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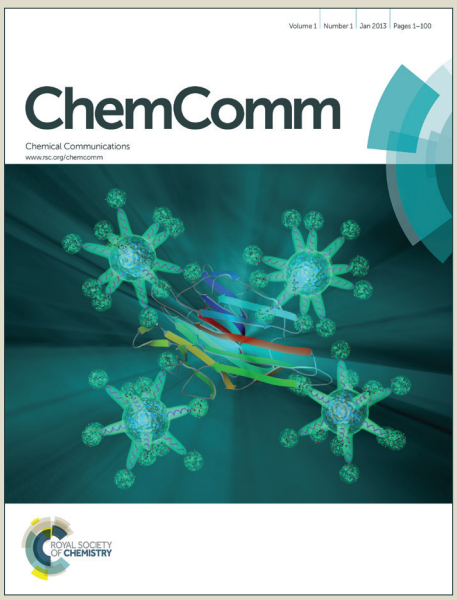

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Room Temperature Spontaneous Conversion of OCS to CO_2 on the Anatase TiO_2 Surface

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High-resolution FT-IR spectroscopy combined with quantum chemical calculations was used to study the chemistry of OCS-disproportionation over the reduced surface of isotopically labelled, nanocrystalline TiO_2. Analysis of the isotopic composition of the product gases has revealed that the reaction involves solely OCS molecules from the gas-phase. Using quantum chemical calculations we propose a plausible mechanistic scenario, in which two reduced Ti^{3+} centres mediate the reaction of the adsorbed OCS molecules.

The Titanium dioxide, TiO_2, is one of the most versatile oxide materials and is used in a wide variety of applications.[1,2,3, 4,5,6,7,8,9,10,11, 12, 13]

The reactions of gaseous carbonyl sulphide (OCS) are of potential importance in atmospheric chemistry. OCS is a predominant sulphur-containing compound in the troposphere (mixing ratio of 500 ppt/v) in the.[14] Approximately 0.64 $Tgyr^{-1}$ of OCS in the troposphere is transported to the stratosphere,[15] where it can be oxidised or photodissociated via reactions with O atoms or OH radicals to form sulphate aerosols. The question of whether OCS can be converted to some other more or less harmful species by reactions like catalytic dismutation is an on-going research challenge. In this paper we describe the conversion of OCS to CO_2 and CS_2 which a model reaction of this kind. We show, that the reaction occurs efficiently over the surface of partly reduced (n-doped) nanocrystalline TiO_2 (anatase) acting as a catalyst.

The partly reduced form of titania can be prepared by the thermal treatment of TiO_2 in vacuum. The formation of initial O vacancies in the surface is followed by the depletion of oxygen from the internal layers of titania. If a neutral oxygen is removed from the lattice, two extra electrons remain and fill the empty states of the titanium ions, forming a point defect in conjunction with three under-coordinated (fivefold) Ti ions.[5] Essentially, two of these Ti ions trap the two electrons and change their formal oxidation state from Ti^{4+} to Ti^{3+}. The resulting spin multiplicity can be a closed-shell singlet or an open-shell singlet and triplet. The corresponding electronic structure is characterised by several defect states in the band gap. These states are localised on both the Ti interstitial and substitution sites. [5, 6, 7, 8, 16, 17, 18, 19, 20, 21]

Previously, we have studied the oxygen atom exchange between gas phase molecules and a reduced titania surface, as well as the photocatalytic effects on this material, using isotopic labelling. [21,22, 23] For this purpose, we synthesised anatase isotopologues:[2, 24, 25] $Ti^{16}O_2$, $Ti^{17}O_2$ and $Ti^{18}O_2$. In the present study, we have extended this approach to examine the interaction of ^{16}OCS with $Ti^{18}O_2$ and describe the reactivity at molecular level.

Similarly to our previous studies focused on the reactivity of reduced titania with CO_2, [11, 25, 26, 27] (which is a homologue of OCS), Fourier transform infrared spectroscopy (HR-FTIR) was used to analyse the products of the reaction.

Two different experiments were conducted to explore the interaction of ^{16}OCS with nanocrystalline $Ti^{18}O_2$. They differed by the ratio of OCS/TiO_2, i.e., by the number of interacting molecules relative to the number of defects in the titania.

a) *Number of bulk defects much higher than the number of ^{16}OCS gas molecules* – low pressure experiment (1.2 Torr of ^{16}OCS).

