

Hindawi Publishing Corporation  
International Journal of Photoenergy  
Volume 2008, Article ID 964721, 9 pages  
doi:10.1155/2008/964721

## Research Article

# Gas-Phase Photodegradation of Decane and Methanol on TiO<sub>2</sub>: Dynamic Surface Chemistry Characterized by Diffuse Reflectance FTIR

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Received 24 July 2007; Accepted 4 January 2008

Recommended by Russell Howe

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to study illuminated TiO<sub>2</sub> surfaces under both vacuum conditions, and in the presence of organic molecules (decane and methanol). In the presence of hole scavengers, electrons are trapped at Ti(III)–OH sites, and free electrons are generated. These free electrons are seen to decay by exposure either to oxygen or to heat; in the case of heating, reinjection of holes into the lattice by loss of sorbed hole scavenger leads to a decrease in Ti(III)–OH centers. Decane adsorption experiments lend support to the theory that removal of surficial hydrocarbon contaminants is responsible for superhydrophilic TiO<sub>2</sub> surfaces. Oxidation of decane led to a mixture of surface-bound organics, while oxidation of methanol leads to the formation of surface-bound formic acid.

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## 1. INTRODUCTION

TiO<sub>2</sub> is of great interest in the field of heterogeneous photo-oxidation catalysis, especially in the area of environmental cleanup. TiO<sub>2</sub> has the advantage of being relatively cheap, nontoxic, and stable, all of which make it attractive for remediation of environmental organic pollutants [1]. Studies on the surface chemistry of TiO<sub>2</sub> help to answer important questions such as the active species for photo-oxidation, the fate of charge carriers, and the mechanism for transfer of charge to species bound to the surface [2]. Previously, we used FTIR (DRIFT) spectroscopy to monitor surface species, surface electron, and hole traps on TiO<sub>2</sub> powders [3–5]; and to attribute broad spectral features to free conduction band electrons [3].

Representative hydrocarbon species (e.g., decane and methanol) were chosen for further investigation of hydrocarbon adsorption and photo-oxidation on the surface of illuminated TiO<sub>2</sub>. The primary objective of these studies is to gain insight into the gas-phase and surface-bound photo-oxidation products.

## 2. EXPERIMENTAL PROCEDURES

TiO<sub>2</sub> (Degussa P25; 25% rutile, and 75% anatase), decane (99.9%, Aldrich), methanol (99.9%, Aldrich), methanol-d<sub>4</sub> (CD<sub>3</sub>OD, 99% isotopic purity, Aldrich), and formic acid (88%, Aldrich) were used as received. Oxygen gas (99.9%) was passed through a water trap before use in FTIR experiments.

DRIFT spectra were acquired using a Bio-Rad FTS-45 spectrometer with a liquid N<sub>2</sub>-cooled MCT detector. Spectra were collected at 8 cm<sup>-1</sup> resolution using a Spectra-Tech Collector diffuse-reflectance accessory. The solid samples were held in the sample cup of a Spectra-Tech high-temperature environmental chamber (HTEC) that could be resistively heated to 1000 K (±1 K), and the chamber evacuated to 10 μTorr. A gas manifold connected to the sample chamber allowed for pure gas samples (e.g., O<sub>2</sub>) or organic vapors (e.g., decane and methanol vapor) to be introduced and removed as needed. The organic samples were attached to the system via a glass bulb, and these samples underwent several freeze-thaw cycles to remove dissolved gases. UV radiation from a 1 kW Oriel Xe lamp was

focused into the HTEC chamber through a moveable mirror and lens system that allowed for photolysis experiments to be conducted without breaking system purge.

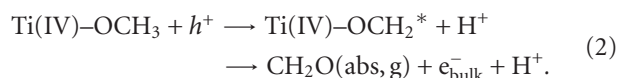
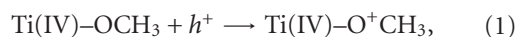
### 3. RESULTS AND DISCUSSION

#### 3.1. Hole and electron trapping on TiO<sub>2</sub> surfaces

One of the primary results of our previous work [3] was an observed rise in the DRIFT spectrum baseline when TiO<sub>2</sub> is irradiated in vacuo, which was caused by the generation of free electrons. The baseline gradually decayed over the course of several hours, leading to a stable trapped electron in a Ti(III)–OH group at 3714 cm<sup>-1</sup>. We now believe that the impurities seen in previously C–H bands found at 2927 and 2859 cm<sup>-1</sup> are indicative of surface-bound species responsible for hole trapping. To test this hypothesis, a small amount of methanol vapor was added to the system, followed by the normal vacuum pumping on the system to remove as much methanol as possible. Experiments conducted in the weeks following the methanol exposure led to a background C–H signal, which had been observed previously, but more importantly led to the expected baseline increase and Ti(III)–OH formation upon irradiation.

Figure 1 shows the DRIFT spectra for TiO<sub>2</sub> powder in vacuo under different conditions. In the untreated powder, bridging hydroxyl groups are seen at 3414 cm<sup>-1</sup> and Ti(IV)–OH stretches are seen around 3645 cm<sup>-1</sup>. There is also a broad adsorption between 3000 and 3600 cm<sup>-1</sup> due to surface-bound water molecules. Upon heating to 200°C, surface water is lost, allowing the bridging hydroxyl groups to be more clearly seen in the spectrum. Furthermore, the Ti(IV)–OH peak becomes more clearly defined as a single peak at around 3645 cm<sup>-1</sup>. Upon irradiation, bridging hydroxyl groups are completely lost, the Ti(IV)–OH peak is reduced in intensity, and a new peak at 3714 cm<sup>-1</sup> is seen, which corresponds to trapped electrons in Ti(III)–OH groups. These results are consistent with our earlier work [3].

