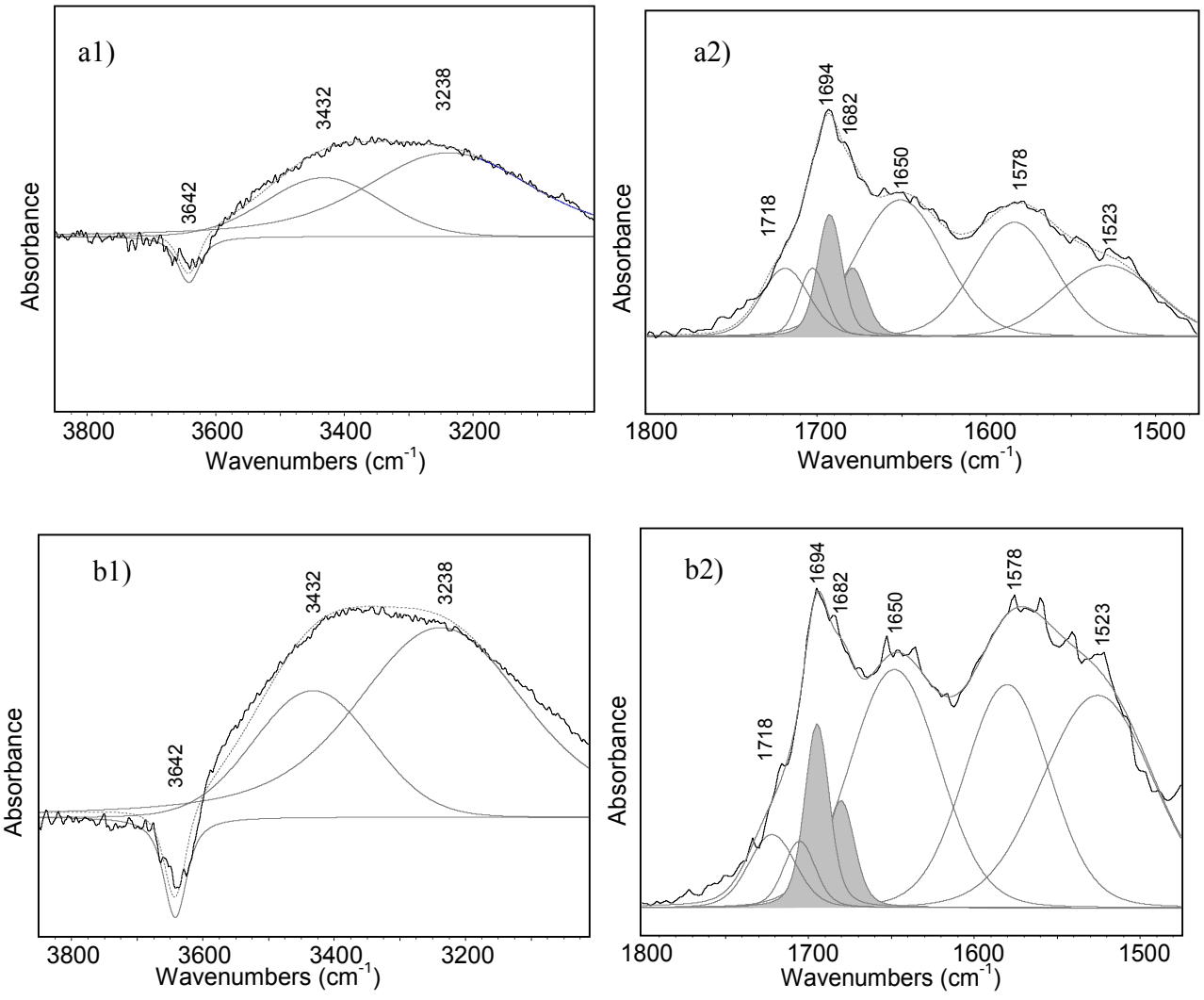
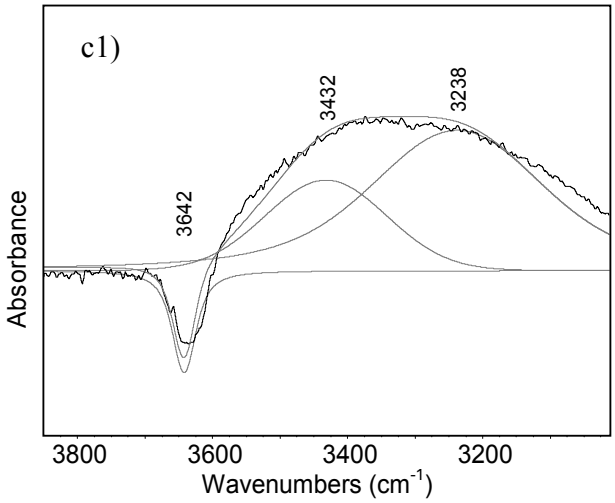
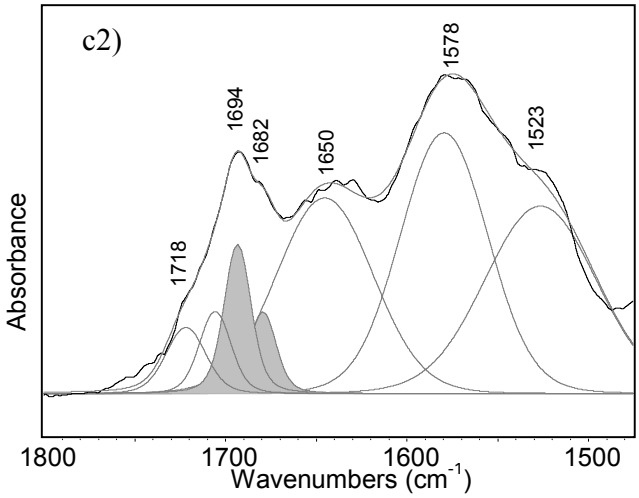
Electronic Supplementary information

