Titanium nanoparticles surface-functionalized with sulfate were prepared by thermal degradation of titanyl sulfate. At 600°C pure anatase phase is obtained. X-ray photoelectron spectroscopy (XPS) showed 1.4 at.% sulfur in the +6 oxidation state. At 700°C anatase was still present, which is attributed to the presence of small amounts of stabilizing sulfate groups only detectable by high-resolution XPS, segregating to the nanoparticle interfaces. Adsorption and photocatalytic degradation of acetaldehyde reactions were studied by in situ diffuse reflectance Fourier transform spectroscopy and 2D correlation spectroscopy, and compared with pure anatase nanoparticles. Aldol condensation of acetaldehyde and subsequent accumulation of crotonaldehyde was lower on sulfate-modified titania. Butanoate was identified as an intermediate, which forms after dimerization and aldol condensation. Much more carboxylates and carbonates accumulated on pure anatase catalysts compared with sulfate-modified anatase during photocatalysis. It is conjectured that surface acidic photocatalysts could be beneficial for achieving sustained activity for photodegradation of organic pollutants.

Introduction

Titanium dioxide (TiO$_2$, titania) is one of the most commonly used photocatalytic semiconductor materials. Early reports of the photocatalytic properties of TiO$_2$ and its ability to oxidize organic molecules under UV illumination were published already in the 1950s.$^{[1]}$ Since then TiO$_2$ has been extensively investigated as an abundant and environmentally benign photocatalyst for both water remediation$^{[2–5]}$ and removal of air pollutants.$^{[6]}$ The basic mechanism of TiO$_2$ photocatalysis for organic photo-degradation is fairly well-established. UV illumination of TiO$_2$ results in interband absorption and electron-hole pair formation. The photoexcited electrons can reduce O$_2$ to O$_2^-$ radicals, and the holes can oxidize water or surface hydroxyls to OH$^+$ radicals. The hydroxyl radical is a stronger oxidizer than the superoxide radical. These two reactive oxygen species (and derivatives of them) are extremely powerful oxidizing agents (energy in excess of 290 kJ mol$^{-1}$), and capable of completely mineralizing organic to CO$_2$, H$_2$O, and possibly (if N, S, or P elements are present), trace amounts of mineral acids, which is makes TiO$_2$ a very attractive photocatalyst for environmental remediation applications.$^{[7–9]}$ Titania has also found application in self-cleaning coatings, utilizing its super-wetting properties, complementing the photocatalytic oxidation activity.$^{[10,11]}$ that efficiently removes pollutants from e.g. glass surfaces by film flow and prevent fogging.

Sulfur dioxide (SO$_2$) is present in the atmosphere, in part originating from combustion of fossil fuels. The interaction between SO$_2$ adsorbate and different metal oxide nanoparticles have been studied in the past. For example, the adsorption of SO$_2$ on $\alpha$-Fe$_2$O$_3$ and $\alpha$-FeOOH in presence of oxygen, and its reactivity towards surface OH groups, was shown to result in formation of sulfite and sulfate.$^{[12]}$ Similarly, SO$_2$ adsorption on TiO$_2$ was shown to yield adsorbed sulfite and bisulfite.$^{[13]}$ Wu and co-workers$^{[14]}$ investigated the oxidation of SO$_2$ on MnO$_2$ surfaces. Significant SO$_2$ adsorption was only observed together with water vapor, and based on $^{18}$OH$_2$ labeling, they concluded that adsorbed SO$_2$ reacted with surface OH groups originating from dissociated water, which eventually led to formation of surface associated sulfate groups. The reactivity of surface OH groups towards solvated SO$_2$ to form sulfate species has also been demonstrated on TiO$_2$ and $\alpha$-Fe$_3$O$_4$.$^{[15,16]}$ While reactions of SO$_2$ with metal oxide surfaces may reduce SO$_2$ emissions, surface modification with sulfate groups can also be employed to modify the (photo)catalytic performance and wetting properties of metal oxides by altering their acid/base surface properties.$^{[17–19]}$ It has previously been demonstrated that surface-modification of titania with sulfate increases the surface acidity which makes the surface oleophobic.$^{[20]}$ Topalian and co-workers$^{[21]}$ developed a method to thermally enhance photo-

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adsorption of \( \text{SO}_2 \) on \( \text{TiO}_2 \) to yield surface-bonded sulfate that is formed via a sulfite intermediate promoted by bonding to a reduced surface Ti atom.\(^{[22]}\)

Although the complete mineralization of organics by photocatalysis is theoretically possible, this is not always the case. Instead, accumulation of degradation products that bind strongly to the catalyst surface can lead to site inhibition (i.e., surface poisoning), and significantly reduce the catalyst activity. This is particularly important in low temperature heterogeneous catalysis, such as typical photocatalytic applications. Hence, modification of the catalyst surface chemical properties to avoid catalyst deactivation is of great interest. Studies of sulfated titania as photocatalyst for degradation of gas-phase acetaldehyde demonstrated less build-up of degradation products on the surface, attributed to an increased surface acidity as compared to non-modified titania.\(^{[20]}\) In this work we have prepared and characterized titania nanoparticles surface-modified with sulfate by means of a simple thermolysis reaction, where titanyl sulfate was employed as a “single-source precursor.” The adsorption of acetaldehyde, a common indoor air contaminant, and its photodegradation on titania under UV illumination, with and without sulfate-modification, were studied by means of in situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) and 2D correlation spectroscopy.