One gram of vacuum-calcinated $Ti^{18}O_2$ (450 °C) was placed into the IR optical cell with 1.2 Torr of ^{16}OCS (99 %). The spectra were obtained every 120 seconds using an InSb detector, in the spectral range of the main CO_2 – OCS infrared absorption bands (1800 – 4000 cm^{-1}). The isotopic composition was determined from calibration measurement of pure standard gases. The evolution of product composition in the low pressure reaction of ^{16}OCS with solid $Ti^{18}O_2$ (0.000146 mol OCS and 0.0125 mol $Ti^{18}O_2$ respectively) is depicted in Figure 1. During the reaction, the partial pressure of ^{16}OCS significantly decreased, while new products appeared: $C^{16}O_2$, $C^{16,18}O_2$ and $C^{18}O_2$, with traces of ^{18}OCS. After 5 days, the reaction gas mixture consisted of 45.8 % $C^{16}O_2$, 42.2 % $C^{18}O_2$, 3.2 % $C^{16,18}O_2$ and 8.8 % ^{16}OCS, with traces of ^{18}OCS. Gaseous CS_2 was not observed.

Based on the analysis of the products, two possible scenarios can be proposed:

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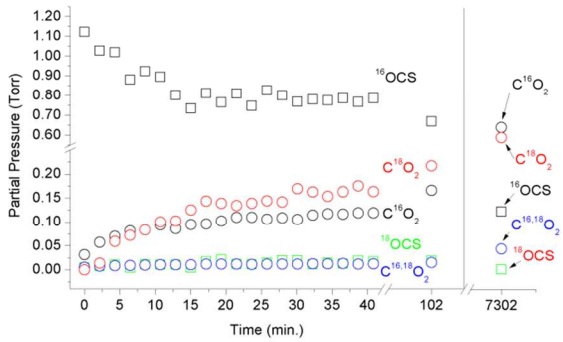

Figure 1: Evolution of the composition of the reaction mixture in the reaction of $Ti^{18}O_2$ (s) + ^{16}OCS (g).

I. Conversion of OCS to CO_2 with the involvement of ^{18}O from titania:

$$Ti^{18}O_2\,(s) + 2\,^{16}OCS\,(g) \rightarrow C^{16,18}O_2\,(g) + Ti^{16,18}O_2\,(s) + CS_2 \qquad (1)$$

II. Disproportionation of OCS to CO_2 without the involvement of ^{18}O from titania:

$$2\,^{16}OCS\,(g) \xrightarrow{Ti^{18}O_2} C^{16}O_2\,(g) + CS_2 \qquad (2)$$

In previous studies,[2,20,25,26] we have observed a quick oxygen isotopic exchange between gaseous $C^{16}O_2$ and solid n-doped $Ti^{18}O_2$. This reaction pathway consists of two steps:

$$Ti^{18}O_2\,(s) + C^{16}O_2\,(g) \rightarrow Ti^{16,18}O_2\,(s) + C^{16,18}O_2\,(g) \qquad (3)$$
$$Ti^{18}O_2\,(s) + C^{16,18}O_2\,(g) \rightarrow Ti^{16,18}O_2 + C^{18}O_2\,(g) \qquad (4)$$

The experimental conditions in the set-up described were similar to our previous study designed to investigate the isotopic exchange. The molar ratio between the gas phase molecules and the solid phase ($Ti^{18}O_2$) species was approximately 1:1000. According to our previous observations, $C^{16}O_2$ immediately reacted at the active sites (surface oxygen vacancies) of $Ti^{18}O_2$ and mutually exchanged the ^{18}O atoms from the titania framework. The $C^{16,18}O_2$ molecule appeared in the reaction mixture as an intermediate (see reaction (3)), and it was present in the gaseous mixture in low concentrations. Assuming that mechanism I is effective in our case, $C^{16,18}O_2$ would rather be the primary product than an intermediate of the ^{16}OCS conversion. In mechanism I, the pathway producing isotopologue $C^{16}O_2$ is absent, because a subsequent isotopic exchange step would involve the formation of $C^{18}O_2$ from $C^{16,18}O_2$ according to reaction (4). This scheme is in obvious disagreement with the spectra depicted in Figure 2, panel B, where all $C^{16}O_2$, $C^{16,18}O_2$ and $C^{18}O_2$ isotopologues have been identified. In contrast to mechanism I, in mechanism II, $C^{16}O_2$ is characterized by a disproportionation reaction according to Eq. (2). The $C^{16}O_2$ may subsequently undergo isotopic exchange reactions with the labelled titania via Eqs. (3) and (4), which leads to the formation of all possible CO_2 isotopologues. This latter scenario is in accordance with our observations.