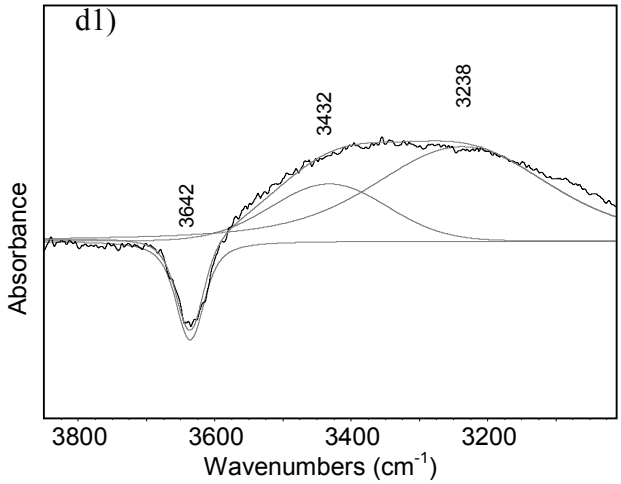
UV illumination conditions

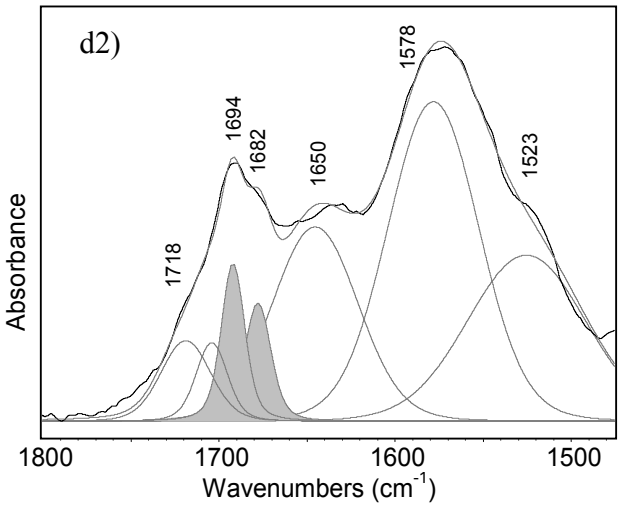
Figure 1 shows the spectrum and its deconvolution after two minutes of cyclohexane photo-oxidation at all temperatures, both in the high and low frequency range.