Alcohols are known to chemisorb to TiO<sub>2</sub> surfaces, [6–8] thus the expected surface species in the case of methanol vapor would be Ti–OCH<sub>3</sub>. This adsorbed species provides a viable hole trap, by either direction hole transfer or through a chemical reaction to form formate:



In either case, free electrons are present in the conduction band, leading to the aforementioned rise in baseline and a change in the color of the powder from white to blue as a result of Ti(III) atoms.

In the reaction described by (2), the injection of an electron into the lattice would create a current-doubling effect, which is well known for the case of organic photo-oxidation by TiO<sub>2</sub> [9–12]. Thus, some of the free electrons observed after photolysis may be a result of such an effect.

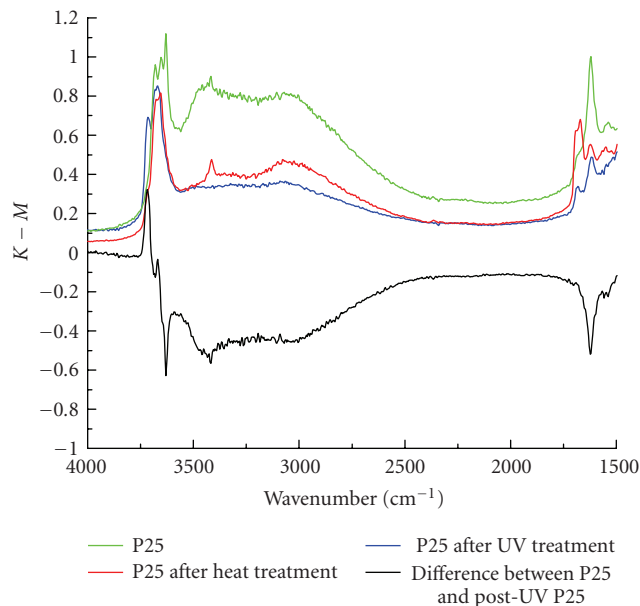


FIGURE 1: DRIFT spectra showing the effect of heating (to 200°C) and UV irradiation on P25 TiO<sub>2</sub> powder in vacuo in presence of hole scavenger contaminants.

The electron-generating reaction would have to proceed under anoxic conditions, and would likely be initiated by the loss of a proton. Figure 2 shows the effect of sequential heat treatment (523 K) and UV treatment in vacuo on a TiO<sub>2</sub> surface which had been exposed to methanol vapor. The heat treatment effectively removed all the water and some of the methanol, but the UV treatment led to an additional decrease in C–H intensity, as seen in the difference spectrum. Thus, there is a photochemical methanol loss pathway, even in vacuo, which supports the mechanism postulated in (2).

When the system was under a constant 1.0 atm N<sub>2</sub> and the fresh TiO<sub>2</sub> sample was not exposed to a vacuum, the baseline did not increase upon irradiation. This was most likely due to the inability of methanol molecules to desorb or detach from the walls and diffuse to the powder surface. The background methanol persisted in the system on the order of weeks and months, unless vigorous cleaning methods (frequent purging of the gas manifold with N<sub>2</sub> or O<sub>2</sub>) were taken. Given the well-known affinity for TiO<sub>2</sub> to sorb hydrocarbons, [2] it is not unlikely that a small amount of impurity in the system could transfer from the walls to the TiO<sub>2</sub> powder, especially given that the amount of manifold surface area is several thousand times larger than the surface area of the powder in the sample compartment. Indeed, work with other organic samples such as methoxychlor and lindane led to a several-month contamination of the experimental setup, as new TiO<sub>2</sub> samples would continually turn orange from picking up these long-lived residual pesticide molecules. The problem of reproducing clean TiO<sub>2</sub> systems is not unique, as seen by the debate over the cause of UV-induced hydrophilicity on TiO<sub>2</sub> crystal surfaces, which has only recently been shown to be a result of the removal of surface hydrocarbon contaminants [13].

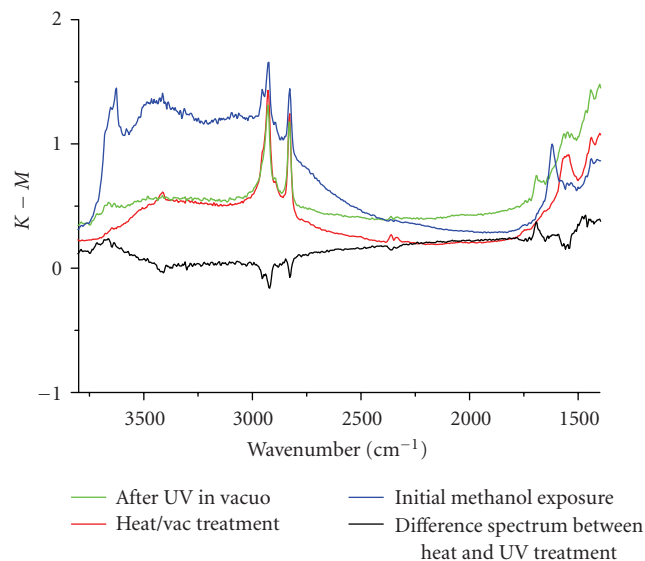
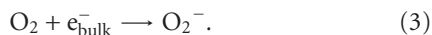
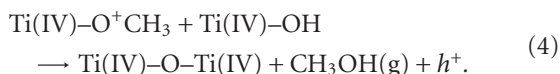


