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Supporting Information to the paper:

Room Temperature Spontaneous Conversion of OCS to CO_2 on the Anatase TiO_2 Surface

by

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Experimental Details.

The measurement was performed with a fully evacuated Bruker IFS 125 HR spectrometer (Bruker, Karlsruhe, Germany) equipped with a 25-cm optical cell in the sample chamber. The system was evacuated or filled with the sample gases in situ (inside the sample chamber of the spectrometer), without manipulation of the optical cell. The experimental set-up is depicted in Figure 1.

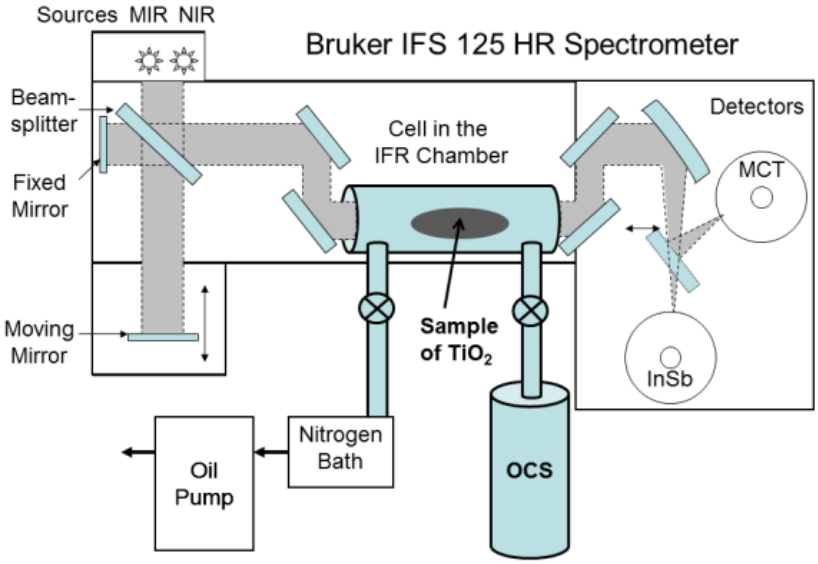

Figure 1: Scheme of the measurement set-up used. The cell with the sample of $Ti^{18}O_2$ was filled by ^{16}OCS from the lecture bottle. BS is the interferometer (IFR) beam splitter, MIR is the middle infrared source, NIR is the near infrared source, HgCdTe and InSb are the semiconductor detectors.

Supplementary panel C of the Figure 3.

