PAPER

Photo-catalytic oxidation of cyclohexane over TiO₂: a novel interpretation of temperature dependent performance[†]

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The rate of cyclohexane photo-catalytic oxidation to cyclohexanone over anatase TiO₂ was studied at temperatures between 23 and 60 °C by *in situ* ATR-FTIR spectroscopy, and the kinetic parameters were estimated using a microkinetic model. At low temperatures, surface cyclohexanone formation is limited by cyclohexane adsorption due to unfavorable desorption of H₂O, rather than previously proposed slow desorption of the product cyclohexanone. Up to 50 °C, the activation energy for photocatalytic cyclohexanone formation is zero, while carboxylates are formed with an activation energy of 18.4 ± 3.3 kJ mol⁻¹. Above 50 °C, significant (thermal) oxidation of cyclohexanone contributes to carboxylate formation. The irreversibly adsorbed carboxylates lead to deactivation of the catalyst, and are most likely the predominant cause of the non-Arrhenius behavior at relatively high reaction temperatures, rather than cyclohexane adsorption limitations. The results imply that elevating the reaction temperature of photocatalytic cyclohexane oxidation reduces selectivity, and is not a means to suppress catalyst deactivation.

Introduction

The photo-catalytic oxidation of cyclohexane to cyclohexanone over TiO_2 catalysts is a potential substitute for the commercially applied, but intrinsically inefficient cyclohexane oxidation process.¹ TiO_2 catalysts show a high selectivity towards the formation of cyclohexanone,² but are also known to suffer from deactivation due to formation of strongly adsorbed carboxylate species.^{3–5} Previously, we have analyzed the TiO_2 surface by *in situ* techniques, and we proposed that slow desorption of cyclohexanone induces the formation of these deactivating species at room temperature.⁶

Few studies have analyzed the effect of elevated temperature on the behavior of the photocatalyst, which might be a means to stimulate cyclohexanone desorption, and thus prevent extensive over-oxidation to carboxylates and the accompanying deactivation. Herrmann *et al.*^{7,8} concluded that the reaction was not limited by adsorption or desorption steps in the temperature interval of 23–55 °C, where the activation energy was estimated at 10.5 kJ mol⁻¹. Product desorption and reactant adsorption were proposed to be limiting reaction rates at lower (<23 °C) and higher temperatures (>55 °C), respectively. This kinetic study was based on the analysis of bulk concentrations only, not considering details of surface chemistry and catalyst deactivation.

In this work, a diamond ATR-FTIR cell was used to run photo-catalytic cyclohexane oxidation at different temperatures, and to evaluate if enhancing temperature is a means to prevent carboxylate accumulation and catalyst deactivation. Furthermore, the activation energy of cyclohexanone formation and the desorption energy of cyclohexanone from the anatase TiO_2 surface were evaluated on the basis of the data and a microkinetic model. This has led to a novel interpretation of the temperature dependent performance of TiO_2 in cyclohexane photo-oxidation, which will be extensively discussed.

Experimental methods

A Specac Golden Gate ATR accessory with a diamond internal reflection element (IRE) was coupled to a Thermo Nicolet 8700 spectrometer. The diamond IRE has a 2 × 2 mm surface and exhibits three internal infrared reflections. The top plate of the Golden Gate ATR accessory can be heated and the temperature in the cell was measured by a thermocouple. The home-made ATR cell has a diameter of 1.2 cm, a height of 1 cm, and is sealed by a quartz window on top, which allows for UV-illumination. An extra pyrex window was placed over the quartz window in order to cut off low wavelengths ($\lambda < 275$ nm), emitted by the UV source.²

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The photocatalyst used was Hombikat UV100 TiO₂ (Sachtleben) of 100% anatase crystallinity. After drying the TiO₂ catalyst for one hour at 120 °C, a suspension of 2.7 mg mL⁻¹ of TiO₂ in distilled water was prepared and sonicated for 30 min. The catalyst coating on the diamond ATR crystal was prepared by placing a 5 μ L droplet of the suspension on the crystal, followed by evacuation of the cell with an 82 mbar membrane pump, while slowly elevating the temperature to 40 °C. The same procedure was repeated two more times, until a coating of TiO₂ covering the complete surface of the crystal was obtained. The coating was dried and evacuated at 120 °C for 30 min and cooled down to the required temperature for the respective experiments. The experiments were run at 23, 30, 40, 50, 55 and 60 °C. After each experiment the catalyst was removed from the diamond crystal and a new TiO₂ coating was prepared. The photo-catalytic tests were performed with cyclohexane of 99.0% purity from Sigma Aldrich, dried over Molsieve (type 4A) overnight to remove traces of water. The cyclohexane was saturated with O₂ by bubbling dry air at 7.65 mL min⁻¹ flow, and introduced in the ATR cell with a syringe filling almost the entire inner volume of the cell.

For the analysis a TRS N₂-cooled detector was used applying a rapid scan mode at 8.8617 cm s⁻¹. The first step of the experiment consisted of recording 500 scans (1.2 min) in the dark followed by 850 scans (2 min) under illumination, and measurements in the dark for 20 min. The initial 500 scans in the dark were used to calculate the background spectrum, while spectra measured during illumination and in subsequent dark conditions were obtained by averaging 25 scans. These spectra represent a time interval of 3.5 s. A 150 W Xe illumination source was shielded by a Uniblitz Shutter (with a VCM-D1 controller), equipped with a diaphragm which opens or closes in synchronization with the infrared measurement. The synchronization between the spectrometer and the shutter was achieved by a home-made Labview method.

A deconvolution method of the Omnic 7.3 software from Thermo Scientific was applied for all spectra between $4000-3010 \text{ cm}^{-1}$ and between $1880-1475 \text{ cm}^{-1}$, with a fixed number of IR bands, before integration of the spectral contributions of water, cyclohexanone and carboxylate, respectively.

oxidation of cyclohexane.