**Results and Discussion**

**Materials properties**

Titanyl sulfate powders were annealed at different temperatures and PXRD patterns were recorded (Figure 1). PXRD of \( \text{TiOSO}_4 \) annealed at 500°C showed amorphous samples, while samples annealed at 550°C were transformed into anatase phase with some minor impurities, which is attributed to titanium (oxo-) sulfates. At 600°C pure anatase structure was obtained, and the crystallinity increased after the 650°C and 700°C annealing treatments, apparent from the PXRD data. However, there were no indications of rutile phase formation. Scherrer analysis (see Experimental section, eqn. 1) was used to estimate the average crystallite sizes (Table 1). The small decrease in average crystallite size for Ti-600 compared to Ti-550 can be explained by removal of the remaining titanium (oxo-) sulfate phases with a subsequent densification of the pure anatase structure.

Micro-strain analysis was performed by the Williamson-Hall method (See Experimental section, Eqn. 2). Figure 2 shows a build-up of strain up to 600°C, followed by relaxation at higher annealing temperatures coinciding with crystallization of the particles and segregation and loss of sulfate as deduced by EDS analysis shown below. The crystallite size obtained from Williamson-Hall micro-strain analysis (eqn. 2) agrees well with result from the Scherrer analysis (eqn. 1).

SEM micrographs (Figure 3) shows a nanoporous sample and a topotactic transformation of the rod-shaped \( \text{TiOSO}_4 \) into aggregates of anatase nanoparticles. There was no apparent change in the macroscopic morphology between the reference \( \text{TiOSO}_4 \) and the sample annealed at 700°C. Elemental EDS analysis revealed a homogenous distribution of sulfur in the Ti-500 to Ti-650 samples, which diminished in intensity with increasing annealing temperature and was below the limit of detection for EDS for the sample annealed at 700°C (Figure S2 and S3).

The BET surface areas were determined to be about 96 m\(^2\)/g and 51 m\(^2\)/g for Ti-600 and Ti-700, respectively, confirming the nanoporous morphology inferred from SEM. In comparison, pristine Hombikat UV100 has a reported surface area of about 330 m\(^2\)/g.\(^{[23,24]}\)

![Figure 1. Powder X-ray diffractograms of Ti-500, Ti-550, Ti-600, Ti-650, and Ti-700. Characteristic anatase diffraction peaks are labeled with an asterisk (JCPDS Card no. 00-021-1272).](image)

![Figure 2. The dependence of the annealing temperature on the micro-strain, \( \varepsilon \).](image)

| Sample  | Average crystallite size | Standard deviation |
|---------|--------------------------|-------------------|
| Ti-700  | 29.9                     | 3.7               |
| Ti-650  | 22.8                     | 3.7               |
| Ti-600  | 14.6                     | 1.5               |
| Ti-550  | 15.4                     | 2.1               |

Table 1. Average anatase crystallite sizes in nanometer after different annealing temperatures indicated by the sample names.
Samples Ti-600 and Ti-700 were further characterized by TEM. From the high-resolution TEM micrographs in Figure 4a and d it is apparent that the rod-like structures consist of well-crystallized primary anatase nanoparticles. The sizes of the primary particles are in good agreement with those calculated from the diffraction data (Table 1). TEM-EDS mapping of Ti-600 and Ti-700 are presented in the Supplementary information, Figure S4 through S6, and show a homogeneous elemental distribution and a decreasing sulfur concentration as a function of annealing temperature. Both Ti-600 and Ti-700 samples exhibit fairly high surface areas considering the high annealing temperature.

To gain insight of the oxidation state of the surface sulfur, high-resolution S 2p X-ray photoelectron spectroscopy (XPS) analysis was employed. Figure 5 shows survey and high-resolution spectra of reference TiOSO₄, Ti-600, and Ti-700 samples. The survey spectra indicated a decreased amount of sulfur in Ti-600 compared to TiOSO₄ in agreement with the EDS analyses in Figure S6. The S 2p/Ti 2p at.% ratio for Ti-600 was calculated to be ca. 0.06 (~1.4 at.% sulfur), while the S/Ti atom ratio from EDS was about 0.02, suggesting higher concentration of sulfur near the surface compared to the bulk, and surface segregation of sulfur species upon annealing.

This is qualitatively corroborated by a theoretical study of sulfur(VI) (i.e. sulfate) doping of anatase, which showed that bulk doping was energetically very unfavorable. Thus, during transformation of titanyl sulfate into crystalline titania, sulfate accumulates on the surface as the total titania surface area decreases with increasing annealing temperature. Surface accumulation of both ligands and dopant atoms during transformation from molecular titanium precursors into titania have previously been observed experimentally. Also, for Ti-700 two very weak signals could be distinguished at 170.27 eV and 176.17 eV in the XPS spectra of Ti-700, which are attributed to the presence of sulfur(VI) species on the surface. These results are consistent with the decreasing sulfur concentration observed in the EDS analyses.

