, evidencing a wide variety of species over the catalyst surface.

The nano-sized catalyst showed higher  $\text{H}_2$  production, by one order of magnitude, compared with the micro-sized system, but normalizing over the surface area the productivity was equal. This allows to conclude that while nanostructuring the  $\text{TiO}_2$  semiconductor enhanced productivity, this effect was merely geometrical and did not depend on changes of intrinsic electronic properties.

The reforming of glycerol may lead to the production of 7 moles of  $\text{H}_2$  per mole of reformed substrate, and it is particularly attractive since glycerol is the major byproduct of biodiesel production. The huge overproduction of glycerol has a negative impact on the global biodiesel economy, since the processes for the economical valorization of glycerol are still limited [189, 190]. In addition, raw glycerol also contains methanol, water, inorganic salts, free fatty acids, triglycerides, and methyl esters, requiring expensive purification for most applications. Therefore, means for the energetic valorization of this polyalcohol are more than welcome, in light of its increasing availability.

0.5 wt% Pt/ $\text{TiO}_2$  was tested for glycerol PR in aqueous solution, increasing the  $\text{H}_2$  production rate by one order of magnitude with respect to pure water [38]. Other examples of glycerol PR over Pd/ $\text{TiO}_2$  and Au/ $\text{TiO}_2$  were proposed in [13], though the catalysts were sensitive to UV light only. Visible light was efficiently harvested by Fu and Lu [191], who used heteropolytungstate/ $\text{TiO}_2$  catalysts. Upon UV irradiation in the presence of an electron donor (glycerol), heteropolytungstate yields dark blue heteropoly blue, absorbing in the visible spectral range.  $\text{H}_2$  production under visible light was effectively achieved, but a dramatic system deactivation took place, mainly due to the light-induced decomposition of the sensitizer.

Luo et al. [14] proposed Pt-B,N-codoped  $\text{TiO}_2$  photocatalysts, while Cu/ $\text{TiO}_2$  catalysts were active for visible light driven PR of glycerol [192]. High activity for the latter catalytic system was ascribed to very high Cu dispersion, also achievable by photodeposition [184, 185]. A significant increase in the absorption at wavelengths shorter than 400 nm can be assigned to the intrinsic bandgap absorption of  $\text{TiO}_2$  enhanced by CuO [193]. High activity can be attributed to the electron transfer from  $\text{TiO}_2$  to the quantum-sized CuO. The optimal CuO content in the photocatalyst was found to be 1.3 wt% with  $\text{H}_2$  production rate of  $2061 \mu\text{mol h}^{-1} \text{g}^{-1}$ , *ca.* 130 times the production rate of pure titania, and the apparent QE was 13.4%.

Glycerol PR has been investigated over Pd/ $\text{TiO}_2$  and Au/ $\text{TiO}_2$  catalysts, achieving *ca.* double  $\text{H}_2$  production rate with respect to methanol, approximately according to the reactions stoichiometries [13]. Pd, though in lower loading than Au, proved almost twice as active. The reaction mechanism, proposed by Bowker and coworkers for Pd-based photocatalysts is similar to that above outlined for methanol. The adsorbed substrate is decomposed into CO and  $\text{H}_2$ . CO is further oxidized to  $\text{CO}_2$  only under irradiation, thanks to the formation of highly oxidizing species over the titania surface, as already discussed for the mechanism of methanol PR.

Glycerol PR has been also investigated over Pt/ $\text{TiO}_2$  catalysts [12]. Glycerol confirmed an efficient scavenger for

oxidizing species (i.e., holes, hydroxyl radicals, etc.) increasing the rate of hydrogen production with respect to direct water splitting. Very dispersed nanocrystallites of Pt played a determinant role in the photocatalytic process, both as electron scavenger and oxidizing catalyst for dark reaction steps. The effect of noble metal concentration was going through a maximum, as described in other references, in this case for 0.1–0.5 wt% loading. Also in this case, the reaction rate first increased with the concentration of the photocatalyst and then decreased for high values due to a shielding effect. Neutral or slightly basic conditions improved the reaction rate. This dependence can be due to the favorable positions of the valence- and conduction-band levels of the semiconductor with respect to those of the redox couples in solution, to the charging behavior of the semiconductor surface, to the speciation of the reactants in liquid phase [12, 194, 195]. A slight increase of temperature (60°C) also proved beneficial to improve reaction rate, likely increasing the rate of the “dark” reaction steps. Many intermediates may also form the most abundant being methanol, which are completely converted to H<sub>2</sub> and CO<sub>2</sub> after proper reaction time. The kind of oxidizing species was also investigated, particularly focusing on the formation of peroxide species on catalyst surface and in solution [122].