FIGURE 2: DRIFT spectra of  $\text{TiO}_2$  powder heated and irradiated in vacuo after absorbing methanol vapor, and the difference spectrum showing the effect of irradiation on the surface which had already undergone heat treatment.

Given this new information, some of the previous conclusions need to be refined, especially in regards to postirradiation baseline relaxation. As reported earlier, both thermal treatment at 423 K as well as exposure to  $\text{O}_2$  at 300 K led to a rapid relaxation of the baseline, as opposed to slow relaxation if the system was left alone [3]. These experiments were repeated, and in the case of relaxation by  $\text{O}_2$ , the resulting peak at  $3714\text{ cm}^{-1}$  is much larger, as seen in Figure 3. This can be explained as follows. The slow relaxation is a result of charge recombination, and has been studied previously [5]. The rapid relaxation from exposure to oxygen is due to electron scavenging by oxygen, as it is a well-known electron acceptor:



The relaxation from thermal treatment is due to injection of trapped holes back into  $\text{TiO}_2$  upon methanol desorption, which begins to occur at 400 K under vacuum conditions [6]. Not all methanol will be removed by this pathway though, as even at 475 K, the  $\text{TiO}_2$  surfaces can contain alkoxides [7]:



The injected holes can then recombine with bulk electrons, that is, annihilation, but they can also combine with the trapped electrons in the form of  $\text{Ti(III)-OH}$  groups:



Thus, since the  $\text{O}_2$  treatment does not remove the surface methanol, there are both less holes injected into the lattice

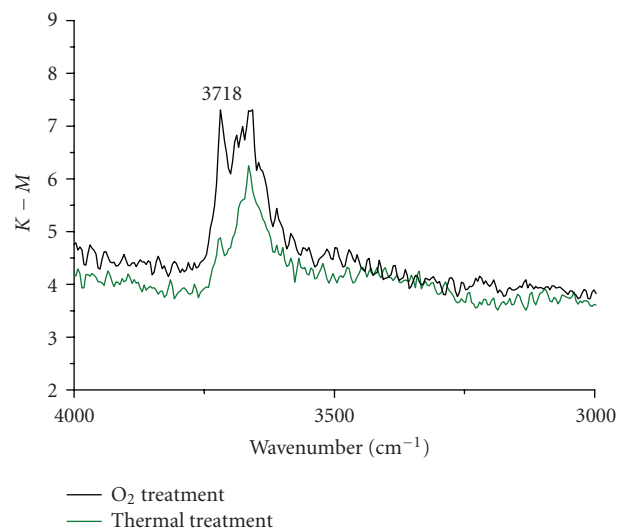


FIGURE 3: DRIFT spectra of  $\text{TiO}_2$  powder irradiated in the presence of methanol vapor, followed by either thermal or  $\text{O}_2$  treatment.

and more hole traps, leading to an increased intensity of the  $\text{Ti(III)-OH}$  peak at  $3714\text{ cm}^{-1}$ .

It was observed that the  $\text{Ti(III)-OH}$  groups could be removed by illumination under  $\text{O}_2$ , but only after being partially rehydrated under  $\text{H}_2\text{O}$  vapor [3]. This result is consistent with loss of chemisorbed methanol (and thus hole injection) upon rehydration as reported elsewhere [14]. Thus, the previous explanation for this observed behavior, which stated that defects were stabilized by surface reconstruction involving OH groups, needs to include the possibility of the methanol loss pathway. Likewise, the role of lattice O-vacancies in the mechanism of hole-trapping, while not completely disproved, cannot account for all the experimental results.

### 3.2. Decane adsorption and degradation on $\text{TiO}_2$ surfaces

A potential practical application of  $\text{TiO}_2$  is in the remediation of oil spills by coated glass beads [15]. In order to gain insight into alkane photocatalysis by  $\text{TiO}_2$ , decane was chosen as a sample hydrocarbon for a series of photoexperiments. The primary reasons for choosing decane were its simplicity (straight-chain alkane) and its vapor pressure ( $\sim 1$  Torr at room temperature, ideal for dosing samples via the gas manifold).