Theoretical methods

A microkinetic model describing the kinetics of cyclohexane photo-oxidation was developed, and, together with a simple batch reactor model, implemented in the software package Athena Visual Studio. The diffusion time of cyclohexanone was estimated to be a few milliseconds, considering a length of 2 µm, which is the penetration depth of the infrared radiation, and a diffusion coefficient of 10^{-9} m² s⁻¹. Therefore all diffusion and mass transfer limitations can be neglected. The microkinetic model was developed based on the reaction mechanism of cyclohexane photo-oxidation proposed previously,⁶ which is presented in Scheme 1. The scheme contains cyclohexane photo-oxidation to cyclohexanone, and the consecutive paths of cyclohexanone desorption. The formation of strongly adsorbed carboxylate species is included as a consecutive oxidation of adsorbed cyclohexanone, as well as via a direct route from cyclohexane. While carbonates have also often been observed as a surface adsorbed species during photocatalytic cyclohexane oxidation, we have not taken this into consideration because of the relatively small contribution of these species in the limited time of exposure to light applied in this study. For simplicity and due to lack of spectroscopic evidence, intermediates leading to formation of cyclohexanone were not considered in the model.

Table 1 shows the reaction steps and the corresponding rate equations considered in the microkinetic model together with the continuity equations required for the reactor simulation and fitting of the experimental data. The rate of the cyclohexanone formation is described by a kinetic equation with a reaction constant k_1 , the occupancy of cyclohexane on the surface (θ_{Cyh}) and the oxygen concentration [O₂]. Due to the low conversion, up to only about 0.6%, the oxygen concentration was assumed to be invariable and for simplicity the reaction order with respect to oxygen was set at unity. Since the time for desorption of cyclohexanone in dark conditions is known to be in the order of minutes,^{9,10} the cyclohexanone desorption rate was considered to be limiting, as shown in Table 1 by reaction (4). The net forward rate of reaction (4) equals the rate of cyclohexanone desorption minus the rate of cyclohexanone adsorption, and is a function of the cyclohexanone desorption constant, k_4 , the cyclohexanone surface occupation, θ_{CyhO} , the cyclohexanone Langmuir constant, K_{CvhO} , the cyclohexanone concentration in the bulk, C_{CvhO} , and the fraction of free sites, θ^* . While still adsorbed, cyclohexanone can be further oxidized, especially in the presence of •OH radicals (reaction (2)). This reaction results in a variety of products that have been identified by in situ ATR-FTIR as carboxylate species. For simplicity it is assumed that only the simplest carboxylate molecule ($C_6H_{11}O$) is formed, which is irreversibly adsorbed on one active TiO₂ site. Reaction (2) is described by its reaction constant, k_2 , and the surface occupation with cyclohexanone, θ_{CyhO} . Reaction (3) describes an alternative path of carboxylate formation, which is the direct oxidation of adsorbed cyclohexane in the presence of O₂ and •OH radicals.

The temperature dependency of the reaction rate constants is described using a modified Arrhenius expression $k_{i,T} = k_{i,T_{\text{ref}}} \exp\left\{\frac{-E_{a,i}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right\}$,¹¹ which avoids a strong



Scheme 1 Applied simplified reaction mechanism of the photo-

 Table 1
 Microkinetic model

Reactions	Equations
$(1) \operatorname{Cyh}^* + \operatorname{O}_2^- \underset{\bullet \operatorname{OH}}{\longrightarrow} \operatorname{CyhO}^* + \operatorname{H}_2\operatorname{O}^*$	Rate $1 = k_1 \theta_{\text{Cyh}} [O_2]^n$
0n	$k_1 = k_{1_296} \exp\left(-E_{a1} \frac{1.0 \times 10^3}{8.314}\right) \left(\frac{1}{T} - \frac{1}{296}\right)$
(2) $\text{CyhO}^* + {}^{\bullet}\text{OH} \rightarrow \text{C}_6\text{H}_{11}\text{O}_2^*$	Rate 2 = $k_2 \theta_{\text{CyhO}}$
	$k_2 = k_{2,296} \exp\left(-E_{a2} \frac{1.0 \times 10^3}{8.314}\right) \left(\frac{1}{T} - \frac{1}{296}\right)$
(3) $Cyh^* + O_2^- + {}^{\bullet}OH \to C_6H_{11}O_2^* + H_2O^*$	Rate 3 = $k_3 \theta_{\text{Cyh}} [O_2]^n$
	$k_3 = k_{3,296} \exp\left(-E_{a3} \frac{1.0 \times 10^3}{8.314}\right) \left(\frac{1}{T} - \frac{1}{296}\right)$
(4) $CyhO^* \rightarrow CyhO + *$	Rate $4 = k_4 \theta_{\text{CyhO}} - k_4 K_{\text{CyhO}} C_{\text{CyhO}} \theta^*$
	$k_4 = k_{4_296} \exp\left(-E_{a4} \frac{1.0 \times 10^3}{8.314}\right) \left(\frac{1}{T} - \frac{1}{296}\right)$
Adsorption equilibria	
$Cyh + * \rightleftharpoons Cyh^*$	$K_{\text{Cyh}} = K_{\text{Cyh}_296} \exp\left(-\Delta H_{\text{Cyh},\text{ads}} \frac{1.0 \times 10^3}{8.314}\right) \left(\frac{1}{T} - \frac{1}{296}\right)$
	With $K_{\text{Cyh}} = \frac{\theta_{\text{Cyh}}}{ \text{Cyh} \theta^*}$
$H_2O^* \rightleftharpoons H_2O + *$	$K_{\rm H_2O} = K_{\rm H_2O_296} \exp\left(-\Delta H_{\rm H_2O,ads} \frac{1.0 \times 10^3}{8.314}\right) \left(\frac{1}{T} - \frac{1}{296}\right)$
	With $K_{\rm H_2O} = \frac{\theta_{\rm H_2O}}{[\rm H_2O]\theta^*}$
Site balance	$1 = \theta^* + \theta_{Cyh} + \theta_{CyhO} + \theta_{H_2O} + \theta_{Carbox}$
Rates of product formation (mol $m^{-3} s^{-1}$)	Rate (Cyh) = $(-\text{rate } 1 - \text{rate } 3) * N_T / V_R$ Rate (CyhQ) = $(\text{rate } 1 - \text{rate } 2) * N / V_R$
	Rate (H ₂ O) = (rate 1 + rate 2) * N_T/V_R Rate (H ₂ O) = (rate 1 + rate 3) * N_T/V_R
Rate of formation of carboxylates species (s^{-1})	Rate (Carbox) = rate $2 + rate 3$