The alcohol may adsorb both in a molecular way or forming alkoxy species, which are more readily oxidized than the H-bonded ones [196, 197]. A correlation between H<sub>2</sub> yield and the polarity of alcohols was also proposed over TiO<sub>2</sub>-based photocatalysts [151].

Polyols (e.g., glycerol or glucose) showed usually higher activity for photoreforming reactions. Surface OH sites showed important since they accept photogenerated holes to form hydroxyl radicals (\*OH) [30, 198–200], one of the principal reactive oxidant in photocatalytic reactions. They also serve as active sites for the adsorption of reactants and intermediates [201]. It was concluded by time-resolved transient absorption spectroscopy [202, 203] that C2–C6 polyols and carbohydrates could scavenge 50–60% of the photogenerated holes of TiO<sub>2</sub> in the time lapse of 6 ns. The scavenging efficiency was higher for increasing the number of OH groups. The adsorption of polyol on TiO<sub>2</sub> can result in levels inside the TiO<sub>2</sub> bandgap, responsible for the fast hole trapping efficiency [35]. By comparing isopropanol, propyleneglycol, and glycerol with increasing number of OH groups in the molecule H<sub>2</sub> production increased and alkanes concentration decreased [204]. Furthermore, undercoordinated surface Ti sites can be stabilized by hydroxyl groups, water, or other hydroxylic molecules, such as alcohols, polyols, and carbohydrates [202, 205, 206]. R-OH molecules bind to Ti atoms through their hydroxyl O and release protons [35]. The conversion of surface Ti to octahedral coordination by the chemisorption of polyols has also been experimentally verified by the observation of Ti K-edge XANES spectra [202]. Two types of adsorption have been observed, however, leading to the same surface intermediate. The role of surface hydroxyls is also of hole scavengers, forming very reactive \*OH radicals which promote substrate oxidation: the higher the number of OH groups in the molecule, the higher the efficiency of the molecule as hole scavenger. The net effect

is the breakup of a C–H bond leaving an adsorbed ketyl radical. A detailed reaction mechanism has been proposed for 2-propanol, supported by FT-IR data [207].

#### 4. Photoreforming of Carbohydrates

Due to the current low efficiency of the WS process, also biomass derived substrates, such as carbohydrates, are gaining increasing interest as an abundant, renewable, and clean feedstock for hydrogen production. Furthermore, the food industry gives a huge amount of solid and liquid wastes (classified as 2nd generation biomass) which have to be valorized. The sewage from food industry contains first of all water-soluble carbohydrates. Until now the sewage from food industry are purified using mainly biological methods. Using pollutants as electron donors shows the promise for integration of wastes decomposition and H<sub>2</sub> production.

The feasibility of H<sub>2</sub> photoproduction from carbohydrates, such as sugars, starches, and/or cellulose, on RuO<sub>2</sub>/TiO<sub>2</sub>/Pt catalysts was first attested by Kawai and Sakata [11]. The abundance of hydroxyls in sugars leads to easier activation of the substrate, though the full degradation of their complex structure is much more complex than simple alcohols. Thus, lower productivity is usually observed. The order of reactivity is consequently starch < sucrose < glucose [10]. The PR of glucose and sucrose over B,N-codoped TiO<sub>2</sub> has been reported even with visible light [14]. A reaction mechanism has been proposed for Pt/TiO<sub>2</sub> [10]. Glucose adsorbs through one of its oxydryls to an under-coordinated Ti(IV) surface site and dissociates leaving a proton and an alkoxide anion. The organic fragment is oxidized by a hole to give a radical, which reacts with another glucose molecule. Further oxidations occur to aldehyde and carboxylic acid derivatives, which are ultimately converted to CO<sub>2</sub>. Adsorbed H<sup>+</sup> can be reduced to hydrogen on Pt sites by using photogenerated electrons.