Figure 3. SEM micrographs of Ti-600 (a, c) and Ti-700 (b, d) displaying rod-shaped aggregates of titania. Scale bars represent 20 μm.

Figure 4. Bright-field TEM micrographs of Ti-600 (a, b, and e) and Ti-700 (c, d, and f). Panels a, b, c, and d shows how the rod-like structures are built up of smaller particles and the high-resolution micrographs (panels e and f) reveal highly crystalline primary particles.

Figure 5. XPS survey spectra of (a) TiOSO₄, (c) Ti-600, and (e) Ti-700. Emission lines due to Ti, S, O, and C are indicated. High-resolution S 2p XPS spectra of (b) TiOSO₄, (d) Ti-600, and (f) Ti-700. Gauss-Lorentz deconvoluted S 2pₓₒ and S 2pₓᵧ peaks are displayed.
169.17 eV, respectively, in the S 2p high-resolution XPS spectrum, that can be assigned to the S 2p$_{1/2}$ and S 2p$_{3/2}$ core-levels (Figure 5f). The S 2p$_{1/2}$ and S 2p$_{3/2}$ positions for all three samples are listed in Table 2, along with the relative S concentration. The residual amounts of surface-bond sulfate presumably contribute to the observed stability of anatase at 700 °C, since the anatase-to-rutile transformation is known to be initiated from the particle surface.[26,29]

Adsorption of acetaldehyde

The surface interaction with acetaldehyde was studied for sulfate-modified anatase (Ti-600 and Ti-700) and commercial pure, sulfate-free anatase (UV100) using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Acetaldehyde is known to spontaneously condense on titania to form crotonaldehyde.[30–32] Dimerization, whereby gas-phase acetaldehyde is directly adsorbed on an adsorbed acetaldehyde molecule is reported to precede crotonaldehyde formation on anatase TiO$_2$.[33] Previous studies have shown that there exists a dose and temperature dependence of acetaldehyde adsorption and aldol condensation on TiO$_2$.[31,32]

Similarly, it has been shown that there is a heterogeneity of products depending on oxidation state of TiO$_2$, and also oxidation to acetate species has been reported.[31,34] Crotonaldehyde (2-butenal) and 2-butenol aldol condensation products were observed on oxidized TiO$_2$ surfaces, whereas 2-butene due to reductive coupling was found on reduced TiO$_2$.[36] The surface interactions between acetaldehyde and sulfate-modified titania samples prepared by SO$_2$ photo-adsorption methods have been studied before by FTIR spectroscopy.[20,33] The acetaldehyde condensation reaction was reported to be significantly suppressed on titania functionalized with surface sulfate.[20]

Figure 6 shows DRIFTS spectra obtained following acetaldehyde adsorption and subsequent UV illumination on the sulfate-modified samples (Ti-600 and Ti-700) compared with the pure Hombikat UV100 titania anatase sample. The interpretation of the IR spectra is based on previous assignments,[26,28–30] and 2D correlation spectroscopy (2D COS) analysis (see Supplementary Information).[35,36] On the pure UV100 sample a broad carbonyl ν(C=O) absorption band centered at 1645 cm$^{-1}$ dominates the DRIFT spectra (Figure 6a). This broad band contains overlapping bands due to acetaldehyde dimers at about 1642 cm$^{-1}$ and crotonaldehyde at about 1652 cm$^{-1}$, which is evident from the time-evolution of the band, and which is further quantified by 2D COS (Figure S7). Similar to previous reports,[38] the dimer ν(C=O) band gradually feeds into the crotonaldehyde ν(C=O) band as a function of dosing time. The band appearing at about 1571 cm$^{-1}$ and the bands around 1489 cm$^{-1}$, 1459 cm$^{-1}$, and 1377 cm$^{-1}$ grow synchronously, and also correlate positively with the growth of the 1653 cm$^{-1}$ ν(C=O) crotonaldehyde band (Figure S7). 2D COS shows that this transformation occurs simultaneously as the water concentration increases on the surface, and precedes crotonaldehyde formation. Since the reaction occurs in oxidizing conditions in synthetic air with water supplied from the aldol condensation reaction, it is reasonable to assume that both 2-butenal,[30] and butanoate[37] form. In particular, butanoate with expected characteristic ν$_s$(OCO) vibration in the ~1550 cm$^{-1}$ region and associated ν$_s$(OCO) vibration in the ~1400 cm$^{-1}$ region agree with the kinetics of the observed bands and 2D COS analysis (Figure S7).[37] The synchronous correlation spectrum for acetaldehyde adsorption on UV100 indicate strong positive correlation for crotonaldehyde (1645 cm$^{-1}$) and butanoate (1571 cm$^{-1}$), which is also apparent in the 1D spectrum (Figure 6a). Significant amounts of oxidation surface products (acetate and formate) are not observed, as evidenced by the decrease of the 1571 cm$^{-1}$, 1459 cm$^{-1}$, and 1377 cm$^{-1}$ bands upon purging in synthetic air (bottom spectrum in Figure 6b).

