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Long-term investigation of the photocatalytic hydrogen production on platinized TiO_2: an isotopic study

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Long-term investigations of the photocatalytic hydrogen production on platinized TiO_2 photocatalysts have been carried out employing different solutions of (deuterated) water and (deuterated) methanol. The results indicate that methanol acts as a sacrificial reagent, *i.e.*, as an "electron donor" and that the amount of evolved molecular hydrogen is equivalent to the amount of H_2 expected from the complete reforming of methanol or even less depending on the used photocatalyst. No evidence for photocatalytic water splitting is observed even in the presence of very low methanol concentrations, *i.e.*, no molecular oxygen has been detected. Based upon the isotopic labelling studies it was confirmed that H_2 is mainly produced by the reduction of protons originating from water.

Broader context

Recently, growing environmental concern and an increasing energy demand are driving the search for new, sustainable sources of energy. In particular, solar molecular hydrogen (H_2) has attracted much attention because it can be regarded as a renewable and clean-burning energy source. Among the proposed technologies for its production, the photocatalytic conversion of biomass derived compounds is currently being discussed. For example, methanol is a biomass derivative from biological substrates and can be considered as a suitable hydrogen source since it contains a rather high hydrogen to carbon ratio (4 : 1). Even though its consumption during photocatalytic hydrogen production is accompanied by carbon dioxide formation, the thus produced carbon dioxide can again be converted into biomass through the plant photosynthesis. Hence, it has been stated that employing sacrificial reagents, in particular biomass derived compounds, for hydrogen gas generation could be a useful intermediate step between the current fossil fuel consumption and the dream of an efficient direct photocatalytic water splitting utilizing solar energy. However, basic investigations aiming at understanding this system are still required for the realization of practical applications in the future.

Introduction

Practically applicable photocatalysts for the efficient release of molecular hydrogen from the photolysis of water have not been discovered to date.[1,2] However, while many metal oxide, nitride, oxynitride, and oxysulfide photocatalysts have been investigated, they were either found to be unstable or to exhibit low solar to hydrogen conversion efficiencies.[3–6] This is related to the fact that the simultaneous reduction and oxidation of water is a complex multistep reaction involving four electrons.[7] To avoid the complexity of the simultaneous formation of molecular hydrogen and oxygen and to enhance the efficiency of the overall process, many researchers employ the so-called organic and/or inorganic sacrificial reagents as "electron donors" instead of water.[8–11] Commonly, methanol is employed here.[12] Indeed, methanol can improve the H_2 production remarkably by reacting with the photogenerated holes at the ps to ns time scale thus greatly reducing the charge carrier recombination.[13] Moreover, methanol is a biomass derivative from biological substrates and can be considered as a suitable hydrogen source since it contains a rather high hydrogen to carbon ratio (4 : 1).[8] Even though its consumption during hydrogen production is accompanied by carbon dioxide formation, the thus produced carbon dioxide can again be converted into biomass through the plant photosynthesis. Consequently, carbon dioxide produced from biomass will not contribute to the global warming provided that the consumption of the biomass will not exceed the natural capacity to convert carbon dioxide into biomass.[8,14] Hence, it has been stated that employing sacrificial reagents, in particular biomass derived compounds, for hydrogen gas generation could be a useful intermediate step between the current fossil fuel consumption and the dream of an efficient direct photocatalytic water splitting utilizing solar energy. However, basic investigations aiming to understand this system are still required for the realization of practical applications in the future.

Herein, details of the mechanism of the photocatalytic hydrogen evolution on platinized titanium dioxide from aqueous methanol solutions have been investigated. Titanium

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dioxide (TiO_2) is considered to be one of the most promising presently known photocatalysts, because of its superior photoreactivity, nontoxicity, long-term stability, and low price.[15] Thus, TiO_2 has been extensively employed for the photocatalytic hydrogen production from aqueous methanol solutions.[12,16,17] However, even though this system is commonly employed, considerable uncertainty still exists concerning the origin of the evolved hydrogen gas. Some authors describe the photocatalytic process as a water splitting reaction,[18,19] while others suggest that it is just a photocatalytic reforming process.[12,20,21] A recent report even states that the water splitting reaction can be assisted by using low methanol concentrations with molecular oxygen being formed simultaneously. Moreover, the amount of evolved hydrogen gas was reported to exceed the amount expected from the complete reforming of methanol.[18] Apparently, water photooxidation seems to compete with the methanol photooxidation. Thus, in the present study, long-term investigations of the photocatalytic hydrogen production on platinized TiO_2 from water–methanol mixtures have been carried out in order to calculate the amount of molecular hydrogen evolved from a known amount of oxidized methanol. Moreover, isotopic labeling experiments have been carried out to define whether the origin of the evolved hydrogen gas is water or methanol. This is expected to provide some very essential information concerning the so-called “sacrificial systems”.