Hydrocarbon oxidation on  $\text{TiO}_2$  has been studied extensively. Several decades ago, Djeghri et al. [16] used a flow-through reactor to study the UV-illuminated photocatalysis of alkanes (methane through octane) in the vapor phase. They found that the alkanes are oxidized to ketones, aldehydes, and  $\text{CO}_2$ , and that steady-state product concentrations are reached within minutes [16]. More recently, Minabe et al. have studied the photo-oxidation of long-chain organics on  $\text{TiO}_2$  thin film, and observed that only  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were produced in the gas phase [17]. They suggest that the initial reactants as well as all intermediates were continuously

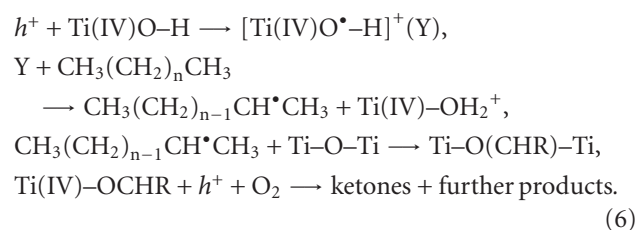
attached to the TiO<sub>2</sub> surface; however, they offered no insight into how the organics were oriented on the surface, or on the nature of the intermediates. The authors prepared their samples by melting their organics, then spreading the liquid on the TiO<sub>2</sub> thin-film surface, whereas Teichner et al. introduced the organics in the gas phase over nonporous anatase particles. These differences in catalyst and sample introduction, as well as the long exposure time of Fujishima's physisorbed organics compared to the gas-phase organics in Teichner's experimental setup, likely account for Fujishima and coworkers inability to detect any intermediates.

In the first set of experiments, decane vapor was introduced to TiO<sub>2</sub> surfaces that had been pretreated by UV irradiation in vacuo, and surface coverage was compared to the nonirradiated case. It was known at the time that UV treatment makes TiO<sub>2</sub> surfaces superhydrophilic, and we believed that the UV pretreatment would affect the ability for decane to adsorb to the surface. Decane dosing was performed by opening a glass bulb containing decane, which was attached to a section of the gas manifold, for 2 minutes. The bulb was then closed, and that segment of the manifold was then opened to the sample chamber. The decane vapor was allowed to equilibrate with the sample for 10 minutes, and an initial FTIR spectrum was taken. The system was then opened to vacuum, and a series of scans were taken as the system was pumping down. Figure 4 shows the results of these experiments. Although initial decane concentrations were different ( $t = 0$ , while sample was sitting nonevacuated under decane vapor), after exposure to vacuum, both samples had near identical decane desorption profiles. Nearly all decane was lost from both the nonirradiated and irradiated surfaces during vacuum treatment, indicating that the decane was weakly bound, that is, physically adsorbed to the surface. These experiments provide support for the theory that hydrocarbon contaminants [13], not UV-induced defects [18] or UV-induced rupture of Ti–OH bonds [19], are responsible for surface hydrophilicity. The experiments suggest that the UV pretreated surface, once exposed to decane vapor, lost its super-hydrophilic character and behaved similarly to the nontreated surface in regards to the amount of decane adsorbed on the surface.

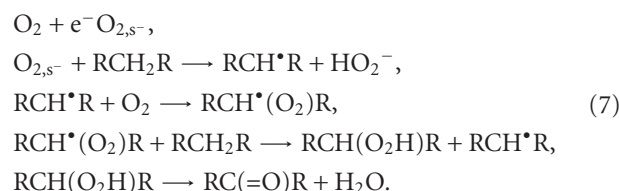
In the next series of experiments, the oxidation of decane on TiO<sub>2</sub> was studied. After dosing the sample with decane, the system was immediately exposed to 1 atm O<sub>2</sub>, so as to prevent the decane from desorbing from the surface. The sample was then irradiated for 5–10-minute intervals, at which point the lamp was turned off and a spectrum was recorded. Total time spent undergoing irradiation was 1 hour. Figure 5 shows the resulting spectra over 2000–4000 cm<sup>-1</sup>. As expected, both water (broad adsorption between 3000 and 3600 cm<sup>-1</sup>) and CO<sub>2</sub> (2320 cm<sup>-1</sup>) are produced, with a loss in hydrocarbon intensity (C–H stretches between 2800 and 3000 cm<sup>-1</sup>). To further probe the reaction products, a series of difference spectra are used, as shown in Figure 6. After one minute of irradiation, water (but not CO<sub>2</sub>) is seen to form, and peaks are seen in the 1350–1750 cm<sup>-1</sup> region, which are indicative of C–O bonds. The initial formation of water indicates that hydrogen abstraction is the first step in decane oxidation [20]. As the oxidation

progressed, these C–O stretches eventually gave way to the C=O stretch at 1737 cm<sup>-1</sup>, simultaneously accompanied by the formation of CO<sub>2</sub>, as seen in the difference spectrum between 5 and 20 minutes of irradiation. At the end of the photoreaction, the system was exposed to vacuum, and some, but not all, of the reaction products were removed. Further oxidation in vacuo was used to remove the more strongly bound surface species.

Two possible mechanisms for the reaction are as follows. The active species for oxidation could be a surface-bound hydroxyl radical, which abstracts a hydrogen atom from a surface decane molecule, forming an alkyl radical. The alkyl radical could then react in any number of ways, such as attachment to a Ti–O–Ti group to form an alkoxy species, which would then undergo further oxidation to ketones and eventually CO<sub>2</sub>:



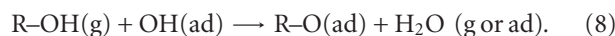
Another possible mechanism involves superoxide formation, which leads to a free-radical-chain mechanism as outlined below:



On the basis of the FTIR data alone, neither mechanism can be proved nor disproved, although ketones are clearly an intermediate product. The spectra are especially complex between 1300 and 1700 cm<sup>-1</sup>, likely due to peak overlap from ethers and ketones of various carbon-chain lengths, making absolute product assignment impossible.