We note that the appearance of bands in the ~1570 cm$^{-1}$ and ~1400 cm$^{-1}$ region upon acetaldehyde adsorption on anatase TiO$_2$ also is evident in previous studies.[26,24,12–24,37]

| Table 2. Peak positions (eV) of S 2p$_{1/2}$ and S 2p$_{3/2}$     |
|-------------|-------|-------|-------|
| Sample      | S 2p$_{1/2}$ | S 2p$_{3/2}$ | S 2p/Ti 2s at.% ratio |
| TiOSO$_4$   | 170.30 | 169.10 | 1.31 |
| Ti-600      | 170.14 | 168.64 | 0.06 |
| Ti-700      | 170.27 | 169.17 | ~0[34] |

[a] Sulfur was below the limit of detection for the elemental XPS survey scan.
although not as pronounced as in the present study, but not consistently attributed to butanoate, which we here identify as intermediate reaction product during adsorption. We conjecture that in many, if not all of those quoted studies, butanoate intermediates form.

Despite its substantially lower sulfur content, the DRIFT spectra in Figure 6c after acetaldehyde adsorption of Ti-700 closely resembles those of Ti-600 shown in Figure 6e; much more than those acquired on Hombikat UV100 in Figure 6a. However, substantially larger amounts of oxidation products (butanoate at about 1570 cm\(^{-1}\) and carboxylate species in the 1560 to 1590 cm\(^{-1}\) region) are apparent on Ti-700 than Ti-600. From Figure 6c and 6e, it is clear that aldol condensation is suppressed on Ti-600 and Ti-700. This is evident from the \(\nu(C=O)\) bands at about 1676 cm\(^{-1}\) and 1693 cm\(^{-1}\), and can be attributed to the interaction of acetaldehyde with surface sulfate species on Ti-600 and Ti-700. The 1693 cm\(^{-1}\) and 1676 cm\(^{-1}\) bands can be assigned to the coordination of the carbonyl carbon to a Ti\(^{4+}\) center and an oxygen vacancy, respectively. Assuming an electron mean free path for the photo-electrons that only collects electrons from the two topmost lattice spacing, an average surface density of Ti surface atoms of 5.14 \(\times 10^{14}\) atoms m\(^{-2}\) (defined to be 1 monolayer (ML)) and a bidentate configuration of surface SO\(^{2-}\), where 1 sulfate group occupies two Ti sites, it is estimated that a close-packed sulfate layer (i.e. 0.5 ML) corresponds to 5.9 at.% sulfur in XPS. Here, Ti-600 is measured to have 1.4 at.% sulfur content, which would correspond to about 1/8 monolayer. Hence, we conclude that there are free Ti sites available for acetaldehyde coordination.

The negative peak seen for Ti-600 and Ti-700 at \(~1360\) cm\(^{-1}\) is assigned to breakage of the S=O double bond when acetaldehyde coordinate to the surface sulfate.\(^{[20,21,38]}\) The small bands at \(~1271\) cm\(^{-1}\) and 1248 cm\(^{-1}\) remains rather constant under dosing and UV illumination and is attributed to the presence of surface-sulfate groups that interacts with adsorbed molecules.\(^{[22]}\) Further, the DRIFT spectra show that decomposition products form on Ti-700, and to a less extent on Ti-600. The broad feature centered at 1585 cm\(^{-1}\) that increases over time is attributed to the \(\nu_{as}(CO)\) mode due to acetate and formate species. It should be mentioned that organic carbonyls are well-known to form diolates by reaction with surface-adsorbed oxygen, with subsequent ejection of organic radicals.\(^{[39]}\) Acetaldehyde has been reported to adsorb on rutile TiO\(_2\) (110) and form an acetaldehyde-oxygen complex, which under UV-illumination transforms into surface-coordinated formate and a gaseous methyl (CH\(_3\)) radical,\(^{[40,41]}\) and further into carbonate species.\(^{[42]}\) However, in the present work we focus on the surface-coordinated reaction products. Formation of acetate is also indicated by the minor \(\nu(C=O)\) (OCO) band at about 1444 cm\(^{-1}\). The collected results for a partly sulfate covered titania surface suggest that the sulfate species have two functions that suppress aldol condensation: (i) They occupy Ti\(^{4+}\) sites and thereby suppress adsorption of acetaldehyde that expose a reactive C atom that otherwise promote dimer and crotonaldehyde formation,\(^{[31]}\) and (ii) the acidic sulfate group attacks the C=O bond which leads to either oxidative decom-

position to acetate and formate, or intermediate formation of e.g. butoxide. In contrast, the chemistry of the free Ti\(^{4+}\) sites are largely unaffected by the sulfate groups, and are responsible for the carboxylate and carbonate formation. Scheme 1 illustrates the different adsorption configurations and observed vibrational frequencies of major DRIFTS bands shown in Figure 6. Table 3 compiles the vibrational frequencies and associated mode assignments.