Experimental

Photocatalyst preparation

Three types of photocatalysts have been employed in this study, *i.e.*, Aeroxide TiO_2 P25, Evonik (BET surface area 52 $m^2\ g^{-1}$, 80 wt% anatase and 20 wt% rutile), Hombikat TiO_2 UV100, Sachtleben (BET surface area 301 $m^2\ g^{-1}$, 100 wt% anatase), and home-made TiO_2 prepared by a sol–gel method as described elsewhere.[18,22] Briefly, titanium isopropoxide (TIP, Sigma-Aldrich, 98%) was first hydrolyzed under vigorous stirring by the addition of 2 mol L^{-1} aqueous solution of hydrochloric acid (with a ratio of 14 mL of TIP per 23.5 mL of HCl solution). After 48 h of aging of the hydrosol at room temperature, polyoxyethylene(10)cetyl ether (Brij 56) was added under stirring and the resulting mixture was dried at room temperature and further at 110 °C for 24 h, before calcination in air at 400 °C for 2 h (heating rate of 2 °C min^{-1}). The obtained TiO_2 powder is denoted as TiO_2-SG. The XRD analysis indicates that TiO_2-SG consists mainly of anatase with a little amount of brookite while the nitrogen adsorption measurements indicate that the BET surface area is 85 $m^2\ g^{-1}$.

Platinized TiO_2 photocatalyst powders have been prepared by the photodeposition method as follows:[23] 0.5 g of the TiO_2 photocatalyst has been suspended by stirring in 100 mL aqueous solution containing the desired concentrations of H_2PtCl_6 to obtain a 0.5 or 1.0 wt% Pt loaded TiO_2 photocatalyst, respectively. The resulting solution was irradiated with UV(A) light employing a Philips fluorescence Hg lamp (illumination intensity: 1.0 mW cm^{-2}) for 2 h under an Ar atmosphere. Afterwards, 1 mL methanol was injected into the solution followed by further illumination for 10 h. The obtained powder was separated by centrifugation, washed with water, and dried at 110 °C for 12 h.

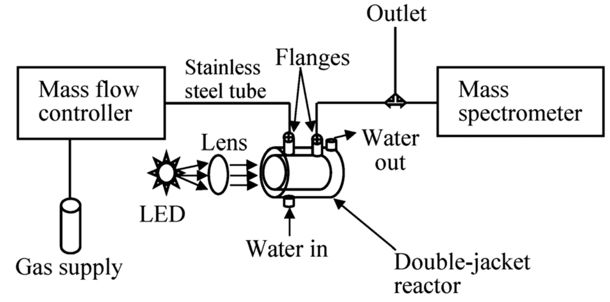

Fig. 1 Continuous flow setup for photocatalytic hydrogen production measurements.

Photocatalytic activity measurements

The photocatalytic hydrogen production tests have been carried out in an experimental setup consisting of a gas supply, a mass flow controller, a 100 cm^3 double jacket Duran and/or a quartz glass reactor with in- and outlets, and a quadrupole mass spectrometer (QMS) for gas analysis (Hiden HPR-20) as schematically shown in Fig. 1. In a typical run, 0.06 g of the Pt loaded TiO_2 photocatalyst were suspended in 50 or 60 mL of an aqueous methanol solution (0.03 M) by sonication. The suspension was transferred into the photoreactor and purged with Ar for 30 min to remove dissolved O_2. Afterwards, the reactor was connected to the mass flow controller and to the Q/C capillary sampling inlet of the QMS through metal flanges and adapters. To remove the air in the headspace of the reactor, an Ar gas stream has continuously been flown through the reactor before irradiation, until no traces of molecular oxygen or nitrogen could be detected by the QMS. The Ar gas flow rate through the reactor was kept constant at 10 $cm^3\ min^{-1}$ during the photocatalytic tests. The inlet flow rate/gas consumption by the QMS is 1 $cm^3\ min^{-1}$ and the excess gas is directed towards the exhaust. The sampling rate of the QMS is in the millisecond time range, thus allowing a fast tracking of the reaction. After stabilization of the system background, the reactor was irradiated from the outside using collimated UV light of a strong 365 nm LED (Thorlabs). For quantitative analysis of H_2 and CO_2, the QMS was calibrated employing standard diluted H_2 and CO_2, respectively, in Ar (Linde Gas, Germany).