The photocatalytic reforming of aqueous solutions of glucose over metal doped titania has been recently investigated [10]. A possible mechanism for the process has been also proposed, but the details of this complex mechanism still need a firm validation. Indeed, glucose behaves as an efficient hole scavenger for titania, though, the interpretation of the experimental results were insufficiently explained by a significant mechanism due to the lack of structural information [202]. A detailed mechanism for glucose photo-oxidation on titania has been introduced in [35]. However, only a single adsorption configuration was considered. The adsorption of  $\alpha$ -D-glucose on the (101) surface of anatase has been computationally investigated [34]. End-on adsorption via a single hydroxyl group, as well as bridge adsorption via two hydroxyl groups, have been considered, in both molecular and dissociative modes. The Ti–O(glucose) bond length showed rather insensitive to the selected hydroxyl group(s) and to the end-on or bridge adsorption mode. By contrast, the bond length decreased significantly when adsorption occurred dissociatively. Ti ions adsorbing glucose in end-on mode showed exposed outward from the surface, while the opposite seems to occur to oxygen ions involved in bridging

adsorption. Molecular adsorption seems more favorable with respect to dissociative one. The highest occupied electronic state is localized almost completely on the glucose molecule and distinct intragap states appear in several cases; this offers an explanation for the experimentally observed hole trapping in photoexcited titania nanoparticles in the presence of glucose.

The effect of various parameters has been evaluated on the PR of mono-, di-, and poly-saccharides [10]. The rate of H<sub>2</sub> evolution decreased with increasing molecular complexity, but microwave pretreatment of soluble starch displayed significantly enhanced H<sub>2</sub> evolution. H<sub>2</sub> evolution increases with increasing glucose amount, though also water takes part in the reaction. However, the reaction rate is dependent on glucose concentration on the catalyst surface rather than on the solution.

The H<sub>2</sub> evolution rate during PR of glucose increased with pH with a maximum at pH = 11 with a very complex effect. The pK<sub>a</sub> of glucose is about 12.3 [208] and when pH  $\ll$  pK<sub>a</sub>, glucose is mainly in its molecular form, preferentially bonding with surface Ti atoms through its hydroxyl [35]. At higher pH, glucose dissociates and the organic anion captures positive holes more efficiently, enhancing activity. If pH > pK<sub>a</sub>, glucose is in the negatively charged form, but TiO<sub>2</sub> surface is negatively charged too (pH higher than the isoelectric point of TiO<sub>2</sub>, *ca.* pH = 6 [209]), limiting adsorption and, thus, H<sub>2</sub> evolution rate. Furthermore, different H<sub>2</sub> production rate was obtained with the two anomers  $\alpha$ - and  $\beta$ -D-glucose. The latter indeed adsorbed in almost planar form over TiO<sub>2</sub>, leading to lower adsorption [210].

The dependence of the PR activity on glucose concentration showed in line with a Langmuir-type kinetic model and the catalytic activity increased in the order Ag, Ru < Pd, Au, Rh < Pt and was correlated with the metal work functions; Pt shows the highest work function and, thus, it may store more efficiently the photogenerated electrons [10, 105].

NiO was used as cocatalyst for TiO<sub>2</sub>-SiO<sub>2</sub> during PR of glucose [211]. An intense absorption onset in the range of 350–400 nm was found for Ni/TiO<sub>2</sub>-SiO<sub>2</sub>, while the support only absorbed UV-light with wavelength lower than 300 nm. Besides effectively decreasing the bandgap extension, Ni addition also allowed to limit CO formation with respect to the bare support.

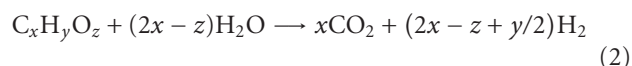
Among alkaline tantalates, NaTaO<sub>3</sub> exhibited the highest activity for H<sub>2</sub> production from glucose solution, as well as for the water splitting reactions, whereas LiTaO<sub>3</sub> showed the lowest activity. This was ascribed to the lower Ta–O–Ta bond angle of LiTaO<sub>3</sub> (143°), with respect to NaTaO<sub>3</sub> (163°) and KTaO<sub>3</sub> (180°). This inhibits the charge migration [212]. Furthermore, the former has wider bandgap energy and poor absorbance [51]. The Fermi level of NiO, used as cocatalyst for such systems is compatible with the energy level of the conduction band of NaTaO<sub>3</sub>, but not with that of KTaO<sub>3</sub>.

Hydrogen production was achieved under visible light by PR of glucose over Bi<sub>x</sub>Y<sub>1-x</sub>VO<sub>4</sub>. It was found that a certain amount of Y doping would promote the transition of BiVO<sub>4</sub> from monoclinic to tetragonal phase and finally lead to the formation of tetragonal solid solution. B/Y ratio of 1 : 1 showed the highest activity for hydrogen production.

The rate of H<sub>2</sub> production decreased after several hours of reaction, but it was recovered after flushing in N<sub>2</sub> [90].