Summarizing the 2D COS analysis (Supplementary information section S4), the following reaction sequence is concluded for acetaldehyde adsorption on pure anatase TiO\(_2\) (UV100 nanoparticles):

![Scheme 1. Different coordination modes of acetaldehyde and its reaction products: (i) Acetaldehyde coordinating via the carbonyl group, (ii) acetaldehyde adsorbing via an oxygen vacancy, (iii) coordinated acetaldehyde interacts with a surface bond sulfate, (iv) the acetaldehyde dimer, (v) crotonaldehyde, and (vi) possible butanoate coordination. Approximate \(\nu(C=O)\) or \(\delta(C=O)\) vibrational frequencies are displayed under each structure. Coordination modes and adsorption frequencies for (i) through (v) are from Topalian et al.\(^{[20]}\) The small (iii) 1562 cm\(^{-1}\) and (v) 1652 cm\(^{-1}\) are attributed to the interaction of acetaldehyde with surface bond sulfate.](image)

| Frequency (cm\(^{-1}\)) | Mode Assignment | Molecule |
|------------------------|----------------|----------|
| 1693                   | \(\nu(C=O)\)-Ti\(^{4+}\) | Acetaldehyde |
| 1676                   | \(\nu(C=O)\)-\(\nu_{as}(O)\) | Acetaldehyde\(^{[20]}\) |
| 1684                   | \(\nu(C=O)\)-\(\delta_{as}(O)\) | Acetaldehyde\(^{[20]}\) |
| 1130                   | \(\nu(C=O)\) | Acetaldehyde |
| 1643                   | \(\nu(C=O)\) | Acetaldehyde dimer |
| 1168                   | \(\nu(C=O)\) | Acetaldehyde + Crotonaldehyde |
| 1562                   | \(\nu(C=O)\) | Crotonaldehyde |
| 1628                   | \(\nu(C=O)\) | Crotonaldehyde |
| 1570                   | \(\nu(O=C-O)\) | Butanoate |
| 1714                   | \(\nu(C=O)\) | Surface coordinated carbonate |
| 1580                   | \(\nu(O=C-O)\) | Formate/Acetate |
| 1550                   | \(\nu(O=C-O)\) | Formate |
| 1376                   | \(\delta(C=H)\) | Formate |
| 1355                   | \(\nu(O=C-O)\) | Formate |
| 1490                   | \(\nu(C=O)\) | Bicarbonate |
| 1480                   | \(\nu(C=O)\) | Bicarbonate |
| 1440                   | \(\nu(O=C-O)\) | Carbonate |
| 1440                   | \(\nu(O=O)\) | Acetate |

[a] Acetaldehyde coordination to an oxygen vacancy. [b] Acetaldehyde interacting with surface sulfate.
acetaldehyde (gas) → acetaldehyde dimer (ads) → crotonaldehyde (ads) → butanoate (ads).

On Ti-600, aldol condensation and hence butanoate formation is suppressed and the reaction pathway therefore proceeds as follows:

\[ \text{acetaldehyde (gas)} \rightarrow \text{acetaldehyde (ads)} + \text{dimer (ads)} \rightarrow \text{acetate}. \]

On Ti-600 aldol condensation and butanoate formation are suppressed. Instead, formation of an intermediate species, presumably acetate \((\sim 1444 \text{ cm}^{-1})\), is evident which is not detected on UV100. Adsorption on Ti-700 exhibits a mixture of pure anatase and Ti-600 adsorption characteristics, albeit more similar to Ti-600.

**Photo-degradation of acetaldehyde**

UV illumination of pure anatase TiO\(_2\) (UV100) results in decomposition of butanoate and crotonaldehyde and evolution of typical \(\nu(C=O)\), \(\nu(C=CH)\), and \(\nu(CH)\) bands due to acetate, formate, and \((bi)\)carbonates (top spectrum in Figure 6, and 2D COS in Figure S8). Similarly, UV illumination of Ti-600 and Ti-700 results in rapid disappearance of acetaldehyde bands, oxidation to formate species, and formation of water and carbonate species, as evidenced by the increase of the gradual increase of the 1550 cm\(^{-1}\) band due to \(\nu(C=O)\) in formate, the \(\nu(C=O)\) water band around 1630 cm\(^{-1}\) region (distorted due to interaction with sulfate species), and the bands at 1713 cm\(^{-1}\) and between 1440 and 1480 cm\(^{-1}\) due to \(\nu(C=O)\) and \(\nu(C=O)\) modes in carbonate ions (Figure 6d and f, and Figure S8). The collected analysis of 1D DRIFT spectra and 2D COS suggests the following reaction pathways. On pure anatase nanoparticles (UV100) we conclude that photo-oxidation of acetaldehyde occurs through the reactions:

\[
\text{crotonaldehyde} + \text{butanoate} \rightarrow \text{acetate} \rightarrow \text{formate} \rightarrow \text{bicarbonate} + \text{carbonate}
\]

On Ti-600 and Ti-700 the photooxidation reaction progress very similarly with the important exceptions that aldol condensation is initially suppressed and that less carbonates form, viz:

\[
\text{acetaldehyde} + \text{dimer} \rightarrow \text{acetate} \rightarrow \text{formate} \rightarrow \text{bicarbonate}.
\]

Clearly, the larger amount of C\(_4\) molecules on pure anatase (UV100) compared with Ti-600 and Ti-700 limits the overall degradation. Moreover, substantial amounts of carboxylate species accumulate on the pure anatase surface.