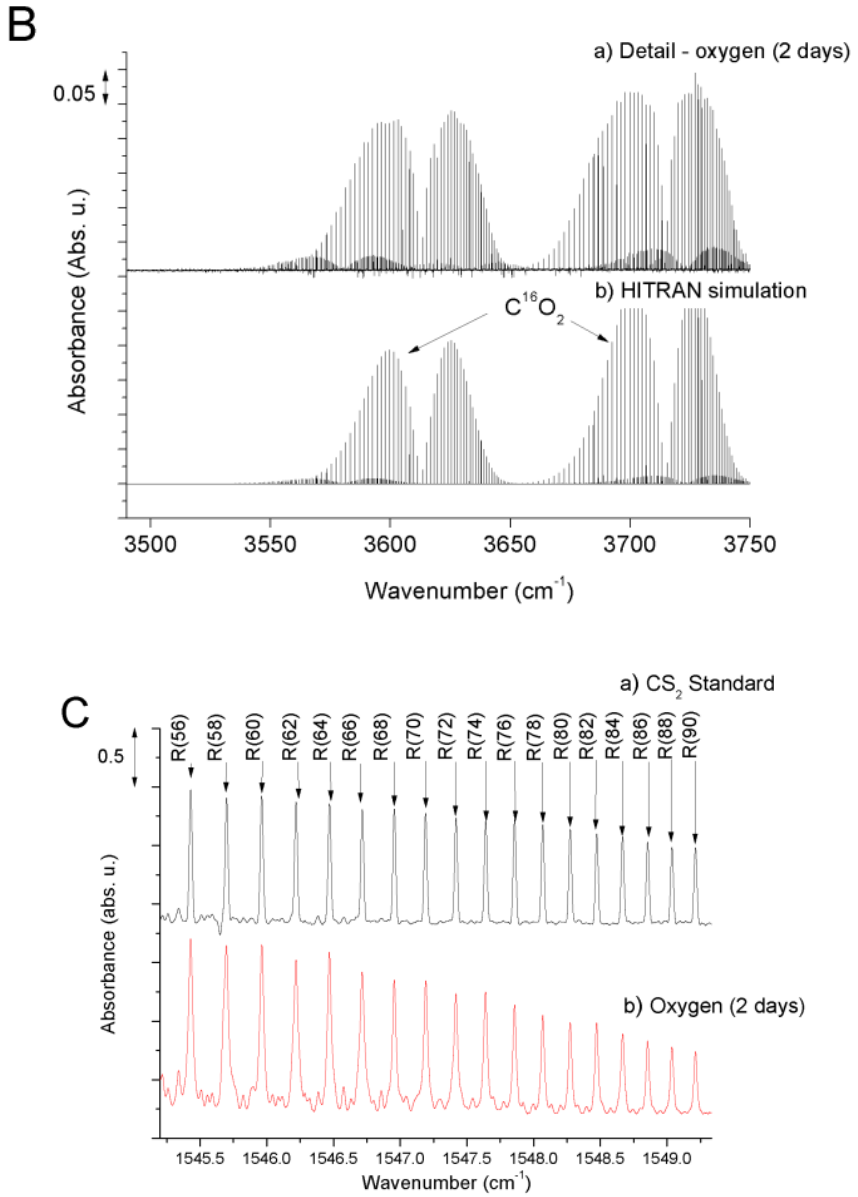

Figure 2: Supplementary panel B of the Figure 3 shows the detail of the $v_1 + v_3$ and $2v_2 + v_3$ bands of $C^{16}O_2$ isotopologues together with the HITRAN simulation. Only the $C^{16}O_2$ isotopologue is present in the spectra. Supplementary panel C of the Figure 3 shows details of the CS_2 spectrum.

Futher Analysis using XPS. To further explore the exposed titania surface, we have carried out the XPS analysis. Throughout the sample manipulation for photoelectron measurement in a dry box filled with Ar, the sample colour faded to the initial white and an unknown adsorbed gas was released (later identified as CS_2). This was the main reason that the photoelectron spectrum measured after six months on the exposed sample did not show any features in the region characteristic of the binding energies of sulphur. Obviously, CS_2 is

rapidly desorbed from titania, if the sample is exposed to Ar atmosphere and/or ultrahigh vacuum during XPS measurement.

Computational Details. Geometries were optimised in gas-phase using the B3LYP density functional theory method with the 6−311++G(2d,2p) basis set of atomic orbitals on the S,C,O and H atoms. Ti was described with the Stuttgart small-core relativistic pseudo-potential (see Ref. 19 in the main text). In the course of the geometry optimisation, no constraints were applied, i.e., all structural parameters were relaxed. The free energies of the studied compounds were obtained as a sum of (i) the total electronic energy obtained at B3LYP/6−311++G(2d,2p) level and (ii) the thermal and entropic correction terms to the Gibbs free energy, which were computed via the harmonic approximation from frequency calculations at the same theoretical level.

All computations were carried out with the Gaussian09 computer code.[Si] The computational model used for description of the catalytic Ti sites comprised two coordinatively unsaturated reduced Ti(III) sites, which were formed by attaching two bridging oxygens and one hydroxyl group to each of the Ti centres, i.e., the total charge of the computed models was 0.

[S] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, *et al.*, *Gaussian, Inc*., **2009,** Wallingford CT.).