Aqueous sucrose solutions were used as model for sugar industry wastewaters and their PR reaction was carried out over metal or anion doped TiO<sub>2</sub> and TiO<sub>2</sub>-SiO<sub>2</sub> [18]. The latter semiconductor showed very similar bandgap energy with respect to titania, whereas the addition of metals variously decreased the absorption edge of the photocatalysts. In particular, 1% V/5% TiO<sub>2</sub>/SiO<sub>2</sub> decreased it to 2.6 eV, likely due to the superposition of the TiO<sub>2</sub> and VO<sub>x</sub> inter-band absorptions. 1% Mn/5% TiO<sub>2</sub>/SiO<sub>2</sub> and 1% Cr/5% TiO<sub>2</sub>/SiO<sub>2</sub> decreased the *E<sub>g</sub>* to 2.8 eV and 2.2 eV, respectively, due to intercalation of doping metals in the TiO<sub>2</sub> framework. By contrast, 0.5% Au/5% TiO<sub>2</sub>/SiO<sub>2</sub> exhibited a pink-violet color due to the surface plasmon resonance originating from the collective oscillations of the electrons on the surface of the gold nanoparticles. Visible light is absorbed by gold nanoparticles due to such plasmon resonance, which leads to a photoexcited state of the gold nanoparticles followed by the transfer of the electrons into TiO<sub>2</sub> [88]. All the metals strongly improved the photocatalytic activity with respect to the Ti-Si support, with an activity scale V > Au > Mn > Cr. Mn and V ions can trap both electrons and holes [213], whereas Cr ion can only trap one type of charge carrier [18] so its activity is lower. In addition, vanadium has a larger capability compared to the other metal to coordinate and release oxygen species. On the contrary, anion doping of TiO<sub>2</sub>-SiO<sub>2</sub> lead to poorer activity, except for sulphur doping.

An increase of H<sub>2</sub> production with respect to WS was achieved by Kondarides et al. [38] by PR of a variety of biomass-derived, including monosaccharides, such as pentoses (ribose, arabinose) and hexoses (glucose, galactose, fructose, mannose), alcohols (methanol, ethanol, propanol, butanol), and organic acids (acetic acid, formic acid). In all cases, H<sub>2</sub> and CO<sub>2</sub> were produced in accordance to the stoichiometry of the general reforming reaction:



The maximum H<sub>2</sub> production rate increased almost linearly with the logarithm of the concentration of the substrate, with temperature (60–80°C) and pH.

## 5. Photoreforming of Other Substrates

**5.1. Waste Solutions.** A very interesting approach is to combine H<sub>2</sub> production and degradation of organic or inorganic pollutants from wastewaters. Various examples have been reported about water solutions containing various alcohols, for example, 2-propanol [214], acids [215, 216], and aldehydes, such as formaldehyde and acetaldehyde [194, 217].

LaNiO<sub>3</sub>-based catalysts were active under visible light for the PR of formaldehyde [194], while the degradation of azo-dyes was performed with simultaneous H<sub>2</sub> production over Pt-TiO<sub>2</sub> [218].

Different examples have been recently reported, such as the treatment of olive mill wastewater over titania, predominantly in the anatase phase, prepared by sol-gel [219].



The rate of  $H_2$  production decreased with time and with prolonged exposure to light due to deactivation of photocatalyst and decreasing reactant concentration. The suppression of the organic fraction, expressed as Chemical Oxygen Demand (COD) removal was 83%, demonstrating the effectiveness of this approach [220–223]. High  $H_2$  productivity was achieved, especially under acidic conditions ( $pH = 3$ ). The effect of  $pH$  is consistent with the point of zero charge of  $TiO_2$  ( $pH = 6.8$ ), which leads to a positively charged surface in acidic medium. This favors the adsorption of organic pollutants onto the  $TiO_2$  surface and facilitates their further degradation [216]. Under these conditions the conduction band position is also favorable to promote the reduction of  $H^+$  [12]. An optimal catalyst concentration of *ca.* 2 g/L was also observed [219], beyond which turbidity induces light scattering and poor absorption [224].

A variety of possible organic pollutants in wastewaters (alcohols, acids, and aldehydes) have been photoreformed over Pt/ $TiO_2$  under variable reaction conditions, achieving in all cases, except with acetaldehyde, full mineralization according to the reforming reaction above reported.  $CO_2$  release in the gas phase was delayed with respect to  $H_2$  due to stronger adsorption of  $CO_2$  on the photocatalyst surface, to the higher solubility of  $CO_2$  in water and/or to mass transfer limitations. It is also likely that the full mineralization of the organic molecule occurs through many consecutive reactions, where the intermediates are slowly oxidized to  $CO_2$  while continuously releasing  $H_2$  in various reaction steps. The rate of reaction was higher with simpler molecules. The reaction rate confirmed higher under neutral or basic conditions, at relatively high temperature (60–80°C) [194].