Results and discussion

The photocatalytic hydrogen production test is usually performed employing a closed system and a gas chromatograph for gas analysis. Under such experimental conditions, it is difficult to carry out long term stability tests due to the generation of overpressure inside the glass reactor and it is also difficult to analyze complex gas mixtures under the same conditions in a single run. Thus, we have built a continuous flow setup adapted to a Quadrupol Mass Spectrometer (QMS) as described in the

Experimental part and schematically shown in Fig. 1. Employing the QMS, fast analysis of complex gas mixtures is readily achieved. For example, the analysis of the photocatalytically evolved gases from a 0.03 M aqueous methanol suspension of platinized TiO_2-P25 photocatalyst powder evinces that only H_2 and CO_2 are formed. No traces of CO, O_2, or CH_4 were detected. Fig. 2 shows the time course of the photocatalytic H_2 and CO_2 evolution in a typical experimental run. It is obvious that the evolution of H_2 and CO_2 suddenly begins as the light is switched on. Subsequently, the observed gas evolution rates are found to gradually decrease most likely due to the consumption of the methanol. However, it is noted that this decrease of the rate of H_2 formation is not linear, however, as evident from Fig. 2 there are different slopes of the rate *vs.* time plot. This behavior can be explained by considering the different intermediates formed during the photocatalytic oxidation of methanol. By spectrophotometric analysis of the illuminated suspensions employing the Nash method[24] and by using high performance ion chromatography (HPIC), it was found that formaldehyde and formic acid are the main products of the photocatalytic oxidation of methanol. The start of CO_2 evolution immediately after the light is switched on indicates that formaldehyde and formic acid can be effectively mineralized on TiO_2 P25. Since the photocatalytic hydrogen production test has been performed under an Ar atmosphere in a sealed photoreactor connected to the QMS, it was not possible to monitor the time profiles of the formaldehyde and the formic acid formation. By integration of the signals shown in Fig. 2, the amounts of evolved molecular hydrogen and CO_2 were calculated to be 5400 ± 200 and 1800 ± 50 μmol, respectively, as shown in the inset of Fig. 2. Assuming that the methanol photooxidation occurs according to eqn (1)–(4),[12,25] the expected amount of H_2 formed from the complete reforming of the methanol employed in this study (*i.e.*, 1.8 mmol) can be calculated to be 5400 μmol according to eqn (5). This value is in good agreement with the experimentally detected amount (5400 ± 200 μmol), evincing that methanol acts as a sacrificial reagent and that the amount of H_2 evolved does not exceed the amount expected from the complete consumption of methanol. These results rather convincingly exclude the possibility of water splitting on Pt loaded TiO_2-P25 even in the presence of low concentrations of methanol. The ratio of evolved H_2 to CO_2 is 3 to 1, which is in good agreement with the proposed mechanism presented in eqn (1)–(5).

$$CH_3OH \xrightarrow{h\nu,\ Pt@TiO_2} CH_2O + H_2 \tag{1}$$

$$CH_2O + H_2O \rightarrow CH_2(OH)_2 \tag{2}$$

$$CH_2(OH)_2 \xrightarrow{h\nu,\ Pt@TiO_2} HCOOH + H_2 \tag{3}$$

$$HCOOH \xrightarrow{h\nu,\ Pt@TiO_2} CO_2 + H_2 \tag{4}$$

$$CH_3OH + H_2O \xrightarrow{h\nu,\ Pt@TiO_2} CO_2 + 3H_2 \tag{5}$$

In order to generalize this finding, long term experiments have also been performed employing a TiO_2 photocatalyst prepared by the sol–gel method (TiO_2-SG) as well as another, commonly used, commercial photocatalyst, *i.e.*, TiO_2-UV100. In the case of TiO_2-SG, once again, no gases other than H_2 and CO_2 have been detected. Fig. 3 shows the time course of H_2 and CO_2 evolution on 0.5 wt% Pt loaded TiO_2-SG. It is clearly seen from this figure that the amount of the evolved H_2 and CO_2 matches the amount of H_2 and CO_2 expected from the complete reforming of methanol (*i.e.*, 1.5 mmol) rather well. Moreover, the amount of the evolved H_2 is three times higher than that of the evolved CO_2. This again confirms that the direct photocatalytic oxidation of water on TiO_2 does not occur in the presence of methanol, in particular, since molecular oxygen has also not been detected under these conditions.

