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In Situ ATR-FTIR Investigation of the Effects of H_2O and D_2O Adsorption on the TiO_2 Surface

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We have investigated the behavior of H_2O and D_2O adsorption on TiO_2 surfaces in the dark and under UV irradiation using *insitu* ATR-FTIR spectroscopy. The influence of an electron scavenger (oxygen) and a hole scavenger (ethanol) on the hydroxyl group and/or hydration water behavior on the TiO_2 surface were also investigated. Adsorption of H_2O–D_2O mixtures revealed an isotopic exchange reaction occurring in the dark onto the surface of the TiO_2 material. Under UV(A) irradiation, the quanitity of both OH and OD groups was found to be increased by the presence of molecular oxygen. On the other hand, the ATR-FTIR study of the ethanol adsorption in H_2O and D_2O revealed a stronger adsorption capacity for ethanol compared to both H_2O and D_2O resulting in molecular and dissociative adsorption of ethanol on the TiO_2 surface. When the system was subsequently illuminated with UV(A) light, the surface becomes enriched with adsorbed water. Different possible mechanisms and hypotheses are discussed in terms of the effect of UV irradiation on the TiO_2 particle network for the photocatalytic reaction and photoinduced hydrophilicity.

Introduction

Photocatalysis and Photoinduced Hydrophilicity have attracted significant attention due to their potential applications in environmental protection [1]. Surface OH groups on TiO_2 materials have been assumed to play important roles in both photocatalytic reactions and photoinduced hydrophilicity [2]. Adsorbed species such as water, substrate and molecular oxygen, however, are expected to affect the hydroxyl group behavior on the TiO_2 surface, which play a major role in the charge transfer and trapping reactions occuring at the TiO_2/water interface under UV (A) irradiation. In oxygenated systems the photogenerated electron reacts with molecular oxygen producing superoxide anion radicals, while the photogenerated holes are either trapped by the surface hydroxyl group or/and water molecules forming reactive hydroxyl radicals or they initiate the direct oxidation of an adsorbed organic donor [3]. It was reported, however, that during UV irradiation not only did the photocatalytic reactions take place on the surface but the photoinduced hydrophilicity also occurred due to the separation and diffusion of photogenerated electrons and holes occurring at the TiO_2/water interface [4]. Additionally, a competitive reaction in aqueous solutions, would take place during UV irradiation between direct oxidation and indirect oxidation of organic molecules due to the different adsorption behaviors of substrates [5]. Alternatively, during UV irradiation the particle network of the TiO_2 material could play a significant role in the absorption of light and adsorption of species [6]. Thus, special attention has been focused on the particle network during photocatalytic reactions and therefore, several mechanisms regarding the effect of UV(A) light on the particle network have been suggested such as the Antenna mechanism and deaggregation concept[1,6]. Although the interfacial substrate/TiO_2 interactions have been extensively studied, the effect of water and oxygen adsorption, together with the associated hydroxyl groups during UV irradiation are, however, still not completely understood for both photocatalytic reactions and photoinduced hydrophilicity.

In this study, Attenuated Total Reflectance-FTIR spectroscopy, was used for an *in-situ* mechanistic investigation at the water/TiO_2 interface. The adsorption behavior of H_2O and D_2O on the TiO_2 surface was investigated in the absence and in the presence of both an electron scavenger (oxygen) and a hole scavenger (ethanol). Several mechanisms considering the interaction of UV(A) light and the hydroxyl groups formation or/and hydration water on the TiO_2 surface have been addressed. This work, therefore,provides new insight into the mechanistic aspects of photoinduced hydrophilicity and photocatalytic reactions on TiO_2 surfaces.

Experimental

Materials

TiO_2 (Hombikat UV100, 100% anatase) was kindly supplied by Sachtleben Chemie. Ethanol (≥99.8%) was purchased from ROTH. The Deuterium oxide (D_2O) (99.9 atom% D) were purchased from Sigma Aldrich. Deionized water (H_2O) was supplied from a Millipore Mill-Q system with a resistivity equal to 18.2 Ω cm at 25 °C.

ATR-FTIR measurement

Attenuated total reflection Fourier transformed infrared (ATR-FTIR) *in-situ* spectra were recorded employing an IFS 66 BRUKER instrument equipped with an internal reflection element 45º ZnSe crystal and a deuterated triglycine sulfate (DTGS) detector.
A thin anatase layer was deposited on the ZnSe ATR crystal (2.3 g m^{-2} and 1-3 µm thick) [7]. Prior to starting the irradiation experiments, spectra of adsorption of H_2O and D_2O on the TiO_2 material were monitored in the dark. The spectrum of the TiO_2-coated crystal were taken as background and used as the blank for the subsequent measurements. When the last spectrum of each experiment had been recorded, the UV(A) lamp was turned on and another sequence of spectra were recorded.