The photocatalytic degradation of azo-dyes, such as Acid Orange 7, in aerated aqueous  $TiO_2$  suspensions has been taken into account [225–227] to achieve full decoloration and the reduction of the chemical oxygen demand of the solution. The reaction was then carried out under anaerobic conditions to explore the possibility of producing hydrogen and to abate dyes such as Acid Orange 7, Basic Blue 41, and Basic Red 46 [218]. Poor photocatalytic activity was achieved with bare  $TiO_2$ , whereas  $H_2$  production increased after addition of Pt, with an apparent activation energy of  $8.9 \pm 1.5$  kcal/mol, and most of all of dyes, acting as hole scavengers. Decoloration of the solution was observed under UV-vis or visible light irradiation, by cleavage of the dye molecule in the vicinity of the azo-bond forming colorless intermediates which may be subsequently oxidized. The amount of  $H_2$  additionally produced with respect to WS was proportional to the amount of dye used.

The photocatalytic  $H_2$  production has been investigated in the presence of chloroacetic acids over Pt/ $TiO_2$ , prepared by photodeposition. Monochloroacetic acid and dichloroacetic acid enhance photocatalytic hydrogen generation, whereas trichloroacetic acid does not. The photocatalytic oxidation of monochloroacetic acid and dichloroacetic acid mainly produces  $CO_2$ , HCl, and formaldehyde, whereas the photocatalytic oxidation of trichloroacetic acid mainly produces  $CO_2$  and HCl [228].

Finally, though it is not strictly an example of biomass based waste stream, a process of simultaneous hydrogen

production and  $H_2S$  removal under visible light irradiation has been investigated over bulk CdS decorated with nanoparticles of  $TiO_2$  [229].

**5.2. Methane Photo-Steam Reforming.** The photo-steam reforming of methane [230, 231] has been studied only marginally due to limitations in the possible feed compositions at low temperature. Furthermore, gas phase applications for  $H_2$  photocatalytic production are much more limited than liquid phase examples. A detailed investigation on methane photo-steam reforming has been proposed by Shimura et al. [232]. Of course the interest would be the application with biogas.  $NaTaO_3$  showed the most interesting sample among different tantalates, though for suitably high  $H_2$  productivity different dopants and cocatalysts were used. In particular, La doping, affecting bandgap energy, and Pt addition, activating methane, were the most effective modifications for  $NaTaO_3$ . NiO, a good cocatalyst for WS over this catalyst was ineffective for methane photo-steam-reforming. Pt was added by photodeposition, but only a subsequent thermal treatment allowed to reach proper catalyst stability. Some limitations in the  $CH_4/H_2O$  ratio derived both by the need to operate in gas phase and by the formation of adsorbed organic intermediates on catalyst surface rendering it hydrophobic.

## 6. Conclusions and Future Perspectives

The research on materials and methods for the PR of organic substrates has thrown its basis and demonstrated the feasibility of  $H_2$  production by this route. From the existing reports it appears that  $TiO_2$ -based photocatalysts have been extensively investigated and sound reaction mechanism has been proposed for the PR of very simple molecules. Further details however are needed to clarify the basic step of the reaction, surface interactions between the adsorbent and the adsorbate and the nature of active species. The reaction mechanism derived for the photoreforming of methanol has been roughly extended to other substrates, but much heavier efforts are needed to better understand the behavior of complex molecules, such as carbohydrates.

One of the key points is to reach an effective separation of the photogenerated charges. This seems achievable by combining the action of the organic substrate, acting as hole scavenger, and a metallic phase drawing the photogenerated electrons and acting as active phase for proton reduction. The data reported mostly refer to UV-absorbing materials. Only few reports focus on photocatalysts active under solar light irradiation, which is a pivotal factor to impart practical relevance to this process.

Finally, the research reports on practically relevant substrates, that is, waste solutions, which enable to couple an environmentally relevant problem (waste disposal) with the need to produce clean fuels, are very limited. The potentiality of application of the PR process in this sense is enormous. The advantage is also the possibility to tune the type of waste to the local needs. However, to really exploit this route, it is of primary importance to focus the attention not only to



the photocatalytic activity of the material, but also to the possible deactivation. Catalyst life represents a key problem when complex (possibly poisoning) substrates are used.

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