correlation between the rate constants and the activation energies. In this equation, $k_{i,T_{ref}}$ is the rate constant of any of the four reactions at the reference temperature, T_{ref} and $E_{a,i}$ is the corresponding apparent activation energy of the reaction. The reference temperature T_{ref} is 296 K.

The total number of active sites (N_T) was determined by NH₃-TPD² to be 4.9 × 10⁻⁸ mol, and it is assumed that this number is constant. The surface is occupied by active sites of basic and acidic character, of which the later occupies 77% of the TiO₂ catalyst, as determined by NH₃-TPD and an Fe(acac)₃ adsorption method.² During the photo-catalytic oxidation the TiO₂ catalyst is occupied by different products, as described in the site balance. The adsorption of cyclohexane and H₂O are assumed to be at equilibrium at all times. The initially adsorbed H₂O molecules are considered as spectators, occupying TiO₂ active sites and reducing the surface occupation with cyclohexane.

The adsorption equilibria of cyclohexane and H₂O are assumed to follow the Langmuir isotherm with the adsorption constants K_{Cyh} and $K_{\text{H}_2\text{O}}$, respectively. Since the adsorption entropy and enthalpy are assumed to be constant in the temperature range covered in the experiments, the temperature dependency of the adsorption constants is expressed using $K_{i,T} = K_{i,T_{\text{ref}}} \exp\left\{\frac{-\Delta H_{\text{ads},i}}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right\}$, with the reference temperature T_{ref} set at 296 K.

The consumption rate of the reactant and the formation rates of the products follow directly from the reaction rates considering the total number of active sites (N_T) and a reactor volume (V_R) of 1.1×10^{-6} m³. In order to fit the IR experimental results, two calibration factors had to be incorporated in the model, to relate the cyclohexanone and H₂O concentrations to their IR peak areas (abs cm⁻¹). Unfortunately, it is not possible to obtain these calibration factors by a direct measurement since the total amount adsorbed, expressed in moles, is always negligibly small compared to the amount in the bulk. Therefore these calibration factors had to be included in the model as fitting factors. The intensity of the absorption band of adsorbed hexanoic acid was compared to that of adsorbed cyclohexanone (not shown) and the first was around two times larger than the second, so the calibration factor of carboxylates was set at two times the value for cyclohexanone. The temperature dependency of the oxygen solubility in cyclohexane^{12,13} has also been taken into account.

The 14 kinetic parameters, consisting of 4 rate constants, 4 activation energies, 3 adsorption constants and 3 adsorption enthalpies, and the 2 calibration factors, were obtained by minimization of the sum of the squared differences between the experimental and the simulated responses. The adsorption enthalpies of cyclohexanone and H₂O on TiO₂ were previously estimated by DFT (Density Functional Theory) calculations.¹⁴ The adsorption enthalpy of cyclohexanone on a dry TiO₂ surface was estimated to be -24 kJ mol⁻¹, while on hydrated surfaces a value of -37 kJ mol^{-1} was calculated.¹⁴ The adsorption energy of water on TiO₂ varied between -57 and -67 kJ mol⁻¹, depending on the extent of hydration.^{6,14–17} Initial guesses for cyclohexanone and H₂O adsorption on TiO₂ of -37 and -65 kJ mol⁻¹ were included in the model and these values were not allowed to vary more than 20 kJ mol⁻¹. The following weighing factors in the microkinetic model were applied to compensate for the differences in the orders of magnitude of the infrared responses: adsorbed cyclohexanone (abs cm⁻¹): 1.0; bulk cyclohexanone (abs cm⁻¹): 0.005; carboxylates (abs cm⁻¹): 0.3; and H₂O (abs cm⁻¹): 0.05.

In the investigation two alternative models were considered, one involving the adsorption of cyclohexanone being at equilibrium at all times, and another assuming that the •OH radical concentration is proportional to the water coverage instead of a constant value. Although both models showed an almost equally good fit, they were disregarded based on physical grounds and available knowledge in literature.^{18,19}

Notation

 $k_{1} (m^{3} mol^{-1} s^{-1}), k_{2} (s^{-1}), k_{3} (m^{3} mol^{-1} s^{-1}), k_{4} (s^{-1}) k_{4} (s^{-1}) k_{1_{2}296} (m^{3} mol^{-1} s^{-1}), k_{2_{2}296} (s^{-1}), k_{3_{2}296} (m^{3} mol^{-1} s^{-1}) and k_{4_{2}296} (s^{-1}) k_{T} (m^{3} mol^{-1} s^{-1})$ $[O_{2}] (mol m^{-3}) n$ $N_{T} (mol)$ $V_{R} (m^{3}) \theta_{CyhO}, \theta_{H_{2}O}, \theta_{Carbox}$