For the ethanol experiments, 18 ml of circulating 30 vol% aqueous ethanol solution was employed at a flow rate of approximately 4 ml min^{-1}. These experiments were started by pumping the background water/D_2O (12.6 ml) through the flow cell at a flow rate of 4 ml min^{-1}, and allowing the TiO_2 deposit to equilibrate with the background solution. One spectrum was used as blank to subtract the signals of the water/D_2O, the pure solution of ethanol (5.4 ml) was subsequently added to the aqueous solution. A new set of spectra were then collected in the dark. Prior to illumination, the last spectrum of the ethanol solution was recorded in the dark with the TiO_2 layer being subtracted, and another spectra was collected during UV irradiation.

The interferometer and the infrared light path in the spectrometer were constantly purged with argon and nitrogen to avoid H_2O and CO_2 contamination. The spectra were recorded with 300 scans at 4 cm^{-1} resolution and analyzed using OPUS version 6.5 software. Irradiation of samples with UV(A) light was carried out using an LED lamp (Model LED-Driver, THORLABS) emitting UV light (365 nm). The distance from the UV lamp to the surface of the test solution was kept 30 cm on which the intensity of UV(A) light was of 1.0 $mWcm^{-2}$ as measured by UV radiometer (Dr. Honle GmbH, Martinsried, Germany).

Results and Discussion

Adsorption of H_2O and D_2O on TiO_2

Figure 1 shows the ATR-FTIR spectra of H_2O–D_2O mixtures adsorbed on the surface of TiO_2 in the dark. The IR spectrum of the adsorbed water on TiO_2 is represented by a strong IR absorbance of an O–H stretching band in the region between 3700 and 2850 cm^{-1} and a bending mode of δ (H–O–H) at 1638 cm^{-1} which is assigned to undissociated water molecules. When D_2O was used instead of water, all the bands that correspond to the adsorbed water on TiO_2 surface were shifted to lower frequency with exchanging H for D, resulting an O–D stretching band in the region between 2750-2050 cm^{-1} and δ (D–O–D) bending band at 1205 cm^{-1}.

It can be clearly seen from these spectra that the intensity of the band in the OH-stretching region decreased gradually with increasing the loading of D_2O. The peak of the isotopologue HDO bending band centred at 1450 cm^{-1} was formed and increased by increasing the concentration of H_2O in D_2O until it approached equimolar proportions [8], and this then decreased again with further increases in the quantities of H_2O in D_2O (Fig. 1 inset).

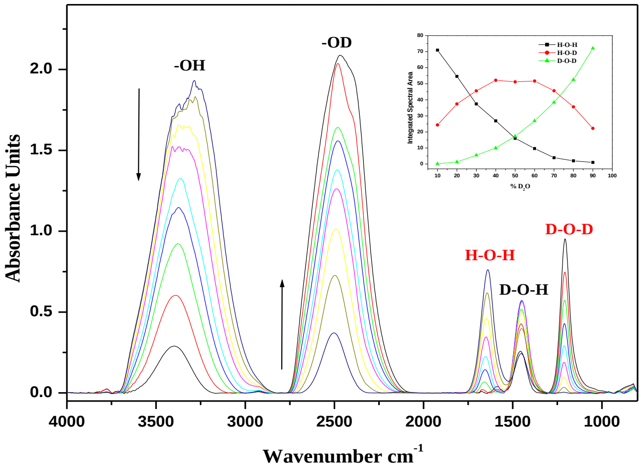


Figure 1. ATR–FTIR spectra of D_2O–H_2O mixtures with different concentrations adsorbed on TiO_2 in the dark. (Copyright 2015 Royal Society of Chemistry.)

Adsorbed D_2O molecules on TiO_2 surfaces are expected to affect the behavior of hydroxyl groups, thus a series of experiments for water adsorption with different ratios of D_2O were performed before and after UV irradiation in the presence of oxygen. Figure 2 shows the time evolution of the intensity of the integrated spectral areas of the OH and OD stretching groups before and after UV(A) irradiation with different ratios (H_2O:D_2O). As can be clearly seen, in the dark, at low concentrations of H_2O ($H_2O\% < D_2O\%$), a strong decrease in the amount of OH stretching was observed. Simultaneously, the amount of OD stretching groups adsorbed on TiO_2 increased during this period until the system reached equilibrium. In contrast, at higher concentrations of H_2O ($H_2O\% > D_2O\%$), both OH and OD stretching bands increased. Interestingly, at an equimolar mixture of 50% H_2O and D_2O, a decrease in intensity of OH stretching with a simultaneous increase in the OD stretching could be observed in the dark. These results suggest that the deuteride ions show a stronger adsorption ability in the dark than hydroxyl ions at the surface of the TiO_2 material. Thus, the deuteride ions could lead to an isotopic exchange process by replacing the hydroxyl groups adsorbed on the TiO_2 surface (reaction 1) [9]:

$$\mathrm{Ti-OH} + \mathrm{OD^-} \longrightarrow \mathrm{Ti-OD} + \mathrm{OH^-} \tag{1}$$