### 3.3. Methanol adsorption and degradation on TiO<sub>2</sub> surfaces

Methanol was chosen as the next molecule to examine, due to the simplicity of possible photo-oxidation products (no long-chain carbon products) as well as the ability for methanol to chemisorb to the TiO<sub>2</sub> surface [6–8]. Samples were dosed with methanol vapor in a similar manner to decane, but unlike decane, the methanol species remained behind on the surface after complete evacuation of the sample chamber. Figure 7 shows the difference spectra before and after methanol and d<sub>4</sub>-methanol adsorption onto the TiO<sub>2</sub> sample. Both samples show a loss of Ti–OH groups, as methanol molecules can displace surface OH groups during chemisorption as seen below:



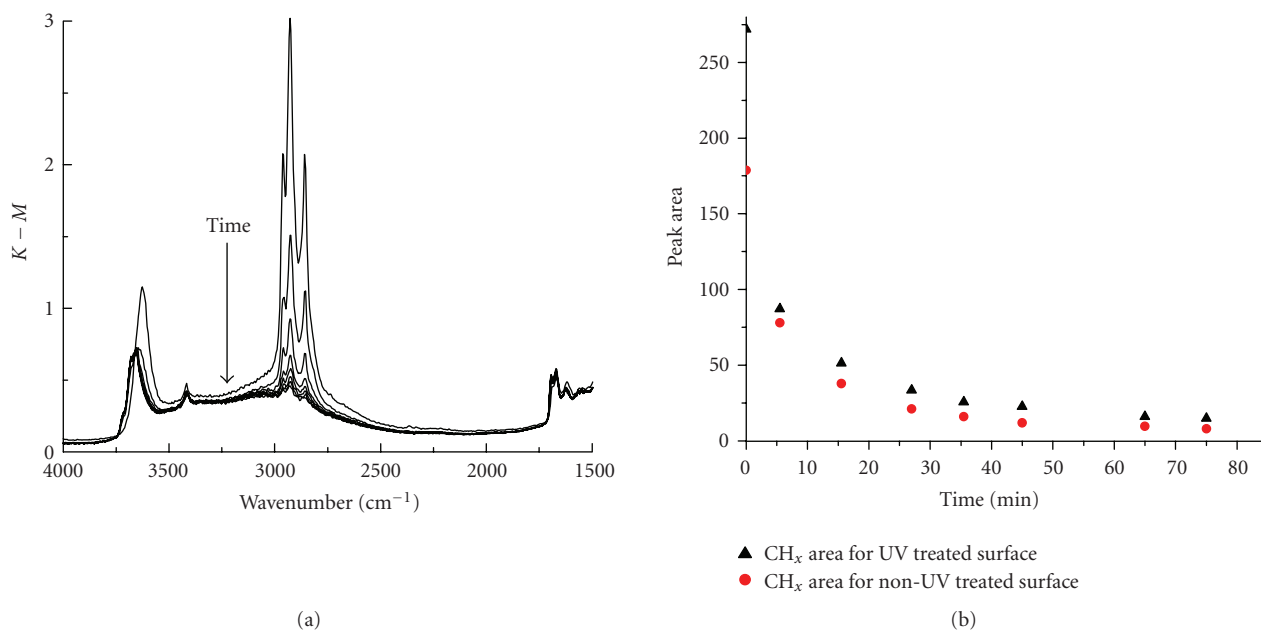


FIGURE 4: Typical time series of decane desorption on TiO<sub>2</sub> in vacuo (a), and hydrocarbon peak intensity of decane absorbed to UV versus non-UV-treated TiO<sub>2</sub> (b).

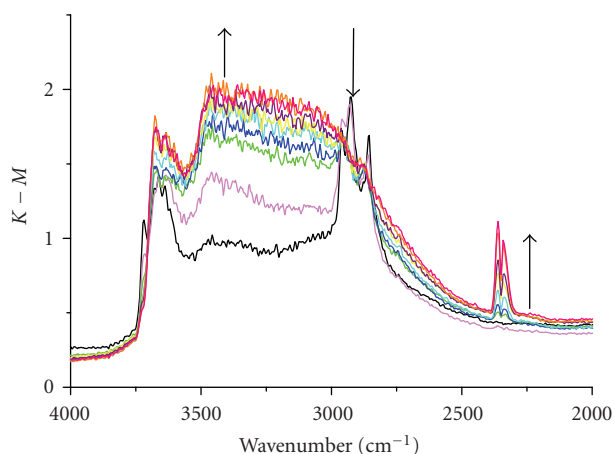


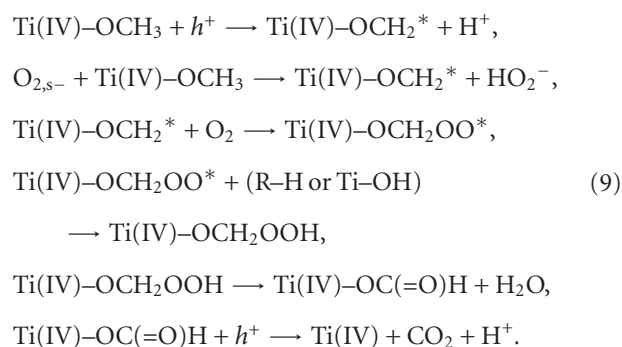
FIGURE 5: DRIFT spectra taken during the course of 1-hour UV oxidation of decane on TiO<sub>2</sub> under 1 atm O<sub>2</sub>. Arrows indicate increase in surface-bound water and CO<sub>2</sub> vapor, and a decrease in hydrocarbon intensity.