 $\begin{array}{l} \theta^{*} \\ K_{\rm Cyh}, K_{\rm CyhO}, K_{\rm H_{2}O} \\ ({\rm m}^{3} \ {\rm mol}^{-1}) \\ K_{\rm Cyh_{2}96}, K_{\rm CyhO_{2}96}, \\ K_{\rm H_{2}O_{2}96} \ ({\rm m}^{3} \ {\rm mol}^{-1}) \\ E_{\rm a1}, E_{\rm a2}, E_{\rm a3}, E_{\rm a4} \ ({\rm kJ} \ {\rm mol}^{-1}) \\ \Delta H_{\rm Cyh, ads}, \Delta H_{\rm CyhO, ads}, \\ \Delta H_{\rm H_{2}O, ads} \ ({\rm kJ} \ {\rm mol}^{-1}) \\ k_{\rm Cyh, ads}, k_{\rm Cyh, des} \ ({\rm s}^{-1}) \end{array}$

 $k_{\rm H_2O,ads}, k_{\rm H_2O,des} \, (s^{-1})$

 $cf_{CyhO,ads}, cf_{H_2O,ads}$ (m³ abs mol⁻¹ cm⁻¹) Rate constants of reactions (1), (2), (3) and (4) Rate constants of reactions (1), (2), (3) and (4) at $T_{\rm ref} = 296 \, {\rm K}$ Rate constants of reaction (1) at each temperature Oxygen concentration Order of reactions (1) and (3) in oxygen concentration Total number of active sites (in the reactor) Reactor volume Occupancy of the active sites with cyclohexane, cyclohexanone, water and carboxylates Fraction of free active sites Adsorption constant of cyclohexane, cyclohexanone and water Adsorption constant of cyclohexane, cyclohexanone and water at 296 K Activation energy of reactions (1), (2), (3) and (4) Adsorption enthalpy of cyclohexane, cyclohexanone and water Rate of cyclohexane adsorption and desorption Rate of water adsorption and desorption Coefficient that relates concentration with infrared peak area; for adsorbed cyclohexanone and water

Results

The photo-catalytic reaction was performed at different temperatures, corresponding to different hydration levels of the TiO₂ surface. This is illustrated in Fig. 1(a). The broad band between 3500 and 3000 cm⁻¹ is characteristic of the OH stretching vibration of water adsorbed on the TiO₂ surface. This water originates from the catalyst layer preparation, and the lab environment to which the layer was exposed before starting the experiment. The very large water band present at 23 °C significantly decreases at higher temperatures. In Fig. 1(b), the peak area of adsorbed H₂O is represented as a function of temperature, showing an exponential decrease. From 23 to 40 °C a decrease of at least 60% in quantity of adsorbed water is observed, while above this temperature surface dehydration becomes less pronounced.

UV illumination conditions

At each temperature, cyclohexane photo-catalytic oxidation was performed for only two minutes with the purpose of analyzing the first steps of the reaction. In general, the first minutes of cyclohexane photo-oxidation at room temperature are characterized by the formation of cyclohexanone in parallel with adsorbed H₂O, but also the formation of carboxylate species causing catalyst deactivation.⁶ Fig. 2 shows the spectrum and its deconvolution after two minutes of cyclohexane photo-oxidation at 23 °C. In the higher frequency range (Fig. 2a), a positive contribution of the OH stretching vibration of H₂O with two characteristic bands can be seen. These peaks have been proposed to correspond to water adsorbed on the TiO₂ active sites (3238 cm^{-1}) and to multilayer hydrogen-bonded water (3432 cm⁻¹).²⁰ A negative contribution for the OH stretching vibration of bridging active sites on TiO₂ is observed at 3642 cm^{-1.21} At the lower frequency range (Fig. 2b), the contribution of the adsorbed reaction product cyclohexanone is visible by its carbonyl vibration at 1694 and 1682 cm^{-1.6} DFT calculations on hydrated (101) TiO₂ surfaces showed that the former band corresponds to the direct adsorption of the carbonyl on TiO₂



Fig. 1 (a) Spectra of cyclohexane adsorbed on TiO_2 at different temperatures, prior to the photo-catalytic reaction, at the region of the OH stretching vibration of adsorbed H₂O (diamond ATR background). (b) Peak area of adsorbed H₂O as a function of temperature, obtained by integration of absorbance intensity between 3590 and 3010 cm⁻¹.



Fig. 2 Spectral deconvolution after two minutes of cyclohexane photo-oxidation on TiO_2 at 23 °C in the (a) high wavenumbers region and (b) low wavenumbers region. The black line represents the original spectra, the grey bands correspond to the deconvoluted peaks and the dashed grey line represents the sum of the deconvoluted peaks. The two grey-shaded peaks in (b) correspond to adsorbed cyclohexanone.

Table 2 Assignment of deconvolution peaks observed during cyclohexane photo-oxidation

Peaks (cm ⁻¹)	Vibration	Assignment ^{6,21–23}	
3642	OH stretching	Bridging OH in TiO ₂	
3432, 3238	OH stretching	Adsorbed H ₂ O	
1718, 1704	C=O stretching	Bulk cyclohexanone	
1694, 1682	C=O stretching	Adsorbed cyclohexanone	
1650	OH bending	Adsorbed water	
1578, 1523	Asymmetric C=O stretching	Adsorbed carboxylates	

adsorption sites, while the latter band is more redshifted because the cyclohexanone is also H-bridged to a neighboring adsorbed H_2O molecule.¹⁴ To improve the spectral deconvolution,¹⁹ the main contribution above 1700 cm⁻¹ was fitted with two peaks that are proposed to correspond to desorbed molecules of cyclohexanone under different environments. Water formation can be observed by its bending vibration at 1650 cm⁻¹, which grows in parallel with the broad contribution between 3600–3000 cm⁻¹. The contribution of the carboxylic acid vibrations is located at 1578 and 1523 cm⁻¹. Table 2 resumes the bands used for spectral deconvolution with their applied assignments.