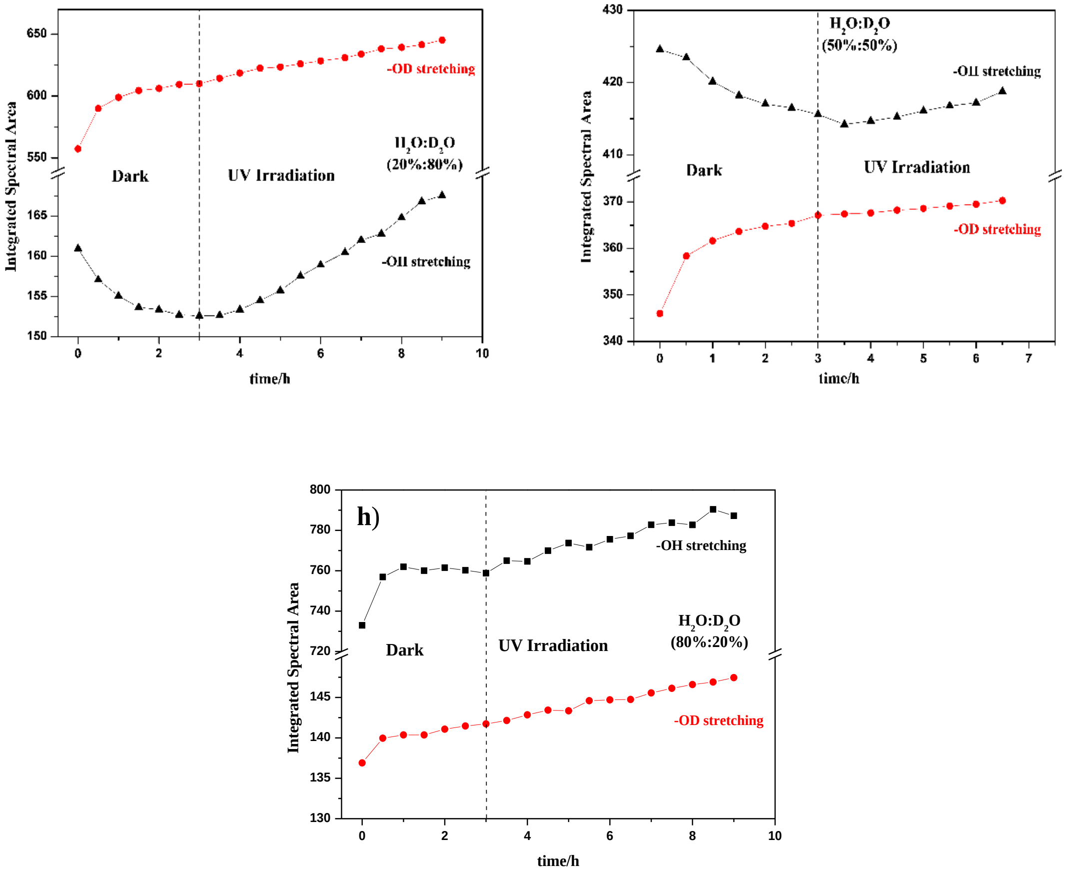


Figure 2. Time evolution of the intensity of the integrated spectral areas of the OH and OD stretching groups before and after UV(A) irradiation with different ratios (H_2O:D_2O). (Copyright 2015 Royal Society of Chemistry.)

When the system was subsequently illuminated with UV(A) light in presence of oxygen, the amount of OH and OD group stretching increased almost immediately. These results indicate that UV irradiation leads to an increase in the number of surface OH groups which in turn increases the hydrophylicity of the TiO_2 surface. These results, however, might be attributed to either an increase in the number of surface OH groups by the formation of new OH and OD groups on the surface or by increasing the amount of H_2O and D_2O molecules chemisorbed on the TiO_2 surface. Several mechanisms have been discussed to explain photoinduced hydrophilicity on TiO_2 surface. Hashimoto *et al.* reported that the increase in the amount of OH groups was believed to be caused by dissociative adsorption of water in vacancies resulting two kinds of hydroxyl groups on the surface i.e., bridging and terminal hydroxyl groups [4]. Another mechanism was proposed by Yates *et al*, who demonstrated that under UV light irradiation the decomposition of organic contaminants can take place leading to the creation of superhydrophilic surfaces [10]. A similar mechanism for UV-induced hydrophilicity proposed by Ohtani *et al.* supposed that all photogenerated holes are consumed to form oxygen vacancies, these can adsorb water, because of the photocatalytic removal of organic contaminants and so hydrophilic conversion is reached [11]. Another study by Nosaka *et al.* using ^{1}H NMR spectroscopy confirmed that the UV light illumination increased the amount of adsorbed on the TiO_2 surface [12].

