Chapter 2

Gas-Phase Photodegradation of Decane and Methanol on TiO$_2$: Dynamic Surface

Chemistry Characterized by Diffuse Reflectance FTIR

Abstract

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to study illuminated TiO_2 surfaces both under vacuum conditions and in the presence of organic molecules (decane and methanol). In the presence of a hole scavenger, electrons are trapped at Ti(III)–OH sites, and a free electrons are generated. These free electrons are seen to decay by either exposure 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 hydrocarbon contaminants is responsible for superhydrophilic TiO_2 surfaces. Oxidation of decane led to an undistinguishable mixture of surface-bound organics, while oxidiation of methanol led to formation of surface-bound formic acid.

Introduction

TiO$_2$ is of great interest in the field of heterogeneous photooxidation catalysis, especially in the area of environmental cleanup. TiO$_2$ has the advantage of being cheap, nontoxic, and stable, all of which make it attractive for remediation of environmental organic pollutants.[1] Studies on the surface chemistry of TiO$_2$ help answer important questions such as the active species for photooxidation, the fate of charge carriers, and the mechanism for transfer of charge to species bound to the surface. These are just some of the topics covered in a recent review paper[2] on TiO$_2$ surface science. Our contribution to the field has been from studies using FTIR spectroscopy to monitor surface species and surface traps on TiO$_2$ powders.[3-5] Spectroscopic features identified distinct species assigned to trapped holes and electrons, as well as more broad features assigned to free conduction band electrons.[3] However, when attempts were made to later repeat this work, some difficulty was encountered in reproducing the results. A better understanding of the role of previously dismissed hydrocarbon species has led to reinterpretation of some of our previous work, as well as an explanation into some of the observed behavior.

In another set of experiments, a simple hydrocarbon species with suitable vapor pressure (decane) was chosen for a study on hydrocarbon adsorption and photoxidation. After results indicated poor adsorption and a hard-to-interpret mix of products, a simpler organic molecule (methanol) was chosen, and the experiments repeated. The goal of these studies was to gain insight into the gas phase and surface-bound photooxidation products.

Experimental Procedures

TiO$_2$ (Degussa P25; 25% rutile, 75% anatase), decane (99.9%, Aldrich), methanol (99.9%, Aldrich), methanol-d4 (CD$_3$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$_2$-cooled MCT detector. Spectra were collected at 8 cm^{-1} 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$_2$) 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.
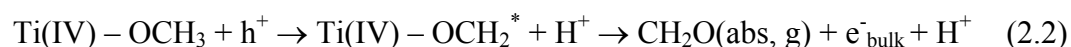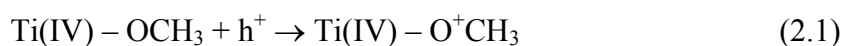
Results and Discussion

Hole and Electron Trapping on TiO$_2$ Surfaces

One of the primary results of our previous work[3] was an observed rise in the DRIFT spectrum baseline when TiO$_2$ 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^{-1}. While there was a period shortly after first inheriting the instrument where I could repeat this result, within several months I could not. One of the possible causes was thought to be loss of vacuum in the system. The previous work stated that IR-transparent lattice O-vacancies are responsible for removing photogenerated holes. If the sample compartment's vacuum was somehow not as good as it was previously, this could perhaps prevent removal of lattice oxygen. However, this did not seem likely, as the vacuum gauge did not register a significant loss of system vacuum. More plausibly, the inability to reproduce the result was not from a loss of vacuum condition, but rather due to an improvement in vacuum due to a decrease in oxygenated carbon impurities. It is believed that the impurities seen in the previous work (C–H bands found at 2927 and 2859 cm^{-1}), which were never fully explained, are indicative of surface-bound species responsible for the 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 as seen previously, but more importantly led to the expected baseline increase and Ti(III)–OH formation upon irradiation.

Figure 2.1 shows the DRIFT spectra for TiO_2 powder *in vacuo* under different treatments. In the untreated powder, bridging hydroxyl groups are seen at 3414 cm^{-1} and Ti(IV)–OH stretches are seen around 3645 cm^{-1}. There is also a broad adsorption between 3000 and 3600 cm^{-1} due to surface-bound water molecules. Upon heating to 200 $^{\circ}$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^{-1}. Upon irradiation, bridging hydroxyl groups are completely lost, the Ti(IV)–OH peak is reduced in intensity, and a new peak at 3714 cm^{-1} 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_2 surfaces,[6-8] thus the expected surface species in the case of methanol vapor would be Ti–OCH$_3$. This adsorbed species provides a viable hole trap, by either direction hole encapsulation or through a chemical reaction to form formate.

$$Ti(IV) - OCH_3 + h^+ \rightarrow Ti(IV) - O^+CH_3 \tag{2.1}$$

$$Ti(IV) - OCH_3 + h^+ \rightarrow Ti(IV) - OCH_2{}^* + H^+ \rightarrow CH_2O(abs, g) + e^-{}_{bulk} + H^+ \tag{2.2}$$

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 equation (2.2), the injection of an electron into the lattice would create a current-doubling effect, which is well known for the case of organic photooxidation by TiO_2.[9-12] Thus, some of the free electrons observed after photolysis may be a result of such an effect. The electron-generating reaction would

have to proceed under anoxic conditions, and would likely be initiated by the loss of a proton. Figure 2.2 shows the effect of sequential heat treatment (523 K) and UV treatment *in vacuo* on a TiO_2 surface that 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 equation (2.2).