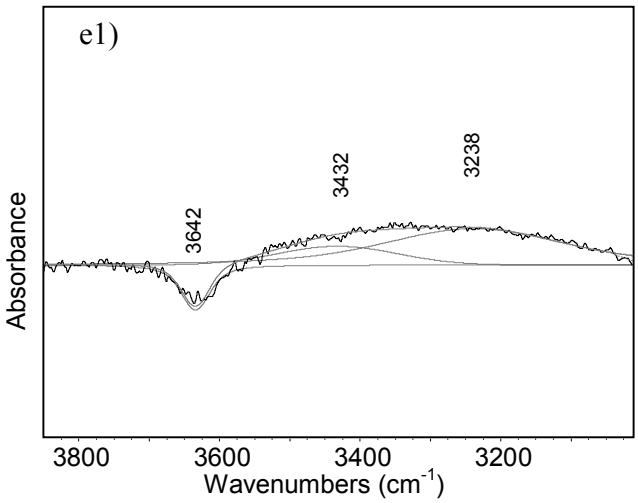


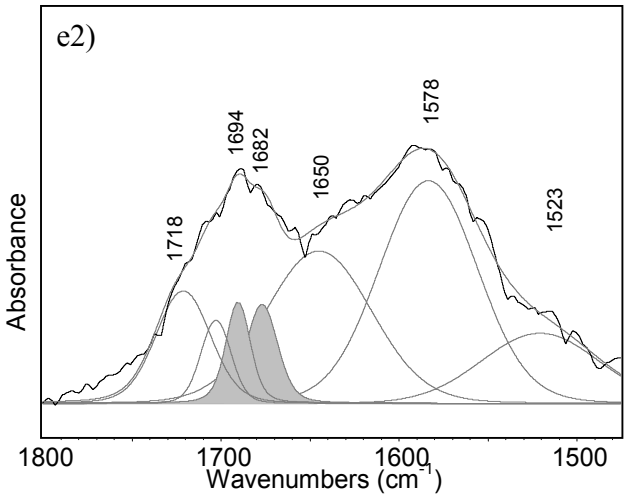

c1)
3642
3432
3238
Absorbance
3800
3600
3400
3200
Wavenumbers (cm-1)


c2)
1718
1694
1682
1650
1578
1523
Absorbance
1800
1700
1600
1500
Wavenumbers (cm-1)


d1)
3642
3432
3238
Absorbance
3800
3600
3400
3200
Wavenumbers (cm-1)


d2)
1718
1694
1682
1650
1578
1523
Absorbance
1800
1700
1600
1500
Wavenumbers (cm-1)


e1)
3642
3432
3238
Absorbance
3800
3600
3400
3200
Wavenumbers (cm-1)


e2)
1718
1694
1682
1650
1578
1523
Absorbance
1800
1700
1600
1500
Wavenumbers (cm-1)