Figure 3 shows the time evolution of the intensity of the integrated spectral areas of the OH and OD stretching groups before and after UV irradiation at prolonged time periods. As can be clearly seen, an isotopic exchange between deuteride ions and hydroxyl groups have been achieved in the dark. Interestingly, after 6 h of UV irradiation, however, no isotopic exchange was detected between hydroxyl groups and deuteride ions during a prolonged time in the dark. From this result, we suggest that the increase of OH and OD stretching groups under irradiation is most likely caused by adsorption of H_2O and D_2O molecules, respectively, and not by the generation of hydroxyl groups.

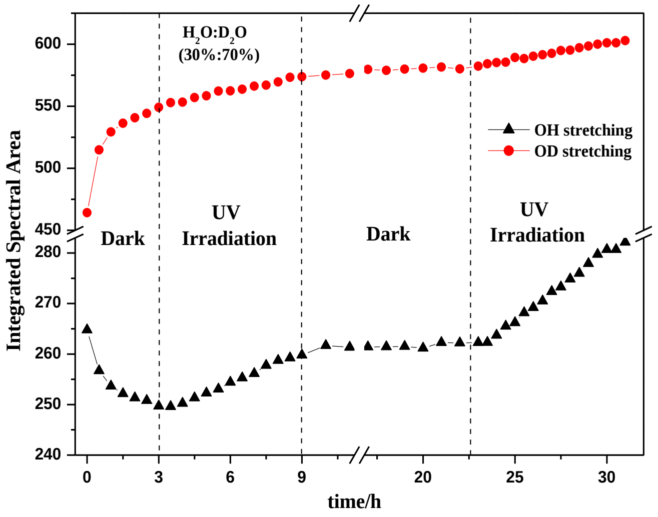
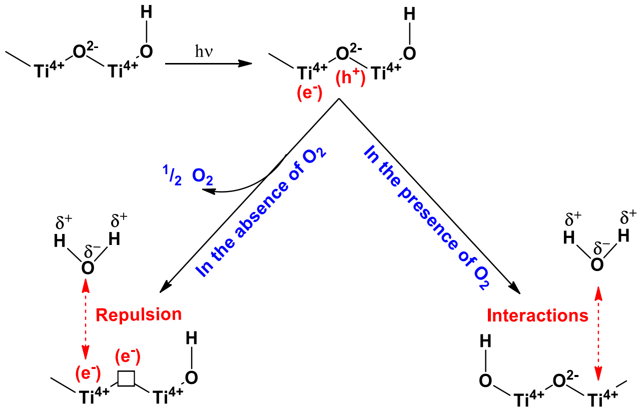


Figure 3. Time evolution of the intensity of the integrated spectral areas of OH and OD stretching groups before and after UV(A) irradiation with prolonged time (Alternately). (Copyright 2015 Royal Society of Chemistry.)

In order to elucidate the mechanism of the adsorption of H_2O and D_2O, the effect of oxygen on the OH and OD group behavior on the TiO_2 surface have been investigated. The integrated intensity of the OH and OD stretching groups increased significantly upon illumination in the presence of molecular oxygen. By contrast, when the sample was purged with nitrogen or argon, no increase in the OH and/or OD stretching group was observed (Figure are not shown). These results clearly indicate that the presence of O_2 is necessary to enhance the photoadsorption of H_2O and D_2O on TiO_2 surfaces during UV(A) irradiation. Our results confirm the critical influence of oxygen on adsorption behavior, resulting in an increase the adsorption of H_2O and D_2O on TiO_2 surfaces which is most likely caused by a photoinduced charge transfer process [9]. Takeuchi *et al.* proposed that when TiO_2 surfaces were irradiated with UV light in the absence of O_2, the electrons trapped on the Ti^{3+} sites were not scavenged by O_2 and the holes trapped on the TiO_2 surface were immediately consumed to oxidize the lattice oxygen, resulting in the formation of oxygen vacancies. Such photoreduced TiO_2 surfaces can behave as negatively charged surfaces. Thus, water molecules hardly adsorb on the photoreduced surfaces due to repulsive effects (Scheme 1) [13].

Scheme 1 Interaction model of adsorbed water during UV(A) light irradiation in the absence and presence of O_2 molecules. (Copyright 2015 Royal Society of Chemistry.)



Adsorption of ethanol in H_2O and D_2O on TiO_2

Figure 4 and 5 show the time evolution of the spectra of adsorbed ethanol on TiO_2 in H_2O a) and D_2O b) respectively, in the dark and under UV(A) irradiation in the presence of O_2. The adsorption of ethanol (30 vol%) and water on TiO_2 were performed in the dark with molecular ratios of 12% and 88% respectively. As shown in figure 4, the adsorption of ethanol on TiO_2 produces several positive absorption bands in the region 3000-2750 cm^{-1} and 1470-1250 cm^{-1} which are assigned to different types of CH vibration of on both CH_2 and CH_3 groups [14,15]. The two most prominent peaks of the adsorbed ethanol appeared at 1043 cm^{-1} and 1085 cm^{-1} which are assigned to the symmetric and asymmetric stretching frequencies of the CO stretching modes [16]. Since water and D_2O were used as the background and over subtraction occurred, a broad negative band assigned to band bending δ (H–O–H)/δ (D–O–D) and hydroxyl group stretching OH/OD were observed.