When the system was under a constant 1.0 atm N_2 and the fresh TiO_2 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 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_2 or O_2) were taken. Given the well-known affinity for TiO_2 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_2 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_2 samples would continually turn orange from picking up these long-lived residual pesticide molecules. The problem of reproducing clean TiO_2 systems is not unique, as seen by the debate over the cause of UV-induced hydrophilicity on TiO_2 crystal surfaces, which has only recently been shown to be a result of removal of surface hydrocarbon contaminants.[13]

Given this new information, some of the previous conclusions need to be refined, especially in regards to post-irradiation baseline relaxation. As reported earlier, both thermal treatment at 423 K as well as exposure to 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 O_2, the resulting peak at 3714 cm^{-1} is much larger, as seen in figure 2.3. 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.

$$O_2 + e^-_{bulk} \rightarrow O_2^- \tag{2.3}$$

The relaxation from thermal treatment is due to injection of trapped holes back into 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 TiO_2 surfaces can contain alkoxides.[7]

$$Ti(IV) - O^+CH_3 + Ti(IV) - OH \rightarrow Ti(IV) - O - Ti(IV) + CH_3OH(g) + h^+ \tag{2.4}$$
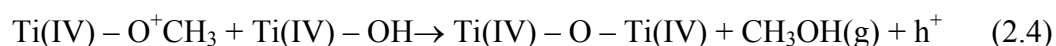
The injected holes can then recombine with bulk electrons, i.e., annihilation, but they can also combine with the trapped electrons in the form of Ti(III)–OH groups.

$$h^+ + Ti(III) - OH \rightarrow Ti(IV) - OH \tag{2.5}$$

Thus, since the O_2 treatment does not remove the surface methanol, there are both fewer holes injected into the lattice and more hole traps, leading to increased intensity of the Ti(III)–OH peak at 3714 cm^{-1}.

It was observed that the Ti(III)–OH groups could be removed by illumination under O_2, but only after being partially rehydrated under H_2O 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.

Decane Adsorption and Degradation on TiO$_2$ Surfaces

A potential practical application of TiO$_2$ is in the remediation of oil spills by coated glass beads.[15] In order to gain insight into alkane photocatalysis by 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 (~1 Torr at room temperature, ideal for dosing samples via the gas manifold).

Hydrocarbon oxidation on TiO$_2$ has been studied extensively. Several decades ago, Teichner 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 CO$_2$, and that steady-state product concentrations are reached within minutes.[16] More recently, Fujishima et al. have studied the photooxidation of long-chain organics on TiO$_2$ thin film, and observed that only CO$_2$ and H$_2$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$_2$ 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_2 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 physi-sorbed organics compared to the gas phase organics in Teichner's experimental setup, likely account for the inability of Fujishima et al. to detect any intermediates.
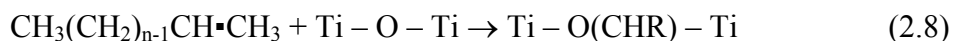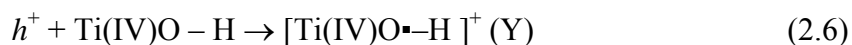
In the first set of experiments, decane vapor was introduced to TiO_2 surfaces that had been pretreated by UV irradiation *in vacuo*, and surface coverage was compared to the nonirradiated case. It was known at the time that UV treatment makes TiO_2 surfaces superhydrophilic, and we believed that the UV pretreatment would affect the ability for decane to absorb 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 2.4 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 the both the nonirradiated and irradiated surface during vacuum treatment, indicating that the decane was weakly bound, i.e., physically absorbed 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 superhydrophilic character and behaved similarly to the nontreated surface in regards to the amount of decane adsorbed on the surface.
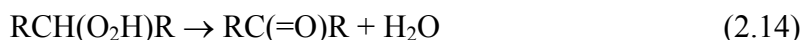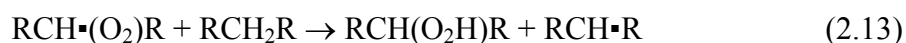
In the next series of experiments, the oxidation of decane on TiO_2 was studied. After dosing the sample with decane, the system was immediately exposed to 1 atm O_2, so as to prevent the decane from desorbing from the surface. The sample was then irradiated for 5-10 minute intervals, at which point the lamp was turned off and a spectrum was recorded. Total time spent undergoing irradiation was 1 hour. Figure 2.5 shows the resulting spectra over 2000 to 4000 cm^{-1}. As expected, both water (broad adsorption between 3000 and 3600 cm^{-1}) and CO_2 (2320 cm^{-1}) are produced, with a loss in hydrocarbon intensity (C–H stretches between 2800 and 3000 cm^{-1}). To further probe the reaction products, a series of difference spectra are used, as shown in figure 2.6. After one minute of irradiation, water (but not CO_2) is seen to form, and peaks are seen in the 1350 to 1750 cm^{-1} 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^{-1}, simultaneously accompanied by the formation of CO_2, 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 hydroxide 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_2.

$$h^+ + Ti(IV)O - H \rightarrow [Ti(IV)O\text{·}–H]^+ (Y) \qquad (2.6)$$

$$Y + CH_3(CH_2)_nCH_3 \rightarrow CH_3(CH_2)_{n-1}CH\text{·}CH_3 + Ti(IV) - OH_2^+ \qquad (2.7)$$

$$CH_3(CH_2)_{n-1}CH\text{·}CH_3 + Ti - O - Ti \rightarrow Ti - O(CHR) - Ti \qquad (2.8)$$

$$Ti(IV) - OCHR + h^+ + O_2 \rightarrow ketones + further\ products \qquad (2.9)$$

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

$$e\text{-} + O_{2,s} \rightarrow O_{2,s\text{-}} \qquad (2.10)$$

$$O_{2,s}\text{-} + RCH_2R \rightarrow RCH\text{·}R + HO_2^- \qquad (2.11)$$

$$RCH\text{·}R + O_2 \rightarrow RCH\text{·}(O_2)R \qquad (2.12)$$

$$RCH\text{·}(O_2)R + RCH_2R \rightarrow RCH(O_2H)R + RCH\text{·}R \qquad (2.13)$$

$$RCH(O_2H)R \rightarrow RC(=O)R + H_2O \qquad (2.14)$$

On the basis of the FTIR data alone, neither mechanism can be proved or disproved, although ketones are clearly an intermediate product. The spectra are especially complex between 1300 and 1700 cm^{-1}, likely due to peak overlap from ethers and ketones of various carbon chain lengths, making absolute product assignment impossible.