Optimized geometries of structures **1-8:**

1

Ti -1.1278 -0.6989 -0.0030

O 0.1026 -0.6675 1.2275

O 0.1382 -0.6751 -1.2576

S -1.7118 1.7396 -0.0023

O -2.4309 -1.9681 -0.0223

C -0.1052 2.2685 0.0313

H -2.7250 -2.7539 0.4397

O 1.0034 1.7787 0.0217

Ti 1.5482 -0.2704 -0.0478

O 3.3457 -0.5354 0.1119

H 4.2255 -0.8252 -0.1217

2

Ti 1.4160 1.3545 -0.0031

O 1.7815 0.1627 -1.2488

O 1.7866 0.1850 1.2513

S -1.0791 1.1633 0.0004

O 2.2040 2.9898 -0.0453

C -1.0585 -0.5172 0.0021

H 2.9097 3.5474 0.2815

O -0.2740 -1.4332 0.0047

S -5.1703 -0.0241 -0.0009

C -3.6241 -0.3723 0.0003

O -2.7005 -1.1776 0.0014

Ti 1.8979 -1.3113 0.0067

O 3.2208 -2.5439 -0.0017

H 4.1232 -2.8532 -0.0615

3

Ti -1.5872 1.3039 -0.0623

O -1.9114 0.0925 1.1909

O -1.7586 0.0762 -1.2913

S 0.9026 1.3591 0.0554

O -2.4876 2.8840 -0.1054

C 1.1707 -0.3442 0.0265

H -3.1566 3.3819 -0.5760

O 0.3695 -1.2770 0.0078

S 5.0417 -0.0718 0.0588

C 3.4709 0.1172 0.0496

O 2.4945 -0.7788 0.0313

Ti -1.7008 -1.3914 -0.0005

O -2.3244 -3.1012 0.0433

H -2.7260 -3.9287 -0.2130

4

Ti -0.7842 1.4752 -0.0586

O -1.7785 0.5316 1.1018

O -1.1932 0.3066 -1.2993

S 1.4861 0.7071 0.6811

O -1.0266 3.2706 -0.2362

C 0.8300 -1.2141 0.4221

H -1.4133 3.9380 -0.8036

O -0.1948 -1.8403 0.2406

S 4.3048 -0.2750 -0.4013

C 2.7860 -0.4687 0.0516

O 2.0439 -1.6398 0.0005

Ti -2.0547 -0.9246 -0.0610

O -3.3943 -2.1153 -0.3877

H -4.2468 -2.5340 -0.2833

5

Ti 0.4971 1.3382 -0.0054

O 1.4638 0.4748 -1.2508

O 1.3696 0.4574 1.2365

S -1.9828 1.1229 -0.0472

O 0.6796 3.1388 0.0059

C -0.4172 -1.2337 -0.0174

H 1.0893 3.8215 0.5395

O 0.5422 -1.9753 -0.0124

S -4.1823 -0.9138 0.0285

C -2.6279 -0.4770 0.0008

O -1.6662 -1.5657 0.0155

Ti 2.2826 -0.7139 -0.0346

O 3.8536 -1.6183 0.1126

H 4.7271 -1.9308 -0.1166

6

Ti -0.4792 1.3246 0.0095

O -1.4430 0.4799 1.2562

O -1.3778 0.4850 -1.2324

S 2.0370 1.1547 0.0190

O -0.6257 3.1320 0.0154

C 0.3824 -1.3456 0.0079

H -1.0380 3.8138 -0.5176

O -0.6463 -2.0105 0.0057

S 4.2018 -0.9634 -0.0168

C 2.7299 -0.3734 -0.0021

O 1.5904 -1.6546 -0.0109

Ti -2.3087 -0.6859 0.0349

O -3.9142 -1.5312 -0.1173

H -4.7907 -1.8158 0.1354

7

Ti 0.4406 1.2464 0.1726

O 0.8781 0.2804 -1.2571

O 1.9923 0.9238 0.8792

S -2.6628 1.1733 -0.2896

O -0.1184 2.9935 0.0811

C 0.0715 -1.0331 1.2502

H 0.2869 3.8491 0.2318

O 1.0359 -1.6811 0.7984

S -3.7383 -1.7424 -0.5141

C -3.1960 -0.2967 -0.4000

O -0.8605 -1.1540 1.9847

Ti 2.3556 -0.5519 -0.3825

O 3.9145 -1.3965 -0.8038

H 4.6266 -1.7717 -1.3179

H 4.6266 -1.7717 -1.3179

H 4.6266 -1.7717 -1.3179

8

Ti 1.2975 -0.6941 0.0022

O 0.0724 -0.8138 -1.2320

O 0.0464 -0.8212 1.2564

S 1.7304 1.7887 0.0038

O 2.7181 -1.8298 0.0268

C 0.1585 2.2357 -0.0131

H 3.0835 -2.5808 -0.4420

S -1.4152 1.8936 -0.0165

Ti -1.4186 -0.6832 0.0383

O -3.1428 -1.2561 -0.0904

H -3.9654 -1.6796 0.1474

Free catalytic site:

Ti -1.3513 0.0000 0.0022

O 0.0002 1.2577 0.0001

O -0.0002 -1.2579 0.0001

O -3.1797 0.0003 -0.0016

H -4.1337 0.0006 -0.0077

Ti 1.3513 -0.0003 -0.0020

O 3.1797 0.0008 0.0010

H 4.1337 -0.0012 0.0067