It can clearly be seen from figure 4a that in the dark the typical bands of adsorbed ethanol increased. Simultaneously, the negative band corresponding to the water adsorption decreased. Even though the molecular ratio of ethanol was very low (12%) compared to water and D_2O (88%), a similar desorption behavior of D_2O, was observed during the dark period. This phenomenon is clearly due to the stronger adsorption of ethanol on the TiO_2 surface compared to water resulting in desorption of water and D_2O molecules. It has previously been reported that alcohol and water adsorb competitively on the oxide surface both molecularly and dissociatively, with the formation of surface hydroxyl and methoxy groups [17]. As shown in Fig. 4b unlike the case of water, the typical bands of adsorbed ethanol, as well as the band centered at 3395 cm^{-1} which is assigned to the OH group of ethanol have increased. These results indicate clearly the adsorption of molecular ethanol on the TiO_2 surface. Simultaneously, a new band at 949 cm^{-1} was observed, which increased during the adsorption of ethanol in the dark. This band has previously been assigned in the literature to OD band bending of deuterated ethanol, Et(OD) [18].

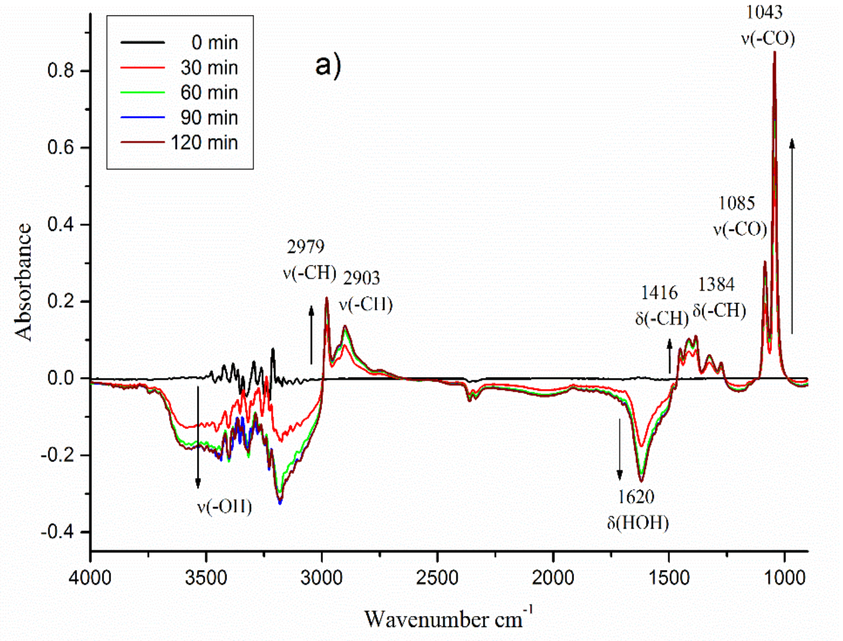
Interestingly, no isotopic exchange was detected in the region 3000-3600 cm^{-1} although the adsorption of ethanol occurred in D_2O. This result also confirmed that molecular ethanol was adsorbed on the TiO_2 surface. It has also been reported that, ethanol dissociates on TiO_2 resulting in sorbed ethoxide groups atop of Lewis acidic Ti^{4+} centers (monodentate) or between two Ti^{4+} centers (bidentate), while the H from the alcohol associates with a neighboring basic surface O to form an OH group [19]. The increasing band bending of OD at 949 cm^{-1} (Fig.4b), indicated the dissociation of deuterated ethanol on the TiO_2 surface resulting ethoxide at Ti^{4+} and the D at a neighboring basic surface.

According to ref. [20] and [17], the proposed dissociation and isotopic exchange reaction of ethanol in the heavy water (D_2O) are as follows:

$$\mathrm{CH_3CH_2OH + D^+ \longrightarrow CH_3CH_2OD + H^+} \qquad (2)$$

$$\mathrm{CH_3CH_2OD \longrightarrow CH_3CH_2O-Ti + O-D} \qquad (3)$$

From this result, we suggest that in the dark, ethanol can adsorb on TiO_2 surface in both, molecular and dissociation forms.