Methanol Adsorption and Degradation on TiO$_2$ Surfaces

Methanol was chosen as the next molecule to examine, due to the simplicity of possible photooxidation products (no long chain carbon products) as well as the ability for methanol to chemisorb to the TiO_2 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 2.7 shows the difference spectra before and after methanol and d4-methanol adsorption onto the TiO_2 sample. Both samples show a loss of Ti–OH groups, as methanol molecules can displace surface OH groups during chemisorption as seen below.
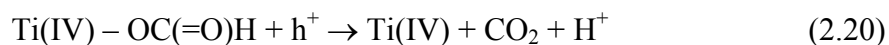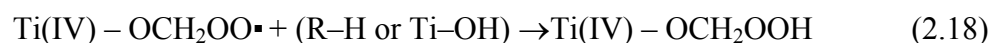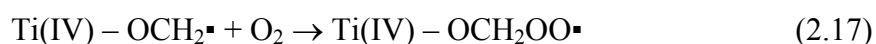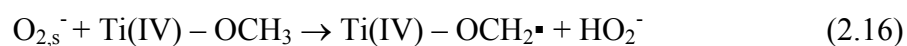
$$R – OH(g) + OH(ad) \rightarrow R – O(ad) + H_2O \text{ (g or ad)} \tag{2.15}$$
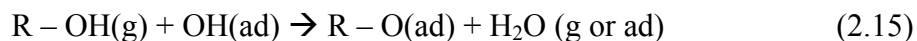
For d4-methanol, CD_3 stretches are seen at 2072 and 2226 cm^{-1}, and the methanol OD stretch is seen as a broad peak centered at 2470 cm^{-1}. An OD stretch corresponding to Ti–OD is also seen at 2716 cm^{-1}, indicating scrambling of surface OH groups with methanol.[3]

Figure 2.8 shows a series of difference spectra taken during the course of methanol oxidation under 1 atm O_2. Within the first 5 minutes, both water and CO_2 are seen to form. There is a decrease in CH_3 stretches at 2916 and 2816 cm^{-1}, and a new peak assigned to a CH_2 stretch at 2862 cm^{-1}. There are also 2 new peaks at 1583 and 1361 cm^{-1}, which are assigned to the asymmetrical and symmetrical stretching bands of carboxylate anion, respectively.[21] These products were also seen in the case of d4-methanol (figure 2.9). 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_2 surface, and the resulting DRIFT spectrum is shown in figure 2.10. 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_2. Upon evacuation, surface water and CO_2 are lost, but an

increase is seen in carboxylate, indicating that it is a surface-bound species that 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_2.

$$Ti(IV) - OCH_3 + h^+ \rightarrow Ti(IV) - OCH_2\cdot + H^+ \tag{2.15}$$

$$O_{2,s}^- + Ti(IV) - OCH_3 \rightarrow Ti(IV) - OCH_2\cdot + HO_2^- \tag{2.16}$$

$$Ti(IV) - OCH_2\cdot + O_2 \rightarrow Ti(IV) - OCH_2OO\cdot \tag{2.17}$$

$$Ti(IV) - OCH_2OO\cdot + (R-H \text{ or } Ti-OH) \rightarrow Ti(IV) - OCH_2OOH \tag{2.18}$$

$$Ti(IV) - OCH_2OOH \rightarrow Ti(IV) - OC(=O)H + H_2O \tag{2.19}$$

$$Ti(IV) - OC(=O)H + h^+ \rightarrow Ti(IV) + CO_2 + H^+ \tag{2.20}$$
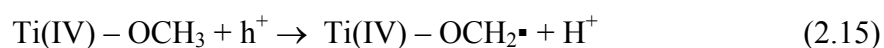
Conclusions