The same deconvolution method was applied at all temperatures and the spectral results can be found in the ESI.† Fig. 3 shows the trends. As expected, the conversion rate of cyclohexane into cyclohexanone increases with temperature up to 50 °C. At 55 °C the contribution of adsorbed cyclohexanone decreases and at 60 °C, a considerable decrease in both adsorbed and bulk cyclohexanone can be seen. The experimental results also show that the formation rate of carboxylate increases with temperature, up to 50 °C.

It appeared that only the experimental data in the temperature range of 23–50 °C could be fitted properly with a single microkinetic model. Above this temperature the production rate of cyclohexanone decreases much faster than the model predicts and therefore it is concluded that the reaction kinetics change significantly above 50 °C. This is probably due to the onset of thermally induced reactions causing additional deactivation, as will be shown later, or total oxidation of cyclohexane into CO_2 and H_2O . The experimental results obtained at 55 °C and 60 °C were therefore not used in the parameter fitting procedure.

Although most product formation profiles are well predicted by the microkinetic model, the carboxylate species show a significant deviation at 23 °C and 30 °C. At 23 °C, the experimental data for carboxylates formation show a clear delay, not predicted by the microkinetic model, which indicates that carboxylates at low temperatures may be a product of a consecutive reaction. At 40 and 50 °C this delay in carboxylate formation is not observed. The peak area of water includes the initial surface adsorbed water shown in Fig. 1, and for higher temperatures it shows a slight decrease at longer UV-illumination times.

Table 3 resumes the kinetic parameters obtained from the parameter estimation using the microkinetic model for cyclohexane photo-oxidation. The obtained value of $-36.9 \text{ kJ mol}^{-1}$ for the adsorption energy of cyclohexanone, $\Delta H_{\text{CyhO,ads}}$, is in excellent agreement with the adsorption energy on a hydrated (101) TiO₂ surface of -37 kJ mol⁻¹, estimated using DFT.¹⁴ The model fit shows an adsorption enthalpy of H₂O on TiO₂ of -47.1 ± 3.2 kJ mol⁻¹, which is smaller than the energy of water adsorption on the (101) crystal phase estimated from DFT calculations,¹⁴ ranging between -57 and -67 kJ mol⁻¹. Although the calculated adsorption enthalpy was lower than expected, the determined $K_{\rm H_2O}$ 296 confirms the high hydrophilicity of the TiO₂ catalyst. The microkinetic model fit shows no thermal enhancement of the formation of adsorbed cyclohexanone ($E_{a1} = 0 \text{ kJ mol}^{-1}$). The rate constant of cyclohexanone formation (k_1) is considerably higher than the rate constants of carboxylate formation $(k_2 \text{ and } k_3)$. Furthermore, according to the optimal fit, the contribution of the reaction of cyclohexanone to carboxylates is negligible (*i.e.* $k_{2,296} = 0 \text{ s}^{-1}$). This is probably due to the very high cyclohexanone desorption rate calculated by the model. Contrary to what was presumed, under illumination cyclohexanone desorption is not rate limiting, confirmed by the 0 kJ mol⁻¹ activation energy determined for cyclohexanone



Fig. 3 Product profiles and simulation results obtained with the fitted kinetic model for adsorbed cyclohexanone (solid squares: $1694 + 1682 \text{ cm}^{-1}$; model fit: black curve), bulk cyclohexanone divided by 1000 (empty squares: $1718 + 1704 \text{ cm}^{-1}$; model fit: black dashed curve), carboxylates (solid grey triangles: $1578 + 1523 \text{ cm}^{-1}$; model fit: grey curve) and water (empty grey triangles: 3432, 3238 cm^{-1} ; model fit: grey dashed curve) formed during photooxidation as a function of time at (a) 23 °C, (b) 30 °C, (c) 40 °C, (e) 55 °C and (f) 60 °C. The right *y*-axis represents the peak area of water.

 Table 3
 Kinetic parameters determined from the microkinetic model

 fitting to experimental data obtained during cyclohexane photooxidation
 photo

Parameter	Prediction	95% confidence range	Units
cf _{CyhO,ads}	0.68	± 0.04	a.u.
cf _{H₂O,ads}	1.29	± 0.06	a.u.
K _{Cyh} 296	0.31	± 0.03	$m^3 mol^{-1}$
$\Delta H_{\rm Cvh.ads}$	-34.4	± 3.7	kJ mol ⁻¹
K _{CvhO 296}	26.9^{a}	± 2.6	$m^3 mol^{-1}$
$\Delta H_{\rm CyhO,ads}$	-36.9	± 3.9	kJ mol ⁻¹
K _{H₂O 296}	766	± 84	$m^3 mol^{-1}$
$\Delta H_{\rm H_2O,ads}$	-47.1^{a}	± 3.2	kJ mol ⁻¹
k _{1 296}	10.84	± 0.25	$m^{3} mol^{-1} s^{-1}$
Eat	0.00^{b}		kJ mol ⁻¹
$k_{2,296}$	0.00^{b}		s^{-1}
E_{a2}	n.a. ^c		kJ mol ⁻¹
$k_{3,296}$	1.74×10^{-3}	$\pm 0.16 \times 10^{-3}$	$m^3 mol^{-1} s^{-1}$
Ea3	18.4	± 3.3	kJ mol ⁻¹
$k_{4 296}$	1286	± 878	s^{-1}
E_{a4}	0.00^{b}	—	kJ mol ⁻¹

^{*a*} Value limited within a narrow range around the value estimated from DFT calculations (see text). ^{*b*} Value limited by its lower boundary. ^{*c*} Not applicable: insignificant parameter.

desorption. It is very important to note that cyclohexanone desorption was observed to be quite slow at 23 °C, as reported previously,19 in agreement with the present result at 23 °C, showing a clear delay in carboxylate formation. This implies that at low temperatures, the oxidation of cyclohexanone to carboxylates is an important deactivation step. Contrarily to cyclohexane photooxidation to cyclohexanone, the model fit shows that cyclohexane photo-oxidation to carboxylate species is thermally enhanced with an activation energy of $18.4 \pm 3.3 \text{ kJ mol}^{-1}$. The correlation matrix of the estimated microkinetic model parameters, calculated under UV illumination conditions, can be found in the ESI.[†] The quite high correlation coefficient between $k_{1,296}$ and $K_{\rm H_2O}$ 296 may have contributed to the relatively large uncertainty in the calculated $K_{\rm H_2O}$ 296. The parameter k_4 296 is associated with an even larger uncertainty, which results from the low sensitivity of the model to this parameter.