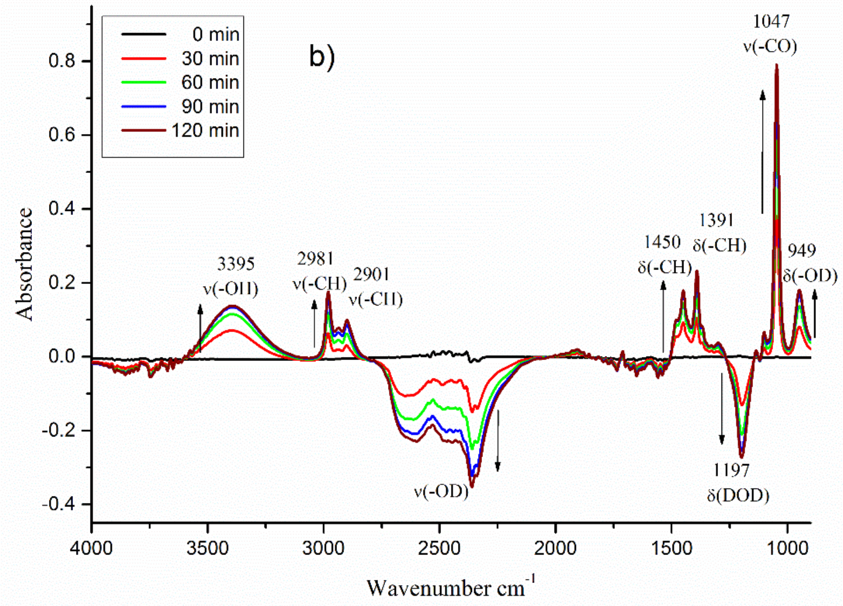


Figure 4. Time evolution of the ATR–FTIR spectra of adsorbed ethanol on TiO_2 in H_2O a) and D_2O b) in the dark.

Figure 5 shows the time evolution of the ATR–FTIR spectra (1800-800 cm^{-1}) of adsorbed ethanol on TiO_2 in H_2O a) and D_2O b) under UV irradiation in the presence of O_2. As can be seen clearly under UV irradiation, the typical bands of adsorbed ethanol solutions have decreased in H_2O and D_2O. A strong decrease in the intensities of the two prominent peaks of the adsorbed ethanol at 1047 cm^{-1} (CO) and 1085 cm^{-1} (C-C) decreased in H_2O as well as in D_2O where the intensities were much higher than in water. Additionally, the bands in the 1740-1710 cm^{-1} and 1600-1520 cm^{-1} regions, which were assigned respectively to carbonyl and carboxylate groups increased gradually. These results indicate that the ethanol was photocatalytically oxidized resulting in the formation of acetaldehyde and acetic acid as photoproducts [19,15].

Interestingly, the typical band of water and D_2O increased when the system was performed under UV irradiation (Figure 5b). This result can tentatively be explained either by photoinduced charge transfer process or by the formation of water as an intermediate product. Lin *et al.* proposed mechanism pathways of the formation of CH_3CO_{ad}, CO_2, and H_2O as photoproducts in the presence of O_2 during the oxidation of ethanol [21,22]. Although, it is well known that the ethanol can be easily adsorbed onto TiO_2 surfaces, however the adsorption mechanism of water and D_2O on TiO_2 surfaces are still unclear.