A variety of C\(_4\) molecules appear as a final product on pure anatase, including carbonates and surface coordinated carbonate species associated with the 1710 cm\(^{-1}\) \(\nu(C=O)\) band that do not form on Ti-600 (Figure S9).\(^{[42]}\) The presence of ketones here is ruled out since they are not final oxidation products and that the 1710 cm\(^{-1}\) band appears last in the 2D COS analysis (Figure S8). The vibrational band at 1489 cm\(^{-1}\) on pure anatase and the broad band at \(\sim 1480 \text{ cm}^{-1}\) on Ti-600 and Ti-700 is assigned to a surface bicarbonate, HCO\(_3^-\) species.\(^{[42]}\)

It appears from the DRIFTS spectra that substantially less intermediate photo-degradation products in the 1400–1600 cm\(^{-1}\) form on Ti-600 and Ti-700 compared with pure anatase (UV100) (Figure 7), after normalization for surface area. After 10 min UV illumination, there are about four times more degradation products on UV100 compared to Ti-600. On Ti-700, an apparent slight negative amount of degradation products is deduced from the spectral analysis. This is explained mainly by loss of acetates which formed during adsorption on Ti-700 to higher extent than on Ti-600 and UV100, which thus counteracts the absorbance-increase due to build-up of intermediates.

To get insight to reaction product formation rates kinetics, the concentration of carboxylate species was estimated by area integration of the 1500–1600 cm\(^{-1}\) region (from Figure 6a and 6c) during UV illumination (Figure 7). For UV100, an initial rapid increase of the concentration of carboxylate species is observed.

\[
\begin{align*}
\text{(a) Integrated absorbance for UV100 (1610–1535 cm}^{-1}\text{)} & \text{ during UV illumination. Black squares are experimental values and the blue line is first order fitting for } y = a(1 - e^{-bt}) \text{, where } a \text{ is the saturation absorbance, and } b \text{ is the rate constant. (b) Integrated absorbance for Ti-700 (1600–1514 cm}^{-1}\text{)} & \text{ during UV illumination. Red squares are the initial increase, followed by decrease (black squares) of absorbance. The blue line is first order fitting for } y = ae^{-bt} \text{ during the decay, where } a \text{ is the initial absorbance, and } b \text{ is the rate constant.}
\end{align*}
\]
in the 1610–1535 cm\(^{-1}\) region, which reached a plateau after about 5 minutes. The normalized reaction rate for carboxylate formation was calculated to 5.6 \(\times\) 10\(^{-6}\) min\(^{-1}\) g\(^{-1}\). An initial rapid increase in the 1600–1514 cm\(^{-1}\) region, although much smaller compared to UV100, was observed also for Ti-700. However, after about 3 minutes of UV illumination the integrated area started to decrease on Ti-700. The reaction rate for the decrease of the carboxylate concentration was calculated to \(-3.2 \times 10^{-7}\) min\(^{-1}\) g\(^{-1}\). In contrast, no major changes in the 1500–1600 cm\(^{-1}\) region was observed for Ti-600 during UV illumination, and the absorbance remained low in this region.

Decomposition of acetaldehyde proceeded very rapidly (millisecond time-scale) under UV illumination and the reaction rates for the parent molecule degradation could not be quantified by the experimental set-up employed in the present study. The reaction rate for bicarbonate formation during UV illumination was estimated for the 1489 cm\(^{-1}\) band for all three samples by integration of the 1460–1530 cm\(^{-1}\) region for UV100 and 1460–1510 cm\(^{-1}\) for Ti-600 and Ti-700. For the first 10 minutes of UV illumination, the carbonate build-up was well approximated by a linear increase. After subtraction of background and normalization for surface area, reaction rates were calculated to 1.7 \(\times\) 10\(^{-6}\) min\(^{-1}\) g\(^{-1}\), 2.4 \(\times\) 10\(^{-6}\) min\(^{-1}\) g\(^{-1}\), and 8.6 \(\times\) 10\(^{-6}\) min\(^{-1}\) g\(^{-1}\) for UV100, Ti-700, and Ti-600, respectively. Thus, bicarbonates build up approximately two orders of magnitude faster on UV100 compared to Ti-600 and Ti-700. Finally, to get an idea of total build-up of degradation products during photocatalysis, the 1400–1600 cm\(^{-1}\) region was integrated for all three samples after about 10 min of UV illumination. Normalized for surface area, the integrated absorbances were 2.6 \(\times\) 10\(^{-4}\) cm\(^{-1}\) m\(^{-2}\), \(-9.10^{-4}\) cm\(^{-1}\) m\(^{-2}\), and 9 \(\times\) 10\(^{-4}\) cm\(^{-1}\) m\(^{-2}\) for Ti-600, Ti-700, and UV100, respectively (The “build-up” for Ti-700 is negative due to the subtraction of the absorbances at the start of UV-illumination which contains species degraded during UV-illumination, thereby decreasing the total absorbance over time). This further supports that substantially less intermediates build up on the sulfated titania samples, being lowest on the Ti-600 sample containing highest amount of sulfate.