Only when TiO$_2$ is irradiated in the presence of a hole scavenger, even at minute contaminant levels, are electrons trapped at Ti(III)–OH sites, and are free electrons generated. Upon heating, the hole scavengers are desorbed, and reinjection of previously trapped holes, which are trapped in the lattice leads to a decrease in detectable Ti(III)–OH centers. The decane adsorption experiments lend support to the theory that removal of hydrocarbon contaminants is responsible for superhydrophilic TiO$_2$ surfaces. While oxidation of decane did not lead to any definitive product assignments, oxidiation of methanol led to identification of surface-bound formic acid.
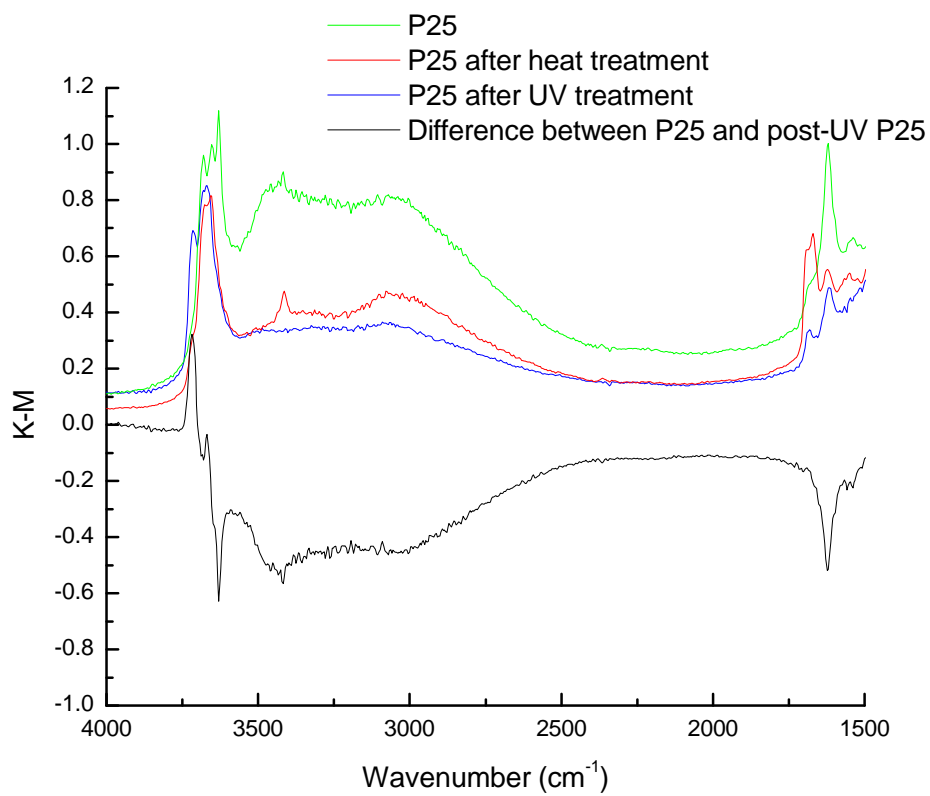
Figure 2.1. DRIFT spectra showing the effect of heating (to 200 °C) and UV irradiation on