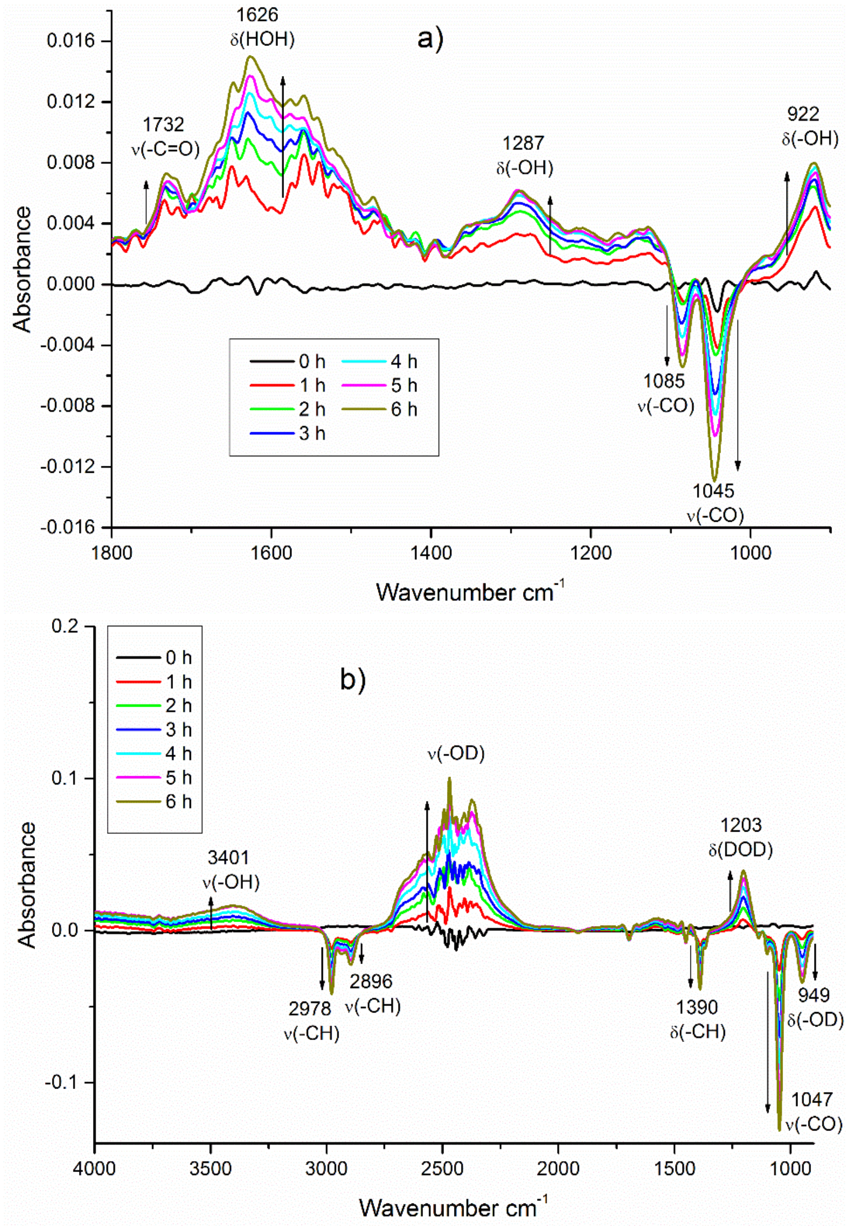


Figure 5. Time evolution of the ATR–FTIR spectra (1800-800 cm^{-1}) of adsorbed ethanol on TiO_2 in H_2O a) and D_2O b) under UV irradiation in the presence of O_2.

In order to clarify the main factors affecting the adsorption of water during UV illumination, the effect of O_2 has been investigated. Figure 6 shows the evolution of the adsorbed ethanol spectra (1800-900 cm^{-1}) under UV irradiation in the absence of O_2 in water a) and D_2O b). In the dark, the adsorption behavior of ethanol in water and D_2O was observed in the IR spectrum (Figure not shown) which were similar to those reported in figure 4.

Under UV irradiation, the typical bands of adsorbed ethanol decreased in water and D_2O (figure 6). In the meantime, the increase of the intensities of carbonyl and carboxylate groups was observed, which is similar to the observation in the presence of oxygen. As expected, the shifting of the background during oxidation of ethanol was observed. The upward baseline shift during irradiation was interpreted as transient and persistent diffuse reflectance infrared signals due to the accumulation of free electrons at the conduction band of TiO_2 particles upon irradiation, where the baseline IR absorption for TiO_2 rises immediately upon UV irradiation [23]. Similar results were reported by Highfield *et al.*, who clearly observed the direct hole oxidation of the adsorbed ethanol molecules by photoinduced holes (h^+) at the valence band of TiO_2 [19]. Interestingly, although the photocatalytic system occurred in the absence of O_2, a similar behavior of the adsorption of water and D_2O has been observed. Additionally, when D_2O was used instead of water, no formation of H_2O was detected in presence and absence of O_2 respectively, in figure 5b and figure 6b. This result would exclude the possibility that the adsorption of water and D_2O in presence of ethanol resulted either from photoinduced charge transfer process or from adsorption of water formed as product.

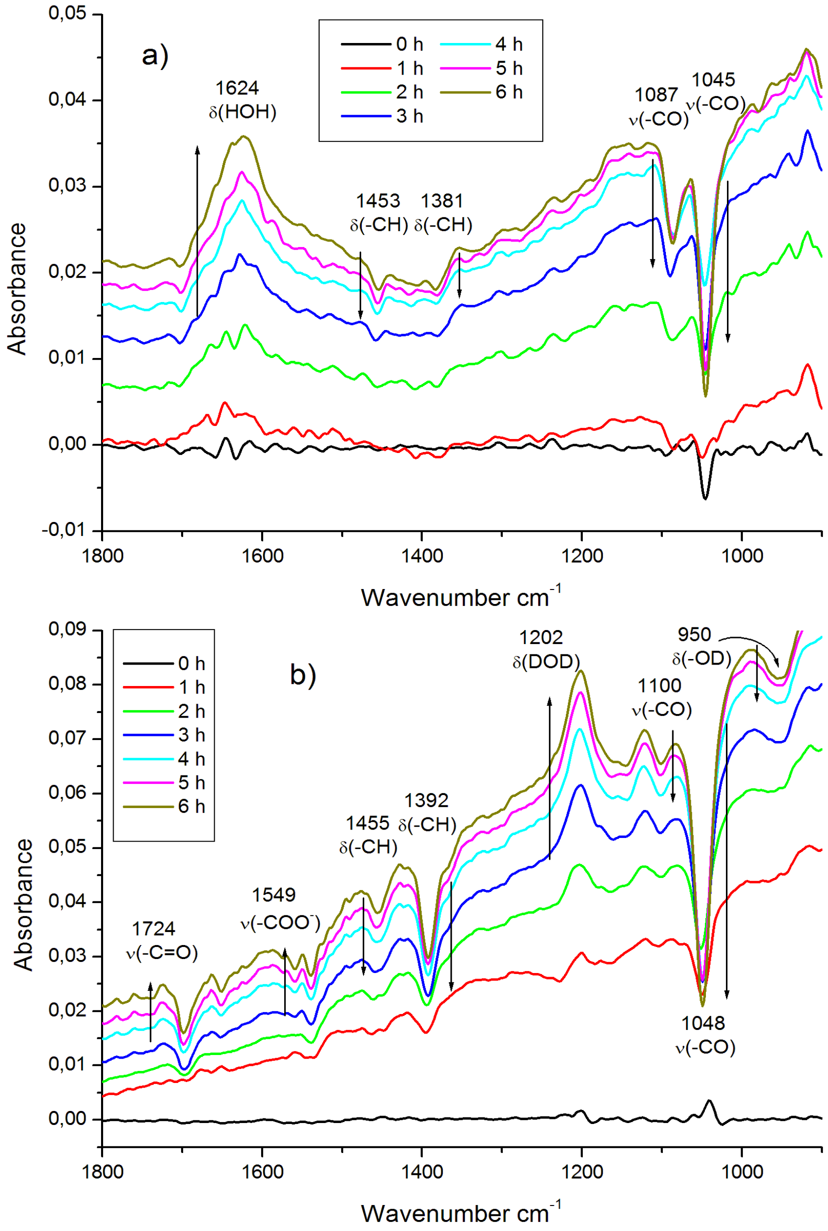
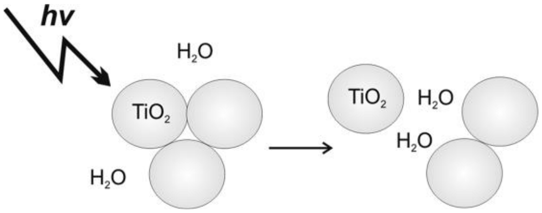