The corresponding surface occupancies of cyclohexane, cyclohexanone, H_2O and carboxylates obtained with the kinetic model are shown in Fig. 4. As mentioned above, the kinetic model is only able to describe the results properly at temperatures up to 50 °C, with the exception of the



Fig. 4 Surface occupation with cyclohexanone (black curve), carboxylates (black dashed curve), cyclohexane (grey curve), and water (grey dashed curve) as a function of time at (a) 23 °C, (b) 30 °C, (c) 40 °C, (d) 50 °C, (e) 55 °C and (f) 60 °C. The right *y*-axis represents the occupancy of cyclohexane and water.

carboxylates prediction at 23 and 30 °C. Above 50 °C the model seems to overestimate the occupancies of cyclohexanone and carboxylates. At room temperature, half of the available adsorption sites are occupied with adsorbed water. At increasing temperatures the water occupancy decreases whereas those of the other components increase. The enhanced product formation is most considerable for the carboxylates species, which is also due to its thermal activation ($E_{a3} > 0$ kJ mol⁻¹). The fraction of free active sites is always very small, in the order of 10⁻⁴, although its fraction increases with temperature (not shown).

The parameter fitting using the experimental data up to 50 °C resulted in a zero activation energy for the cyclohexanone formation reaction. In order to get more insight whether this result is really acceptable, the parameter estimation has also been carried out separately at all temperatures. In these estimations the rate constants k_1 , k_2 , k_3 and k_4 were allowed to vary whereas the two calibration factors and the six parameters related with the adsorption constants were kept at the values presented in Table 3. The resulting rate constants of the cyclohexanone formation at the



Fig. 5 Arrhenius plot of the dependency of the constant of cyclohexanone formation with the inverse of reaction temperature. The horizontal line corresponds to the k_1 (m³ mol⁻¹ s⁻¹) value in Table 3 and the squares correspond to the k_T (m³ mol⁻¹ s⁻¹) values, determined at a single temperature using the microkinetic model.



Fig. 6 Selectivity of cyclohexane photo-oxidation to cyclohexanone, calculated by $k_1/(k_1 + k_3)$. The line corresponds to the $k_1/(k_1 + k_3)$ values reported in Table 3, and the squares correspond to the $k_1/(k_1 + k_3)$ values, determined at a single temperature using the microkinetic model.

different temperatures ($k_{\rm T}$) are plotted in an Arrhenius plot in Fig. 5, with the straight line corresponding to the microkinetic model fit at all temperatures, *i.e.* $E_{\rm a} = 0$ kJ mol⁻¹. It appears that the individual results for the cyclohexanone formation constant also correspond, with a small experimental error, to a zero activation energy up to 55 °C. Above this temperature the rate decreases significantly, probably due to the onset of one or more reactions not accounted for in the kinetic model, such as the thermally activated oxidation of cyclohexanone to carboxylates, as will be discussed later.

The selectivity of the cyclohexane photo-oxidation reaction to cyclohexanone, shown in Fig. 6, is calculated dividing the rate of cyclohexanone formation by the sum of the rates of cyclohexanone and carboxylates formation, which corresponds to $k_1/(k_1 + k_3)$. The values of the rate constants k_1 and k_3 were calculated using k_{1_296} , k_{3_296} , E_{a1} , and E_{a3} in Table 3, and the modified Arrhenius equation. The selectivity to the desired product is very high and slowly decreasing with temperature, although the non-selective product carboxylate is very detrimental causing irreversible deactivation. Fig. 6 shows the selectivity at all temperatures while above 50 °C the microkinetic model does not apply (Fig. 3e and f). It is noted that the real selectivity to cyclohexanone is probably lower than calculated here since the cyclohexane photo-oxidation reaction on TiO₂ is known to produce up to 5% of cyclohexanol.^{24,25} The small cyclohexanol contribution was not included in the microkinetic model since the amount cannot be estimated reliably due to a large overlap of its IR bands with the other bands.

Dark conditions

When the UV-illumination is turned off, the cyclohexanone formation stops and photon-independent phenomena, like desorption, can be isolated. The decrease of the adsorbed cyclohexanone peak under dark conditions was recorded and fitted using the microkinetic model, considering that the photon-induced reactions do not occur. The results are shown in Fig. 7 for all temperatures studied and these show that the desorption of cyclohexanone in dark conditions is a slow process, in the order of minutes, in agreement with previous studies.^{18,19} At higher temperature the rate of desorption increases, but complete desorption was not reached up to 60 °C. The results show that the relative concentration of irreversibly adsorbed cyclohexanone *vs*. the initial concentration increases with reaction temperature.