In the case of TiO_2-UV100, as shown in Fig. 4, it is clearly observed that the amount of the evolved H_2 is about three times higher than the amount of the evolved CO_2 for both, loading

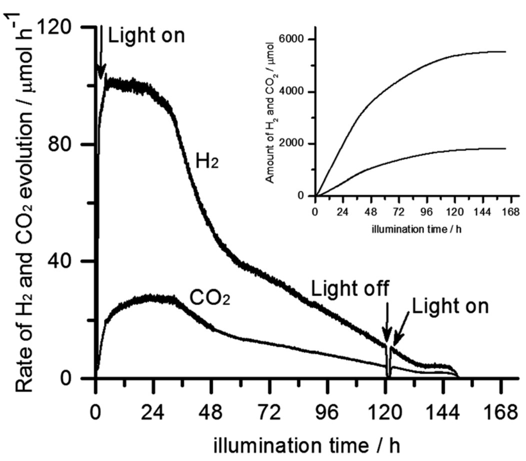

Fig. 2 Photocatalytic H_2 and CO_2 evolution on platinized TiO_2-P25 from 30 mM CH_3OH–H_2O solution: 1.0 g L^{-1} photocatalyst, 60 mL suspensions, and UV illumination employing 365 nm LED (light intensity 44 mW cm^{-2}).

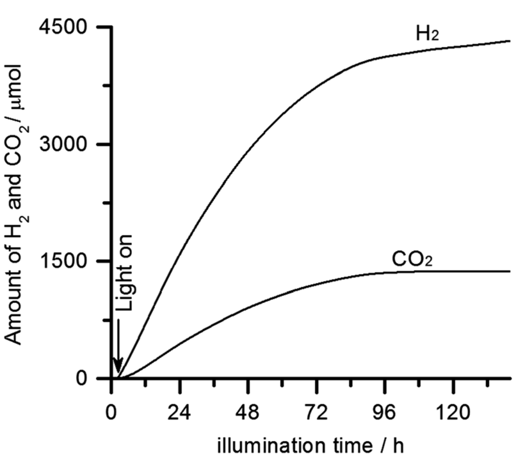

Fig. 3 Photocatalytic H_2 and CO_2 evolution on platinized TiO_2-SG from 30 mM CH_3OH–H_2O solution: 1.0 g L^{-1} photocatalyst, 50 mL suspensions, and UV illumination employing 365 nm LED (light intensity 44 mW cm^{-2}).

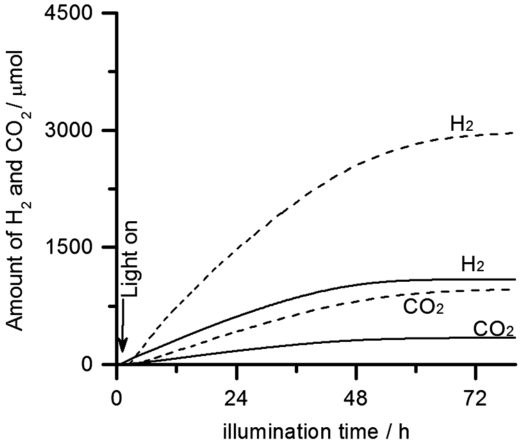

Fig. 4 Photocatalytic H_2 and CO_2 evolution on platinized TiO_2-UV100 from 30 mM $CH_3OH–H_2O$ solution: 1.0 g L^{-1} photocatalyst, 50 mL suspensions, and UV illumination employing 365 nm LED (0.5 wt% Pt solid line and 1.0 wt% Pt dashed line), (light intensity 44 mW cm^{-2}).