Figure 6. Time evolution of the ATR–FTIR spectra of adsorbed ethanol on TiO_2 in H_2O a) and D_2O b) in the absence of O_2.

Considering the effect of UV light on TiO_2 particles, however it seems that the particle network resulting under UV light irradiation might be responsible for the enhancement of water adsorption on TiO_2 particles due to a new distribution of the particles.

Several interpretations of the mechanism of the UV-induced hydrophilicity have been reported in the literature which can explain the behavior of water adsorption. Yates *et al.*, reported that only under UV light illumination could the decomposition of organic contaminants take place leading to the generation of hydrophilic surfaces [10]. On the other hand, Wang *et al.* found that the total TiO_2 exposed surface increased under UV(A) illumination leading to an increase in the surface area due to de-aggregation of particle agglomerates which in turn enhanced the photonic efficiency [6]. The same mechanism was considered by Mendive *et al.* who demonstrated that due to de-aggregation of particle the water molecule could fill the space between the particles (Scheme 2), which was demonstrated by the increase in the IR band corresponding to the bending mode of water [24]. In other studies, Thermal chemistry showed that there were mainly two reaction channels for ethanol desorption which lead to the suggestion of a mechanism involving the creation of new adsorption sites for water adsorption by means of a photothermal-desorption of adsorbed ethanol molecules [17]. The behavior of the preadsorption of water on the thermal desorption reaction of ethoxy has been reported by Gamble *et al.* [25]. From these results we suggest that the adsorption of water and D_2O are most likely to occur via photothermic rather than photoelectronic processes.

Scheme 2. Proposed Mechanism of TiO_2 Nanoparticle Layer Expansion (Copyright 2011 American Chemical Society.)



Based on the hypotheses reported in the literature, i.e., the de-aggregation concept, super-hydrophilicity phenomena and photo-induced removal of impurities, we suggest that the adsorption of H_2O and D_2O molecules on TiO_2 surfaces during UV light irradiation occurred not only by photoinduced charge transfer processes (photoinduced adsorption/desorption and photocatalytic reaction) but also by thermal processes (thermal desorption and de-aggregation of particle).

Conclusion

The behavior of adsorbed H_2O and D_2O in photocatalytic processes and in photoinduced hydrophilicity on TiO_2 surfaces has been studied in the presence and absence electron (O_2) and holes (ethanol) scavenger. Adsorption of H_2O with different ratios of D_2O on TiO_2 revealed different isotopic exchange reactions, which take place in the dark. Upon illumination with UV light in the presence of O_2, both OH and OD groups are formed leading to increase the hydrophilicity of the TiO_2 surface. The increase in the amount of OH and OD groups is suggested to be caused by photoinduced charge transfer allowing the adsorption of H_2O and D_2O onto the TiO_2 surface. The FTIR spectra of ethanol in the dark shows the coexistence of ethanol adsorption both, in molecular and in dissociation forms. Under UV(A) illumination the typical EtOH bands decreased on the surface while the adsorption of water and D_2O increased. Several mechanisms reported in the literature can explain this behavior, such as replacement of surface impurities that are photocatalytically destroyed, exchange of adsorbed water molecules by thermal desorption of ethanol and increase of hydroxylation by augmentation of surface area due to the deaggregation of particles agglomerates.

Acknowledgments

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