The four kinetic parameters obtained for the microkinetic fitting under dark conditions are compared with the values obtained under UV illumination, in Table 4. The results show a very large value of K_{CyhO} (2663 ± 210) compared to the value found under UV illumination (26.9 ± 2.6). The large cyclohexanone adsorption constant calculated under dark conditions is affected by the significant extent of irreversible adsorption visible in Fig. 7. The cyclohexanone adsorption constant this irreversible adsorption does not occur under UV light, which apparently causes a modification of the TiO₂ surface.²⁶

The results also show that in dark conditions the activation energy for cyclohexanone desorption from the TiO₂ surface amounts to 58.5 ± 5.3 kJ mol⁻¹, while a value of zero was found under photo-catalytic conditions. Apparently the rate of desorption is much lower under dark conditions than in the presence of UV light. It is therefore concluded that the adsorption characteristics of cyclohexanone on TiO₂ under UV illumination and dark conditions are not comparable; under UV illumination the cyclohexanone adsorption appears to be in equilibrium, whereas in dark conditions the cyclohexanone desorption is slow. The correlation matrix of



Fig. 7 Desorption of cyclohexanone from the TiO₂ catalyst in dark conditions at (a) 23 °C (black squares), 30 °C (empty squares) and 40 °C (grey squares); and (b) 50 °C (black triangles), 55 °C (empty triangles) and 60 °C (grey triangles). The curves are the fits obtained with the adapted parameters in Table 4.

	UV illuminati	UV illumination		Dark		
Parameter	Prediction	95% confidence range	Units	Prediction	95% confidence range	Units
$\begin{array}{c} K_{\rm CyhO_296} \\ \Delta H_{\rm CyhO,ads} \\ k_{4_296} \\ E_{\rm a4} \end{array}$	26.9 -39.9 1286 0.00	$ \begin{array}{c} \pm 2.6 \\ \pm 3.9 \\ \pm 878 \\ \end{array} $	$\begin{array}{c} m^3 \text{ mol}^{-1} \\ kJ \text{ mol}^{-1} \\ s^{-1} \\ kJ \text{ mol}^{-1} \end{array}$	$2663 \\ -14.7 \\ 7.27 \times 10^{-3} \\ 58.5$	± 210 ± 3.1 $\pm 0.68 \times 10^{-3}$ ± 5.3	$\frac{m^3 \text{ mol}^{-1}}{kJ \text{ mol}^{-1}}$ $\frac{s^{-1}}{kJ \text{ mol}^{-1}}$

 Table 4
 Comparison between the kinetic parameters determined from the microkinetic model fitting to experimental data obtained under UV illumination and under dark conditions



Fig. 8 Profiles of adsorbed carboxylates (1578, 1523 cm⁻¹) at (a) 23 °C (black dots), 30 °C (empty dots), 40 °C (grey dots) and (b) 50 °C (black triangles), 55 °C (empty triangles) and 60 °C (grey triangles). The first two minutes represent the illumination conditions and the remainder dark conditions. The curves were drawn to guide the eye.

the microkinetic model parameters, calculated under dark conditions, can be found in the ESI.[†] No strong dependency between any of the estimated parameters was found.

The development of the carboxylate peak area as a function of time at all temperatures is shown in Fig. 8. Below 50 °C the carboxylates peak grows under illumination, but starts to decrease when switching to dark conditions (Fig. 8a). This decrease is relatively small and could therefore also be caused by inaccuracy in the deconvolution procedure. Above 50 °C the carboxylates peak clearly continues growing after switching to dark conditions (Fig. 8b), although the formation rates are lower than under illumination conditions. This shows that the formation of carboxylates occurs almost exclusively photocatalytically below 50 °C, but above 50 °C both photocatalytically and thermally. Above 50 °C, the increase of the carboxylate peaks is opposed by a decrease in the peaks of adsorbed cyclohexanone (compare Fig. 8b and 7b). This suggests that a serial reaction scheme is operative: cyclohexanone is thermally oxidized to carboxylates.

Discussion

Activation energy for cyclohexanone formation

Photocatalytic reactions are activated by photon absorption, and an energy of $300-350 \text{ kJ mol}^{-1}$ is required to initiate the process of electron-hole separation.²⁷ Nevertheless, the activation energy of a photo-catalytic reaction, like the selective oxidation of cyclohexane is expected to be small. From pulse radiolysis it was found that for the reaction of organic molecules with •OH radicals the typical activation energy is in the range of 5–13 kJ mol⁻¹;²⁸ similarly, an activation energy for the formation of the superoxide anion was estimated as $11 \text{ kJ mol}^{-1.29}$

It is striking that our study, based on activity measurements using ATR-FTIR analysis, provided an estimate of 0 kJ mol⁻¹ for the apparent activation energy for the selective cyclohexane photo-oxidation to cyclohexanone (Table 3), implying that this reaction is not thermally activated. Herrmann *et al.* estimated an apparent activation energy of 10.5 kJ mol⁻¹ between 23–55 °C for the same reaction.⁷ While the apparent activation energy determined in our work is based on the formation rate constant of adsorbed cyclohexanone, previous studies only evaluated the formation rate of desorbed cyclohexanone.^{7,8} This may explain the difference in apparent activation energies found, since the latter is influenced by sorption effects. The *in situ* ATR-FTIR technique appeared very suitable for distinguishing these effects.

Herrmann et al. reported the highest activation energy (58 kJ mol⁻¹) at temperatures below 23 °C,^{7,8} which was ascribed to cyclohexanone desorption limitations. Although we did not study the reactivity below 23 °C, the results in Table 3 indicate that cyclohexanone desorption in not limiting under photo-catalytic conditions. Our data suggest that the high apparent activation energy reported by Herrmann et al. is related to a variation of the degree of surface adsorbed water. The results in Fig. 1 clearly show that the number of adsorption sites available for cyclohexane adsorption is not constant but dependent on the extent of surface hydration. This is particularly significant at low temperatures, at 23 °C more than 50% of the surface is occupied by adsorbed H_2O , resulting in a lower product formation rate (Fig. 3a). Below 23 °C the effect of surface hydration is likely to be even stronger. Therefore at low temperatures the apparent activation energy of the cyclohexanone formation is more

accurately predicted from: $E_{app} = E_a + (1 - \theta_{Cyh})\Delta H_{Cyh} - \theta_{H_2O}\Delta H_{H_2O}$.³⁰ In our study a water adsorption enthalpy of -47.1 kJ mol⁻¹ was estimated, indicating that the apparent activation energy calculated below 23 °C by Herrmann *et al.* may partly correspond to the desorption of H₂O from a considerably hydrated TiO₂ surface. The other part of the difference in the value of the activation energy might be due to the decrease in number of active sites by the formation of carboxylates, maybe in combination with irreversibly adsorbed cyclohexanone, as shown in Fig. 7.