For d<sub>4</sub>-methanol, CD<sub>3</sub> stretches are seen at 2072 and 2226 cm<sup>-1</sup>, and the methanol OD stretch is seen as a broad peak centered at 2470 cm<sup>-1</sup>. An OD stretch corresponding to Ti-OD is also seen at 2716 cm<sup>-1</sup>, indicating scrambling of surface OH groups with methanol [3].

Figure 8 shows a series of difference spectra taken during the course of methanol oxidation under 1 atm O<sub>2</sub>. Within the first 5 minutes, both water and CO<sub>2</sub> are seen to form. There is a decrease in CH<sub>3</sub> stretches at 2916 and 2816 cm<sup>-1</sup>, and a new peak assigned to a CH<sub>2</sub> stretch at 2862 cm<sup>-1</sup>. There are also 2 new peaks at 1583 and 1361 cm<sup>-1</sup>, which are assigned to the asymmetrical and symmetrical stretching bands of

carboxylate anion, respectively [21]. These products were also seen in the case of d<sub>4</sub>-methanol (Figure 9). To further validate that formic acid is indeed the intermediate species identified in the difference spectra, a drop of formic acid was placed directly on a fresh TiO<sub>2</sub> surface, and the resulting DRIFT spectrum is shown in Figure 10. Carboxylate peaks are observed in the same location as the peaks from the difference spectra, confirming the assignment.

After 15 more minutes of irradiation, there is a decrease in the carboxylate species, and an increase in CO<sub>2</sub> occurs. Upon evacuation, surface water and CO<sub>2</sub> are lost, but an increase is seen in carboxylate, indicating that it is a surface-bound species which now has increased signal strength, possibly due to readsorption of gas-phase carboxylic acid molecules once surface water was removed. A possible mechanism for the reaction, which is consistent with the spectral evidence presented above, is as follows. The initiating step is hydrogen abstraction, either by direct hole transfer or superoxide. A hydroperoxy species is formed, which rearranges to a surface-bound formic acid, which can then be released as CO<sub>2</sub>:



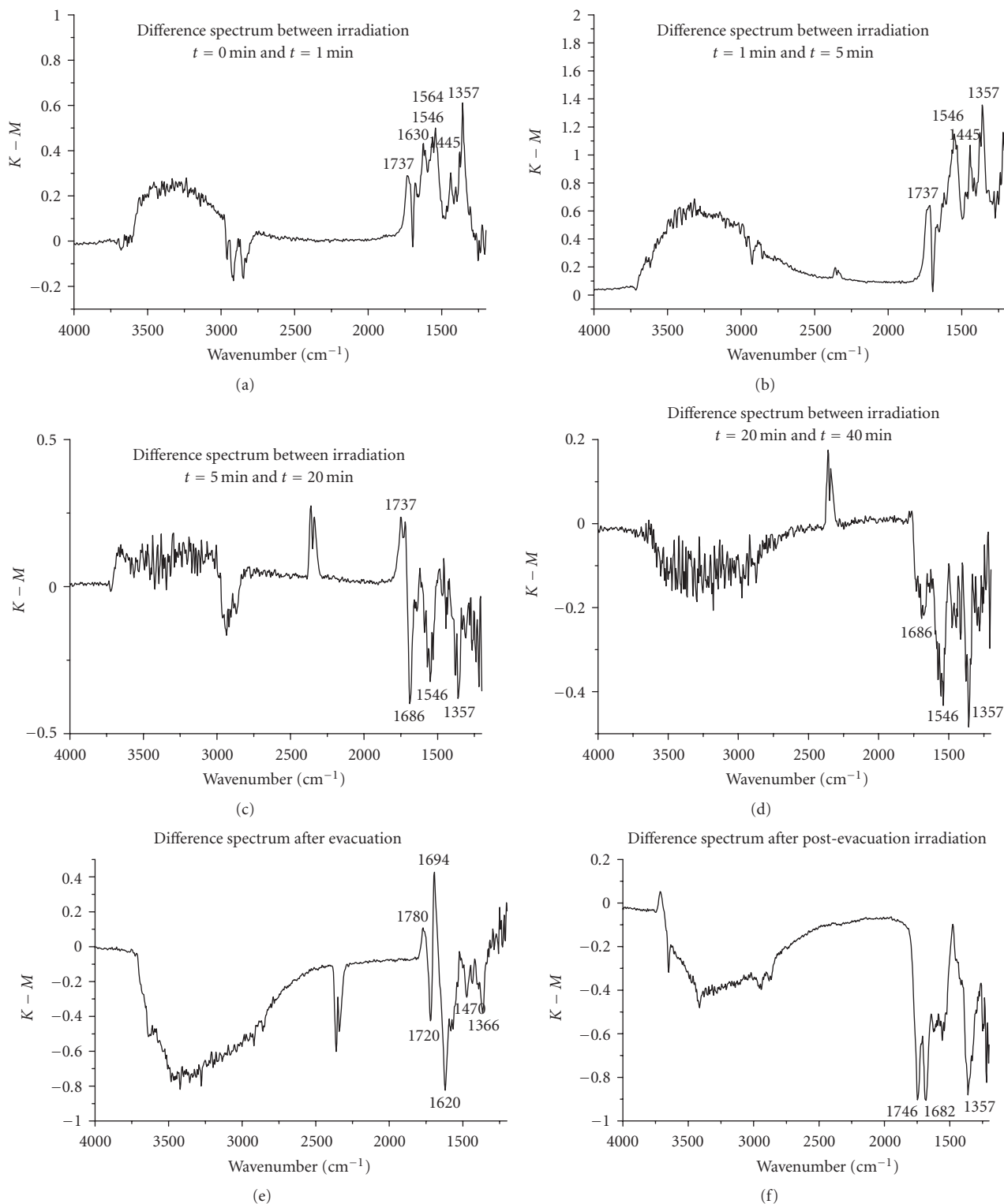


FIGURE 6: Time series DRIFT difference spectra following course of decane oxidation.

#### 4. CONCLUSIONS

Only when  $\text{TiO}_2$  is irradiated in the presence of a hole scavenger, even at very low surficial concentrations, electrons are trapped at  $\text{Ti(III)-OH}$  sites, and free electrons are also

generated. Upon heating, the hole scavengers are desorbed and with the consequent reinjection of previously trapped holes. This leads to a decrease in detectable  $\text{Ti(III)-OH}$  centers. Decane adsorption experiments lend support to the theory that removal of hydrocarbon contaminants is

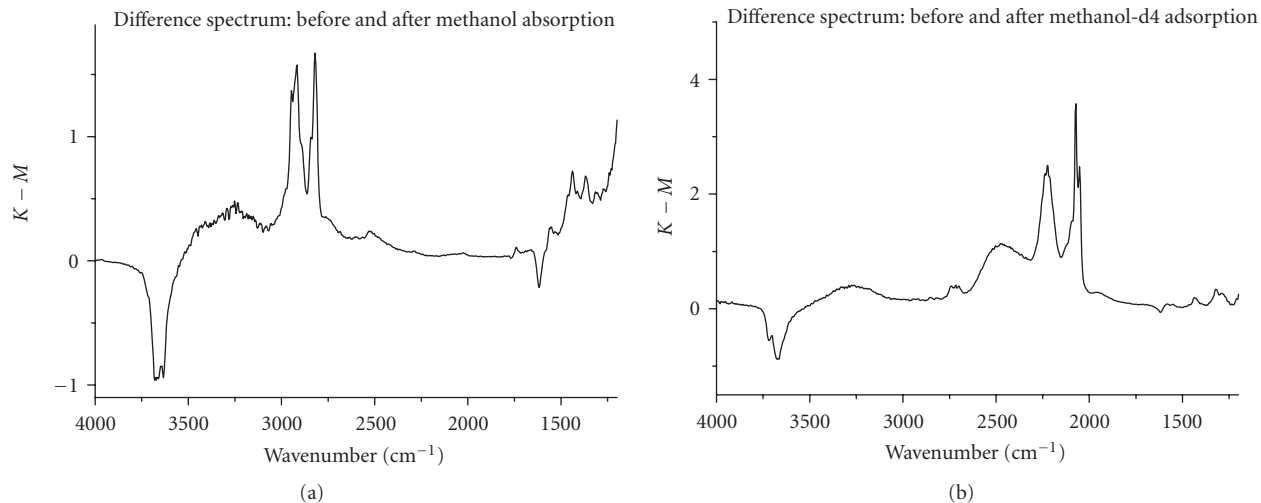


FIGURE 7: DRIFT spectra showing surface coverage of methanol and methanol-d<sub>4</sub>.