P25 TiO$_2$ powder *in vacuo* in presence of hole scavenger contaminants.
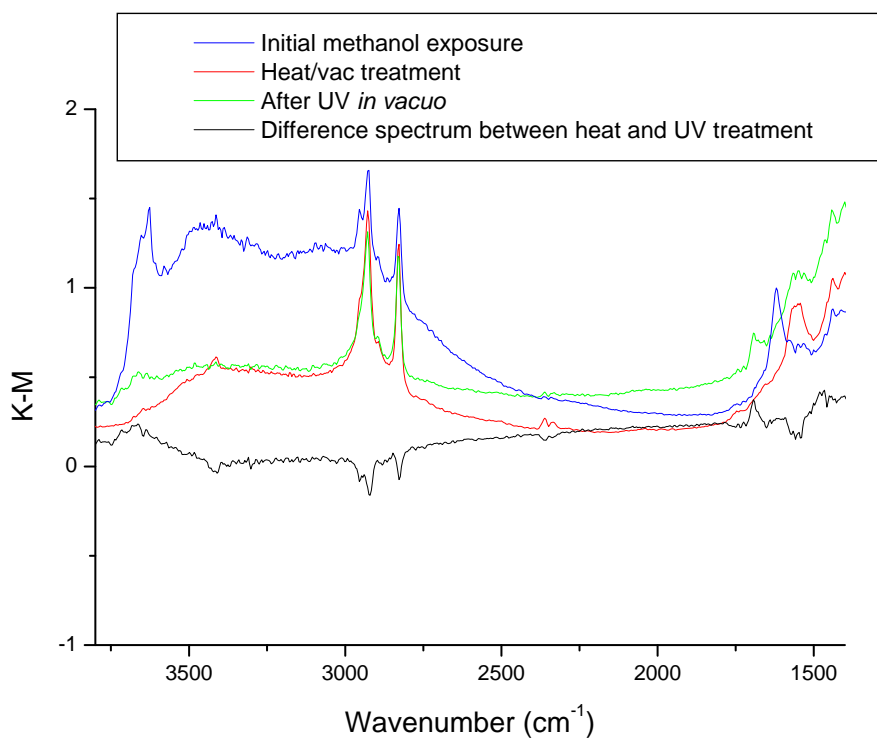
Figure 2.2. DRIFT spectra of TiO_2 powder heated and irradiated *in vacuo* after absorbing methanol vapor, and the difference spectrum showing the effect of irradiation on the surface that had already undergone heat treatment.
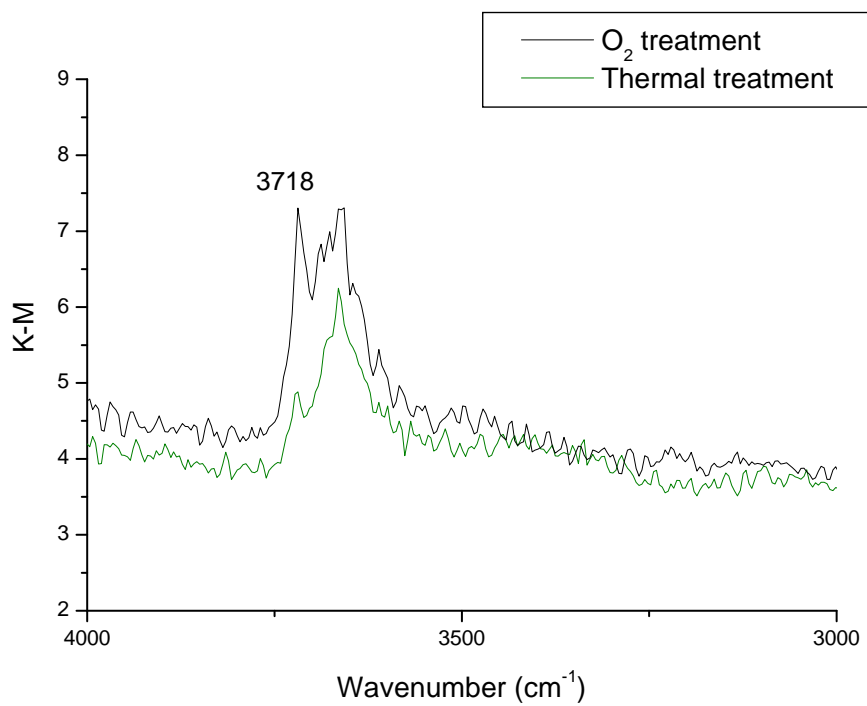
Figure 2.3. DRIFT spectra of TiO_2 powder irradiated in the presence of methanol vapor, followed by either thermal or O_2 treatment.
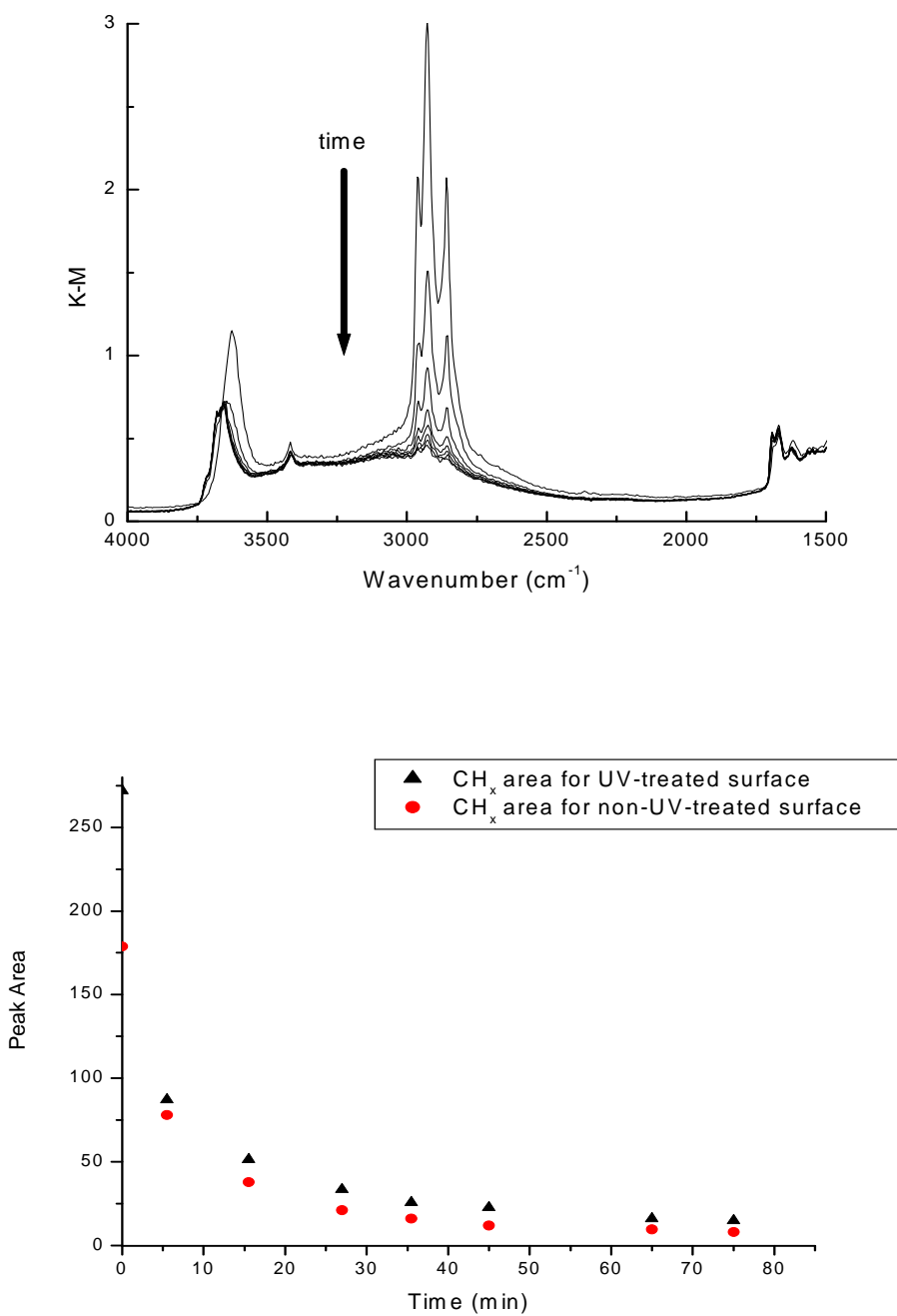