**Conclusion**

In this work we have demonstrated a simple and scalable method to produce sulfate-modified titania nanoparticles by employing titanyl sulfate as a “single-source precursor”. As the annealing temperature increases, sulfate accumulates on the titania surface and is gradually removed. Eventually, the nanoparticles progress towards essentially pure anatase phase. Thus, the sulfate coverage can be adjusted by using different annealing temperatures. It was demonstrated that even small amounts of surface-sulfate species can have substantial effect on the adsorption properties of acetaldehyde on the titania nanoparticles. The different reaction pathways for adsorption and photo-degradation on pure and sulfate-modified TiO\(_2\) was determined using in situ DRIFTS and 2D correlation spectroscopy analysis. The formation of butanoate as an oxidation product of crotonaldehyde on pure anatase TiO\(_2\) was established. Formation of aldol condensation products and butanoate was observed to be suppressed on sulfate-modified titania. Moreover, build-up of photo-oxidation products during UV illumination were considerably lower for Ti-600 as compared to pure anatase TiO\(_2\), which is attributed to the presence of surface sulfate groups on Ti-600, which both acts as Brønsted acid facilitating bond cleavage of reactive C bonds, and also block reactive surface sites, which otherwise are engaged in bonding of reaction products.

Notably, coordinated carbonates were not detected on sulfate-modified titania. Thus, titania surface-functionalized with coordinated sulfate groups may provide an economical and environmentally benign solution to increase catalyst life-time during gas-phase photocatalysis by means of suppressing accumulation of reaction products while still providing active sites for photo-oxidation. The acid properties of the sulfate-modified titania can also be used to tuned by adjusting the annealing temperature and provide means to prepare oleophilic nanoparticles.

**Experimental Section**

**Materials**

Titanyl sulfate hydrate (TiOSO\(_4\), nH\(_2\)O) was purchased from Sigma-Aldrich and used as received. About 0.5 grams of titanyl sulfate was placed in a ceramic crucible and annealed in air for two hours at 500 °C, 550 °C, 600 °C, 650 °C, or 700 °C employing a 1-hour heating ramp to reach the target temperature. The powder was evenly spread out to a few mm thickness. The samples were designated Ti-500, Ti-550, Ti-600, Ti-650, and Ti-700, respectively. Hombikat UV100 anatase titania (UV100, Sachtleben Chemie GmbH) was used as non-sulfated reference material. The UV100 particle size was measured to be about 8 nm from Scherrer analysis of XRD data, in good agreement with literature data. The choice of UV100 as a reference material is because of the similar particle size and anatase phase purity, as in the prepared Ti-series.

**Materials characterization**

Powder X-ray diffraction (PXRD) data for all samples were recorded using a Siemens D5000 powder X-ray diffractometer with Cu K\(_{\alpha}\) radiation (\(\lambda = 1.5418 \text{Å}\)). A step size of 0.02° and divergence- and anti-scattering slit width of 1° were used. Data treatment was performed in EVA version 11.0. The average crystallite sizes (D) of the different treatments were calculated using the Scherrer equation:

\[
D = \frac{K\lambda}{\beta_{\text{c}, \text{cost} \theta}}
\]  
(1)

Where K is the shape factor (0.9 for spherical particles which we use here as an approximation), \(\lambda\) is the wavelength of the X-rays, \(\beta_{\text{c}}\) is full width at half maximum (FWHM), calculated using the Origin 2019 software corrected for instrumental broadening, and \(\theta\) is the Bragg angle in radians. Correction for instrumental broadening was performed using a NIST 1976 Al\(_2\)O\(_3\) standard. The average crystallite sizes for the samples were calculated using all diffraction peaks of anatase between 20 angles 20° to 65°.
The micro-strain, ε, in the titania particles was estimated by the Williamson-Hall method:

\[ \beta_c \cos \theta = \varepsilon (4 \sin \theta) + \frac{K \lambda}{D} \]  

(2)

Here, \( \theta \) is the Bragg angle in radians, \( \beta_c \) is FWHM, \( \lambda \) is the wavelength of the X-rays, \( D \) is crystallite size, and \( K \) is the shape factor.[9] A plot of \( \beta_c \cos \theta \) against \( 4 \sin \theta \) yields \( \varepsilon \) as the slope of the straight line, and the intercept is inversely proportional to the particle size, \( K \lambda / D \) (Figure S1).

A Zeiss LEO 1550 scanning electron microscope (SEM) equipped with a field emission gun (operated between 5 and 8 keV) and an Oxford Aztec energy dispersive X-ray spectroscopy (EDS) system was used for imaging and elemental composition analysis. The sample powders were dispersed on carbon tape for analysis.