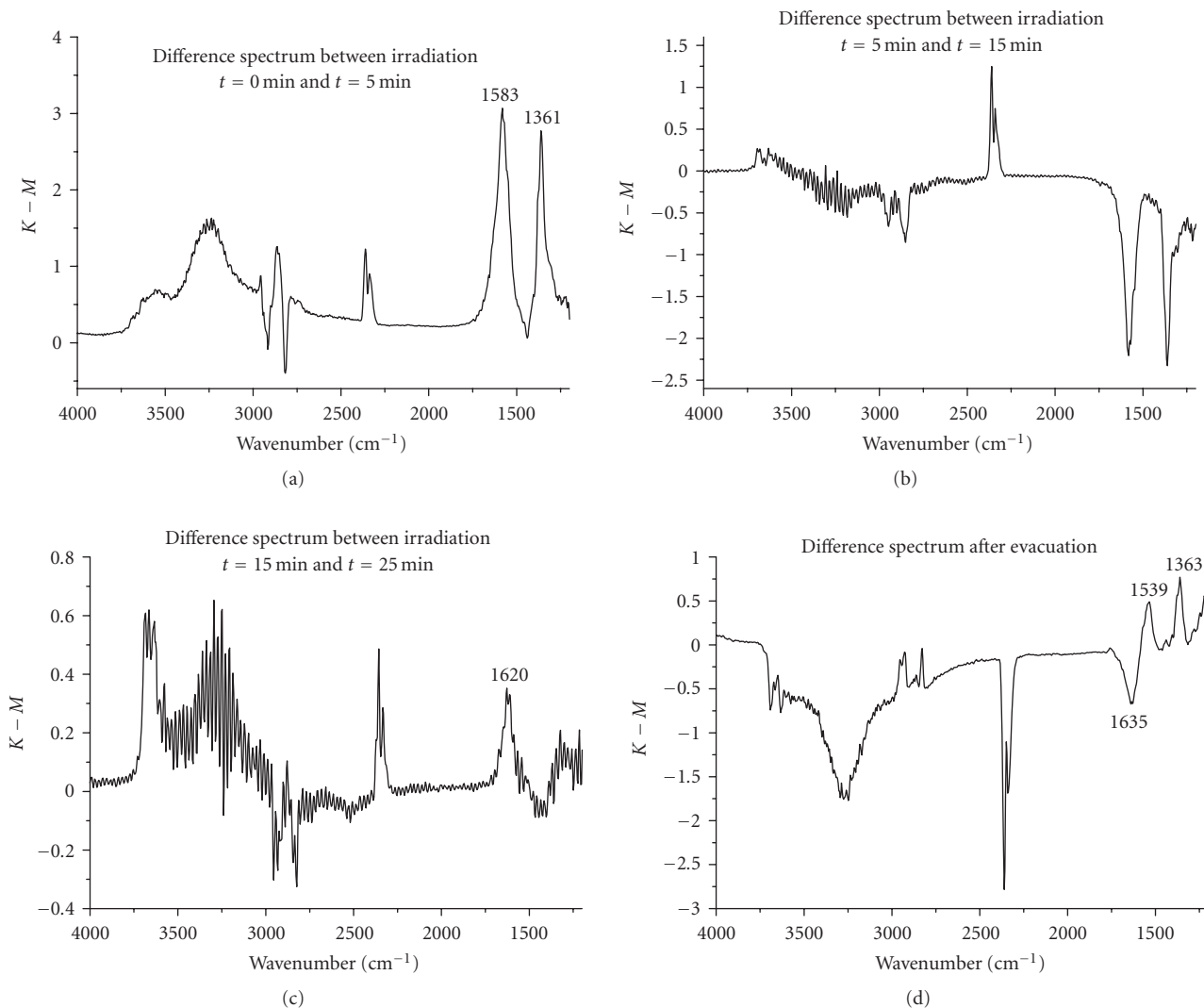


FIGURE 8: Time series DRIFT difference spectra following course of methanol oxidation.

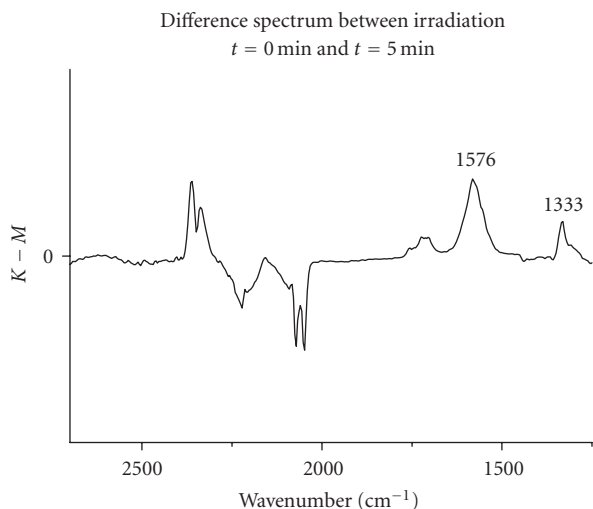


FIGURE 9: Initial products of d4-methanol oxidation.

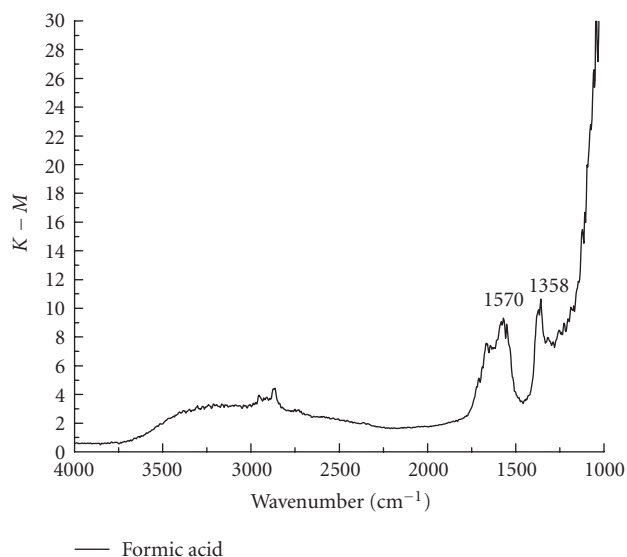


FIGURE 10: Formic acid absorbed on  $\text{TiO}_2$ .

responsible for the appearance of super-hydrophilic  $\text{TiO}_2$  surfaces. While the oxidation of decane did not lead to any definitive product assignments, the oxidation of methanol led to identification of surface-bound formic acid.

## ACKNOWLEDGMENTS

We are grateful to the Hydrogen Energy Research & Development Center and 21st Century Frontier Research and Development Program of the Ministry of Science and Technology of Korea for research support. Supplementary support was generously provided by the Northrop-Grumman Corporation. Special issue dedicated to the second international conference on semiconductor photochemistry.

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