At temperatures above 55 °C the microkinetic model is not applicable since other reactions not considered in the model interfere with the kinetics of cyclohexane photo-oxidation, resulting in lower rates than predicted by the model. Herrmann *et al.* observed a similar effect, reported as a negative value of the apparent activation energy at higher temperature, which they, however, explained by cyclohexane adsorption limitation instead of deactivation. Our model does not predict cyclohexane adsorption limitations (Fig. 4) under UV illumination up to 50 °C. Only the results at 55 and particularly 60 °C (Fig. 3e and f), showing a significantly lower reaction rate than at lower temperature, might partially be related to adsorption limitations.

The results in Fig. 8 indicate that above 50 °C, besides the photo-catalytic route, a thermal route must be taken into account in the carboxylate formation. The contribution of the thermal deactivation is the largest at 60 °C, which is accompanied by a decreased product formation. Based on these results, the apparent activation energy at temperatures above 55 °C can be estimated with $E_{\rm app} = E_{\rm a} + (1 - \theta_{\rm Cyh})\Delta H_{\rm Cyh} - E_{\rm deact}$.³⁰ The activation energy for the thermal deactivation route was not estimated since it was only significant in the 60 °C experiment of which the results were not used in the microkinetic model.

From our findings it has become evident that apparent activation energies estimated using a simple Arrhenius method based on liquid phase concentrations, must be interpreted with care since the values are influenced significantly by competitive adsorption and deactivation phenomena. More mechanistic insight is obtained using *in situ* techniques, which are able to analyze these phenomena. This is particularly important for the highly hydrophilic and easily deactivated TiO_2 photo-catalysts for organic transformations, as demonstrated herein.

Temperature effect on selectivity

The kinetic model contains two routes to carboxylate formation: (i) an indirect route *via* oxidation of cyclohexanone to carboxylates, and (ii) a direct route *via* formation of carboxylates from cyclohexane. The results of the kinetic parameter estimation show that the direct route is clearly the predominant one; only at 23 °C this seems not true since then the formation of carboxylates shows a clear delay. This indicates that the oxidation of cyclohexanone to carboxylates is an important deactivation route at low temperatures. The fact that this reaction is negligible according to our modeling might be due to the high cyclohexanone desorption rate constant under illumination, resulting in a low cyclohexanone occupancy within the error of the calculations.

The results show that selectivity towards cyclohexanone formation decreases with reaction temperature (Fig. 4). Scheme 2 resumes by a simplified illustration, the surface occupation according to our model at different temperatures, under dark conditions as well as under illumination conditions. At 23 °C, competitive water adsorption hinders the cyclohexane adsorption, resulting in a low reaction rate. Although H₂O is included in the microkinetic model as a spectator only, it may in reality also intervene in the reaction, e.g. in the formation of •OH radicals or by inducing a lower product selectivity. The carboxylates are represented with chemical bonds to the active sites to stress that these species are irreversibly adsorbed, causing deactivation. At temperatures up to 50 °C, the surface hydration decreases and cyclohexane adsorption increases, increasing the yield under UV illumination conditions. At 60 °C the yield decreases significantly, probably due to the thermal formation of carboxylates, (Fig. 8b), although also a limitation in the cyclohexane adsorption may play a role.



Scheme 2 Schematic representation of the expected species covering the surface of the TiO_2 catalyst under dark conditions (prior to reaction) and during photo-catalytic oxidation of cyclohexane (UV illumination), at (a) low temperatures and (b) high temperatures. The –OH site represented in the scheme is a simplification of the multiplicity of sites present in the TiO_2 surface. The solid lines represent irreversible adsorption while the dotted lines represent weak H-bonded adsorption.

The kinetics of cyclohexanone desorption under dark conditions, not shown in Scheme 2, proved to be unrelated to the desorption of cyclohexanone under UV illumination. According to our results the TiO_2 catalyst *during* photon absorption shows a much "cleaner" surface, while in dark conditions, *after* the exposure to UV light, cyclohexanone is much more strongly or even irreversibly adsorbed on the surface, in agreement with a previous study.¹⁹ Apparently not only a high degree of surface hydration *before* photon-induced conversion,¹⁹ but also the presence of photo-activated states *during* reaction largely promote desorption of the ketone.

Conclusions

The temperature dependence of the photo-catalytic cyclohexane oxidation on TiO₂ was evaluated using in situ ATR-FTIR, allowing the analysis of surface adsorbed species. The experimental data were fitted using a microkinetic model, which predicts the absence of a temperature effect on the rate of selective formation of cyclohexanone ($E_{a1} = 0 \text{ kJ mol}^{-1}$). The cyclohexane photo-catalytic oxidation is significantly limited by both competitive water adsorption and catalyst deactivation. The formation of carboxylates, which according to the model fit are mainly formed by direct cyclohexane oxidation under UV illumination, showed an activation energy of 18.4 \pm 3.3 kJ mol⁻¹. Above 50 °C carboxylates are also formed by consecutive oxidation of cyclohexanone, as demonstrated by spectral changes in dark conditions. The results imply that elevating the reaction temperature of photocatalytic cyclohexane oxidation reduces selectivity, and is not a means to suppress catalyst deactivation.

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