Figure 2.4. Typical time series of decane desorption on TiO_2 *in vacuo* (top), and hydrocarbon peak intensity of decane absorbed to UV- vs. non-UV-treated TiO_2 (bottom).
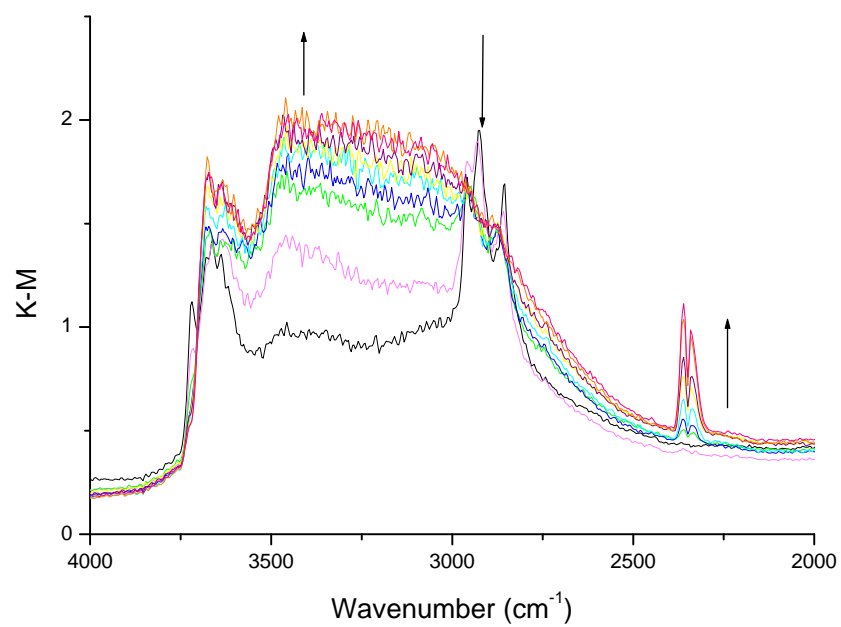
Figure 2.5. DRIFT spectra taken during the course of 1 hour UV oxidation of decane on TiO$_2$ under 1 atm O$_2$.   Arrows indicate increase in surface-bound water and CO$_2$ vapor, and decrease in hydrocarbon intensity.
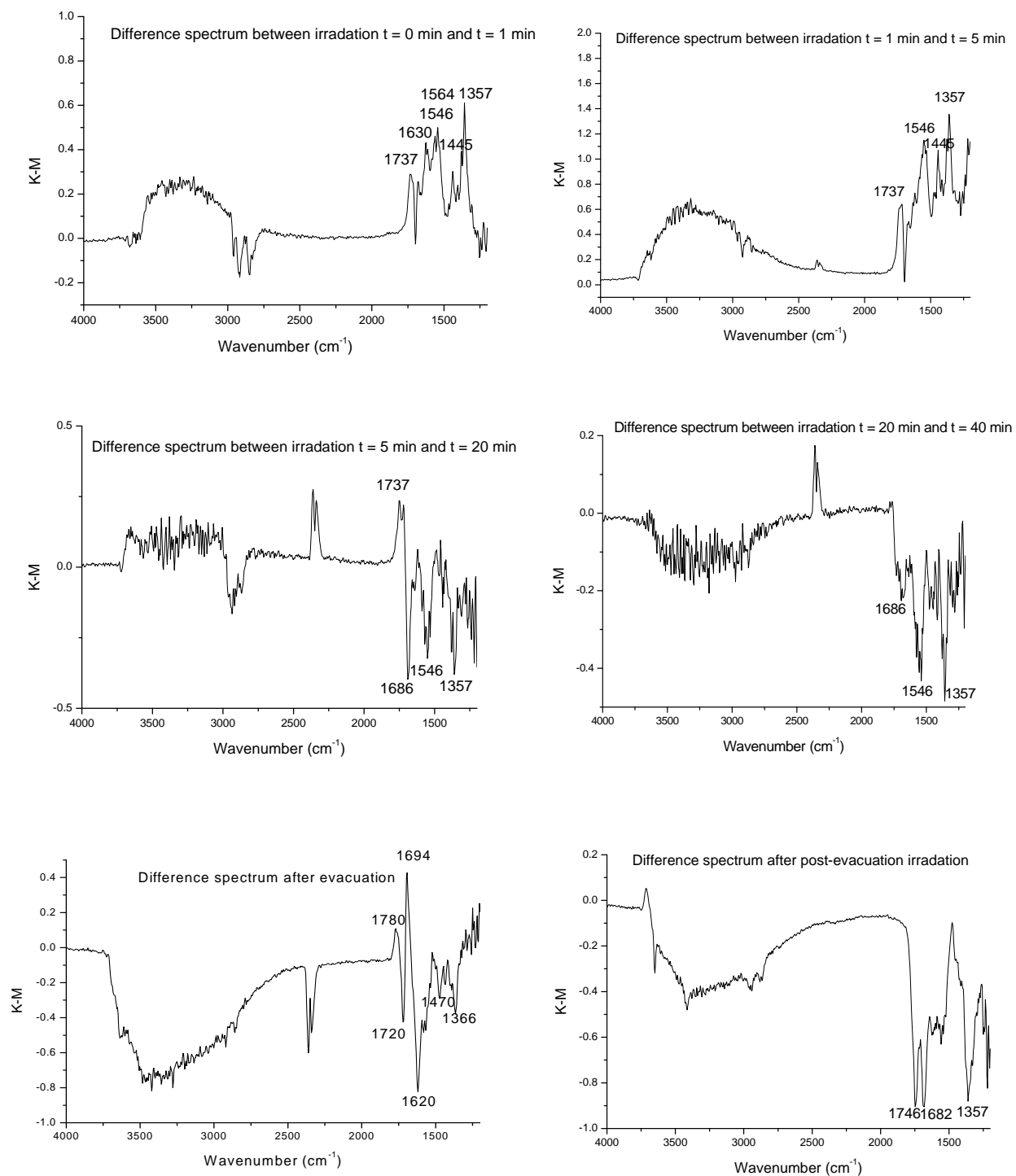
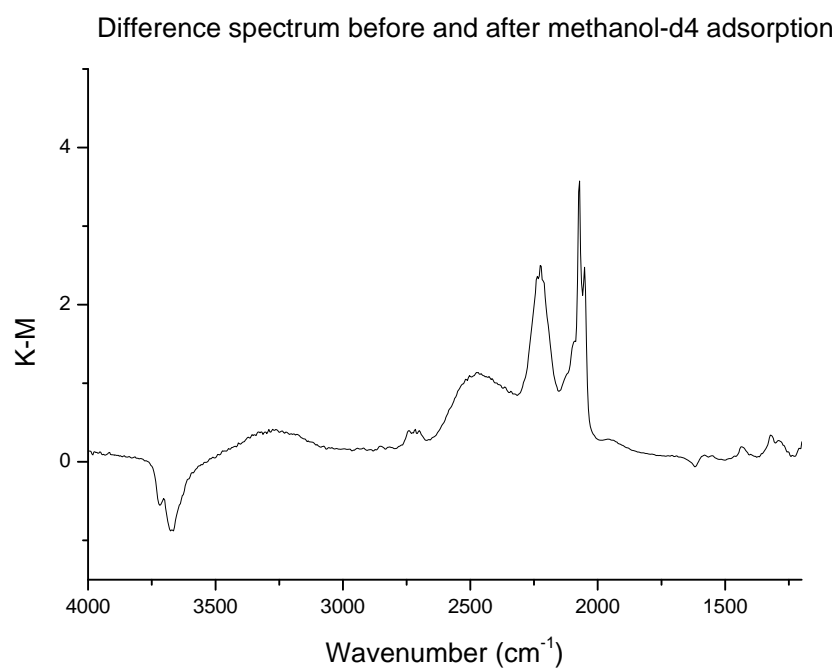**Figure 2.6**. Time series DRIFT difference spectra following course of decane oxidation.