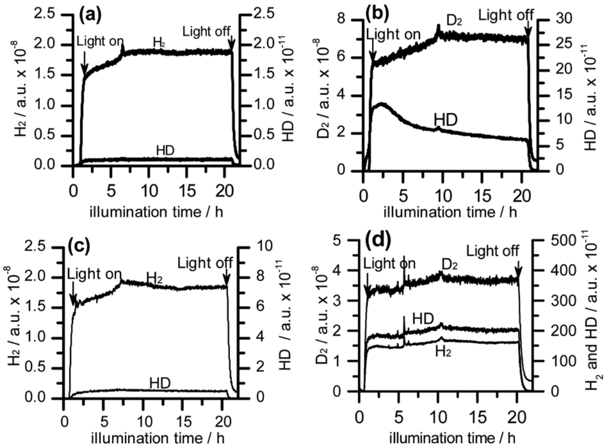

Fig. 5 Photocatalytic H_2, HD, and D_2 evolution on platinized TiO_2-P25 from (a) $CH_3OH–H_2O$, (b) $CD_3OD–D_2O$, (c) $CD_3OD–H_2O$, and (d) $CH_3OH–D_2O$ solutions. *Experimental conditions*: 1.0 g L^{-1} photocatalyst, 60 mL suspension, and UV illumination employing 365 nm LED (light intensity 44 mW cm^{-2}).

TiO_2-UV100 with 0.5 and 1.0 wt% Pt, respectively. However, it is also obvious that the total amount of H_2 evolved on 0.5 and 1.0 wt% Pt TiO_2-UV100 is only 34 and 64%, respectively, of the amount expected for the complete reforming of methanol. These results suggest that the Pt loading plays a crucial role in enhancing the photocatalytic activity of the photocatalysts. In fact, in this study, a Pt loading of 0.5 wt% has been found to be optimal in the case of TiO_2-P25 and TiO_2-SG, while for TiO_2-UV100 the optimum loading to obtain the highest H_2 evolution rate is 1.0 wt%. However, even employing the optimum Pt loading for TiO_2-UV100 does not result in the complete reforming of the entire amount of methanol present evincing that the TiO_2 type also plays an important role. It seems that at low concentrations of methanol and/or its photooxidation products, *i.e.*, mainly formaldehyde and formic acid, Pt loaded TiO_2 UV100 is not able to photocatalyze the hydrogen evolution reaction. The main conclusion from these long-term illumination experiments is, however, that the amount of H_2 detected on the three different investigated photocatalysts does under no circumstance exceed the amount expected from the complete reforming of methanol. Moreover, in neither case has molecular oxygen been detected as a product of the photocatalytic reaction. Hence, the assumption of photocatalytic water splitting into H_2 and O_2 in the presence of methanol appears to be highly unreasonable. As the formation of molecular hydrogen ceases once the initially present methanol has been entirely depleted, it can moreover be concluded that TiO_2 cannot photocatalytically split water even in the absence of methanol.[12,26]

To identify the origin of the evolved hydrogen gas, a series of photocatalytic hydrogen production tests on TiO_2-P25, *i.e.*, the benchmark photocatalyst that is usually taken as a reference, have been performed employing the following (deuterated) water and (deuterated) methanol mixtures: (a) $CH_3OH–H_2O$, (b) $CD_3OD–D_2O$, (c) $CD_3OD–H_2O$, and (d) $CH_3OH–D_2O$. The initial concentrations of CH_3OH and CD_3OD were 0.03 M. The evolved gases, *i.e.*, H_2, HD, and D_2, have been simultaneously analyzed and the results are presented in Fig. 5. In cases (a) and (b), only H_2 and D_2 were detected as shown in Fig. 5a and b, respectively. It is worth mentioning that a minute change in the QMS signal at $m/z = 3$ has been observed. This change is readily explained by the overlap of the H_2 or D_2 signal with that of HD. In case (c), when a $CD_3OD–H_2O$ mixture has been employed, the evolved gas is mainly H_2 evincing that the evolved H_2 is formed by the reduction of H^+ mainly originating from H_2O (see Fig. 5c). If H_2 would originate from methanol, a notable amount of HD, at least, should be detected supposing that methanol will be photooxidized by hydrogen abstraction and release D^+ and H^+ from the fully deuterated methyl group and from the hydroxyl group, respectively.[27] Note that a rapid H^+/D^+ exchange is highly expected according to eqn (6). If the released D^+ and H^+ will be directly reduced at the surface of the Pt-cocatalyst, a notable amount of HD gas will be evolved as schematically shown in Fig. 6a. Since, however, the evolved gas is mainly H_2 it is more likely that the photooxidation and the photoreduction take place at separate sites. Most probably, the photogenerated holes are reacting with methanol while, at the same time, the photogenerated electrons reduce adsorbed H^+ originally coming from H_2O as illustrated schematically in Fig. 6b. Consequently, however, even though methanol acts as a sacrificial reagent, the evolved molecular hydrogen originates from water. It is important to mention here that even though the H_2 is most