Detailed particle morphology and energy-dispersive X-ray spectroscopy (EDS) mapping was performed using field-emission transmission electron microscopy (FE-TEM, JEM-2100F, JEOL) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Quantera II Scanning XPS Microscope from Physical Electronics equipped with an Al K\( \alpha \) source. A low-energy flood-gun, set at 1.0 V and 20.0 \( \mu \)A, was employed for charge compensation. For the survey spectra, a pass energy of 224 eV and a resolution of 0.8 eV was used, and for the high-resolution spectra a pass energy of 55 eV and 0.1 eV resolution were employed. Sample powders were suspended in water and dropped on clean glass slides with subsequent evaporation of the solvent under a desktop lamp. The binding energy was calibrated against the C 1s line of adventitious carbon. Data was treated and analyzed using the CASA XPS software.[46] The spectra were smoothed using a Savitzky-Golay algorithm with a 9-point window. Specific surface areas of the samples were determined using a Micromeritics ASAP 2020 instrument employing BET analysis.

**Acetaldehyde adsorption and photo-induced degradation**

Acetaldehyde adsorption and catalytic surface reactions were measured by means of in situ diffuse reflectance Fourier transform spectroscopy (DRIFTS) employing a vacuum pumped Fourier transform infrared spectrometer (Vertex 80, Bruker Optics, Ettlingen, Germany) equipped with a custom modified HPHT reaction cell placed in a Praying Mantis DRIFTS accessory (Harrick Scientific Products, Inc. NY, USA) and a liquid nitrogen-cooled HgCdTe detector.[46] A 365 nm LED light source (Prizmatix Ltd., Holon, Israel) was used as UV source in the photocatalytic measurements. The catalytic surface was exposed to an irradiance of 22.8 mW cm\(^{-2}\) during UV illumination as measured by a thermopile detector (Ophir Photonics, Jerusalem, Israel).

All samples were pre-treated in 50 mL/min synthetic air flow at 400 °C for 25 min and subsequently cooled down to room temperature prior to experiments. In the experiments, 30 ppm acetaldehyde was dosed in synthetic air at 50 mL/min flow rate over the catalyst powders.

First, acetaldehyde was dosed over the surface for about 8 minutes, followed by a purging for about 10 minutes and then UV illumination for another 10 minutes. Repeated DRIFT spectra were recorded between 1000 cm\(^{-1}\) and 4000 cm\(^{-1}\) as a function of illumination time every 16 s with 4 cm\(^{-1}\) resolution and with each spectrum averaged over 30 scans. The IR spectra were manually baseline-corrected and smoothed employing a Savitzky-Golay algorithm with a 9-point window. The absorbance, A, was determined from the measured transmittance T, after appropriate baseline line corrections, from the relation A = \log(1/T) valid in low absorptive sample approximation. OPUS (version 7.5, Bruker Optics) was used for recording and processing of the DRIFT spectra. The 2Dshige software was used for 2D correlation spectroscopy analysis of the DRIFT spectra.[46]

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**Conflicts of interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Titania · sulfate · titanyl sulfate · photocatalysis · acetaldehyde

[1] M. C. Markham, J. Chem. Educ. 1955, 32, 540–543.
[2] M. Pérez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O’Shea, M. H. Entezari, D. D. Dionysiou, Appl. Catal. B 2012, 125, 331–349.
[3] Y. Lee, S. J. Park, J. Ind. Eng. Chem. 2013, 19, 1761–1769.
[4] R. Krakowiak, J. Musial, P. Bakun, M. Szychala, B. Czarzynska-Goslińska, D. T. Mlynarczyk, T. Kozcirowski, L. Sobotta, B. Stanisz, T. Gosliński, Appl. Sci. 2021, 11, 8674.
[5] K. Nakata, A. Fujishima, J. Photochem. Photobiol. C 2012, 13, 169–189.
[6] Z. Shayegan, C. S. Lee, F. Haghighat, Chem. Eng. J. 2018, 334, 2408–2439.
[7] R. Fagan, D. E. McCormack, D. Dionysiou, S. C. Pillai, Mater. Sci. Semicond. Process. 2016, 42, 2–14.
[8] W. Y. Teoh, J. A. Scott, R. Amal, J. Phys. Chem. Lett. 2012, 3, 629–639.
[9] T. Ochiai, A. Fujishima, J. Photochem. Photobiol. C 2012, 13, 247–262.
[10] S. Banerjee, D. D. Dionysiou, S. C. Pillai, Appl. Catal. B 2015, 176, 396–428.
[11] M. Takeuchi, K. Sakamoto, G. Martin, S. Coluccia, M. Anpo, J. Phys. Chem. B 2005, 109, 15422–15428.
[12] J. Bultrasaitis, D. M. Ciwertyn, V. H. Grassian, Phys. Chem. Chem. Phys. 2007, 9, 5542–5554.
[13] C. E. Nanayakkara, J Petitbonne, V. H. Grassian, Phys. Chem. Chem. Phys. 2012, 14, 6957–6966.
[14] H. D. Wu, W. M. Cai, M. C. Long, H. R. Wang, Z. P. Wang, C. Chen, H. F. Hu, X. J. Yu, Environ. Sci. Technol. 2016, 50, 5809–5816.
[15] C. E. Nanayakkara, W. A. Larish, V. H. Grassian, J. Phys. Chem. C. 2014, 718, 23011–23021.