Difference spectrum before and after methanol absorption

Difference spectrum before and after methanol-d4 adsorption
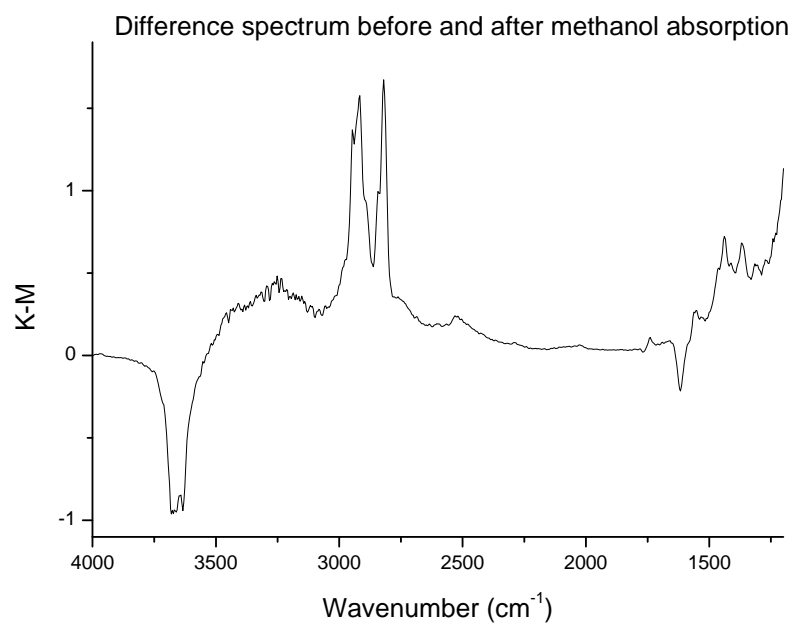