60C

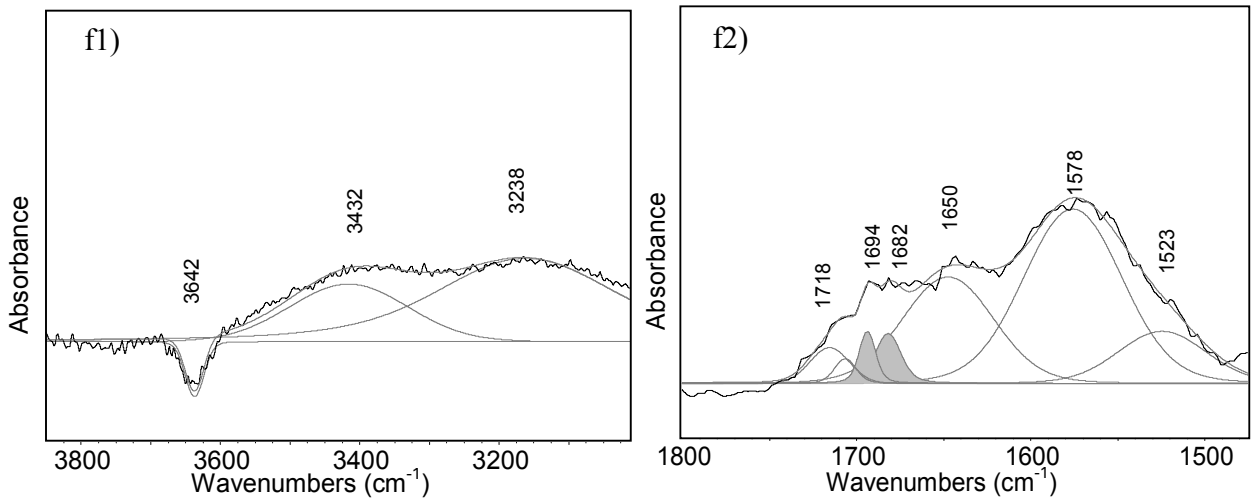


Figure 1. Spectral deconvolution after two minutes of cyclohexane photo-oxidation on TiO_2 at (a) 23ºC, (b) 30ºC, (c) 40ºC, (d) 50ºC, (e) 55ºC and (f) 60ºC for the 1) high wavenumbers region and 2) low wavenumbers region. The spectra are represented in common scale of absorbance among the same wavenumber 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 correspond to adsorbed cyclohexanone.

Table 1 shows the correlation matrix of the 11 parameters that could be fitted, without becoming limited by the boundaries that were set to avoid the values moving into physically unacceptable ranges. None of the absolute values of the correlation coefficients between different parameters exceeds the value of 0.99 indicating the absence of a strong correlation between any of the estimated parameters[1]. The quite high correlation coefficient of 0.97 between k_{1_296} and K_{H2O_296} may have contributed to the relatively large uncertainty in the calculated K_{H2O_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.

Table 1. Correlation matrix of the estimated microkinetic model parameters, calculated under UV illumination conditions.

Parameter	$cf_{CyhOads}$	cf_{H2Oads}	$\Delta Hads_{Cyh}$	K_{CyhO_296}	$\Delta Hads_{CyhO}$	K_{H2O_296}	$\Delta Hads_{H2O}$	k_{1_296}	k_{3_296}	Ea_3	k_{4_296}
$cf_{CyhOads}$	1										
cf_{H2Oads}	-0.82	1									
$\Delta Hads_{Cyh}$	-0.77	0.90	1								
K_{CyhO_296}	-0.24	-0.20	-0.24	1							
$\Delta Hads_{CyhO}$	-0.59	0.70	0.76	-0.46	1						
K_{H2O_296}	0.64	-0.92	-0.90	0.49	-0.77	1					
$\Delta Hads_{H2O}$	-0.66	0.80	0.88	-0.35	0.84	-0.89	1				
k_{1_296}	0.66	-0.94	-0.93	0.43	-0.72	0.97	-0.83	1			
k_{3_296}	-0.32	-0.11	-0.21	0.74	-0.22	0.40	-0.30	0.37	1		
Ea_3	0.12	-0.17	-0.08	-0.07	0.09	0.05	0.12	0.12	-0.47	1	
k_{4_296}	0.15	-0.27	-0.26	0.52	-0.24	0.36	-0.25	0.36	0.23	0.04	1

Dark conditions

Table 2 shows the correlation matrix of the 4 parameters that were fitted to the ATR-FTIR results under dark conditions. Since the absolute values of all the correlation coefficients between different parameters are significantly lower than 0.99, it can be concluded that there is no strong dependency between any of the estimated parameters.

Table 2. Correlation matrix of the microkinetic model parameters, calculated under dark conditions.

Parameter	K_{CyhO_296}	$\Delta Hads_{CyhO}$	k_{4_296}	Ea_4
K_{CyhO_296}	1			
$\Delta Hads_{CyhO}$	-0.89	1		
k_{4_296}	0.60	-0.56	1	
Ea_4	-0.42	0.54	-0.77	1

References

1 Caracotsios, M., Personal Communication, 1997