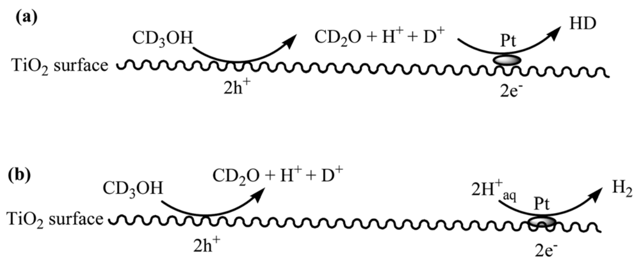

Fig. 6 Proposed mechanism of the photocatalytic H_2 formation from aqueous methanol solutions.

likely originating from water, this does not mean that indeed a water splitting reaction is being observed!

In fact, in order to produce formaldehyde from methanol, the CD_3OH molecule must lose one hydrogen atom and one deuterium atom from the hydroxyl group and the fully deuterated methyl group, respectively. Guo *et al.*[26] have investigated the photocatalytic transformation of partially deuterated methanol (CD_3OH) on the $TiO_2(110)$ surface. They found that CD_2O is produced on the five-fold coordinated Ti sites whereas H and D atoms are produced on the bridge-bonded oxygen (BBO) sites. Moreover, these authors noted that the transfer rate of H-atoms from the hydroxyl group of CD_3OH to the BBO sites is faster than the D-atom transfer from the D_3-methyl group evincing a photocatalyzed H-atom and D-atom abstraction from CD_3OH. Apparently, the two hydrogen transfer steps towards the formation of formaldehyde do not occur simultaneously or concertedly. Thus, the probability of D and H atoms to be reduced at the Pt cocatalyst to produce HD is much lower than the probability of the reduction of two H-atoms originating from water. Therefore, the evolution of only H_2 in case (c), however, where fully deuterated CD_3OD has been employed, can be readily explained by statistical considerations. The ratio of H atoms to D atoms is calculated for this experiment to be 925 to 1. Hence, the probability of H^+ reduction by conduction band electrons is much higher than the reduction of D^+ formed *via* the oxidation of CD_3OH by valance band holes taking into consideration the H/D exchange (eqn. (7)–(11)). The exchange between the H-atom from water and the surface adsorbed D-atom originating from the photocatalytically oxidized CD_3OH, thus, should be considered whenever deuterated methanol is being employed.

$$CD_3OD + H_2O \Leftrightarrow CD_3OH + HOD \tag{6}$$

$$CD_3OD + h_{VB}^+ \rightarrow {}^{\bullet}CD_2OH + D^+ \tag{7}$$

$$D^+ + H_2O \rightarrow HOD + H^+ \tag{8}$$

$$H^+ + e^-_{CB} \rightarrow H^{\bullet} \tag{9}$$

$$D^+ + e^-_{CB} \rightarrow D^{\bullet} \tag{10}$$

$$H^{\bullet} + D^{\bullet} \rightarrow HD \tag{11}$$

In case (d), where a CH_3OH–D_2O mixture was employed, the evolved gas is mainly D_2 with a notable amount of H_2 and HD as shown in Fig. 5d. The detection of H_2 and HD in this experiment can be explained by the fact that the reduction of H^+ is easier than that of D^+, *i.e.*, it occurs at a more positive potential, thus, the reduction of the former by conduction band electrons competes with the reduction of the later.[28] However, by statistical considerations the amount of H^+ present in the reaction mixture is much smaller than that of D^+ and, thus, D_2 is detected as the main gas component. This confirms that the hydrogen gas photocatalytically evolved from aqueous methanol solutions indeed mainly originates from water. The evolution of a notable amount of H_2 and HD, *i.e.*, in case (d), can also be explained by considering that methanol can be photocatalytically dissociated on the TiO_2 surface more easily than water.[26] Thus, H atoms originating from methanol dissociation adsorbed at the TiO_2 surface can contribute to the hydrogen evolution even though their concentration is very low in comparison with the D atoms originating from D_2O.

Conclusions

In conclusion, the current results confirm that methanol acts as a sacrificial reagent for the photocatalytic molecular hydrogen production over platinized TiO_2. No evidence for direct water splitting even in the presence of low methanol concentrations has been observed. The amount of photocatalytically evolved hydrogen does not exceed the amount expected from the complete reforming of methanol. Investigations of the photocatalytic hydrogen production employing different mixtures of (deuterated) water and (deuterated) methanol indicate that H_2 is mainly produced by the reduction of protons originating from water as evinced from the statistical considerations.

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