Figure 2.7. DRIFT spectra showing surface coverage of methanol and methanol-d4.
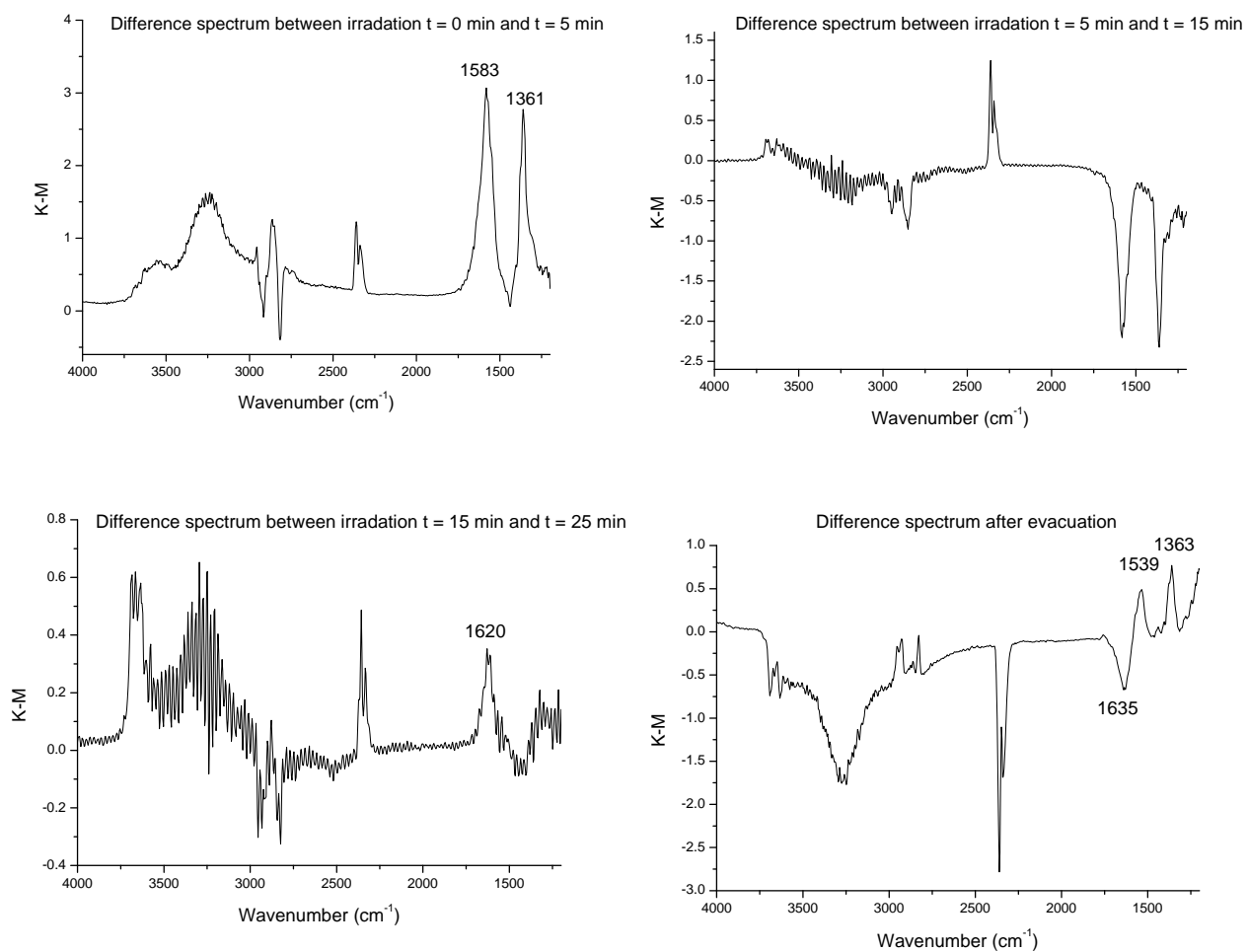
Figure 2.8. Time series DRIFT difference spectra following course of methanol oxidation.
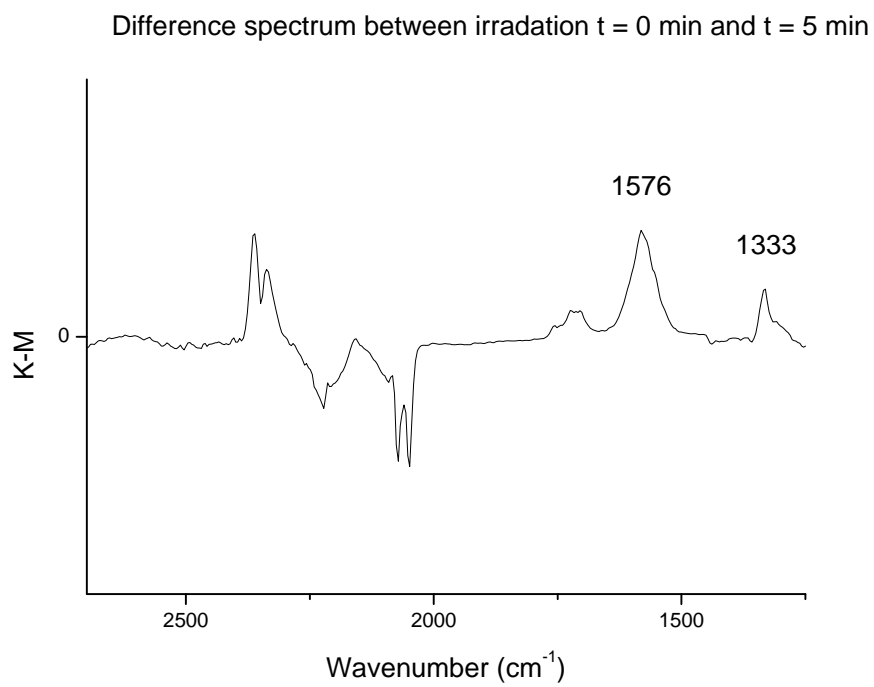
Difference spectrum between irradation t = 0 min and t = 5 min

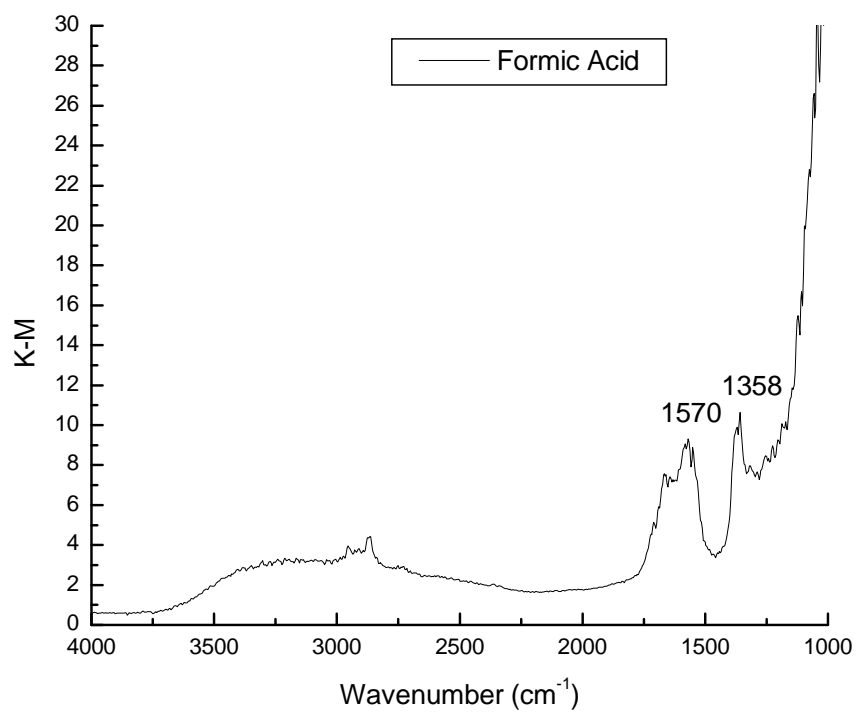**Figure 2.9**. Initial products of d4-methanol oxidation.

Figure 2.10. Formic acid absorbed on TiO_2.

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