b) *The number of $Ti^{18}O_2$ bulk defects is comparable to (or less than) the number of ^{16}OCS molecules* – atmospheric pressure experiment (760 Torr of OCS).

In parallel to the previous low pressure ^{16}OCS experiment, a reference high pressure experiment was carried out using 0.0125 mol of $Ti^{18}O_2$ and 0.017 mol of ^{16}OCS. An identical cell was filled with 1 g of vacuum-calcined $Ti^{18}O_2$ powder and blown with carbonyl sulphide until atmospheric pressure was reached. To achieve a

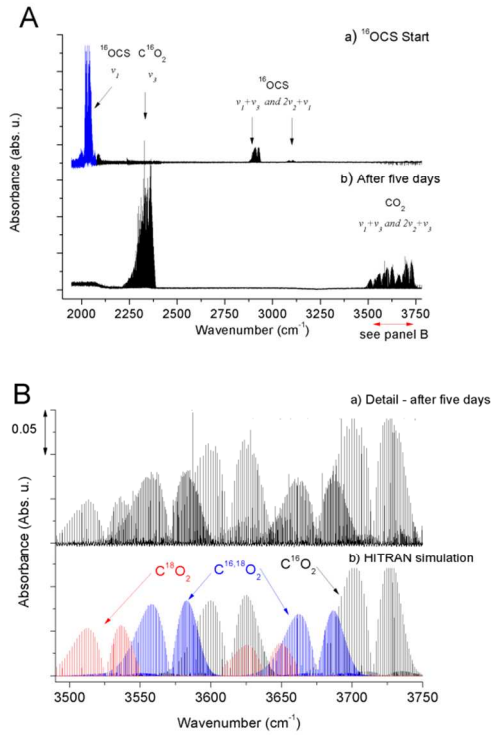

Figure 2: Spectra of the reaction mixture formed from 1.2 Torr ^{16}OCS kept over solid $Ti^{18}O_2$ are depicted in panel A at the beginning of the experiment (a) and after five days (b). All OCS has been completely exchanged to CO_2, and equilibrium has been achieved. Panel B shows details of the $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ bands of all CO_2 isotopologues. For comparison, the spectrum of CO_2 isotopologues was simulated using the Winproof program and parameters of the absorption lines taken from the HITRAN database.[28]

higher detection limit, 1 ml of the reaction mixture was analysed in the 30 m multipass cell using a high resolution Bruker IFS 120 spectrometer after one and six months. Initially, only traces of $C^{16}O_2$ were detected (see the weak band ν_3 in Figure 3, panel A, spectrum b). After the first month, the concentration of $C^{16}O_2$ gradually grew to 2 %, and after six months it reached 37 % (Figure 3, panel A, spectrum c). The ^{16}OCS molecule was present at a high concentration and reacted at the surface of the $Ti^{18}O_2$, where it filled the oxygen vacancies, according to reaction (2). The resulting CS_2 was adsorbed onto the $Ti^{18}O_2$ surface in the same manner as water,[20] hindering the subsequent isotopic exchange between $C^{16}O_2$ and $Ti^{18}O_2$. Only $C^{16}O_2$ from the parent ^{16}OCS remained in the mixture. The CS_2 was present in the gas phase at a 12 % concentration (compare to Figure 3, panel A, CS_2 standard spectrum a) and spectrum c).

The adsorption of CS_2 on the $Ti^{18}O_2$ surface changed the colour of the sample from the initial white-yellow to an ochre-brown after 6 months. This colour suggests the possible interaction of sulphur-containing species with TiO_2. However, no shifts of the characteristic $Ti^{18}O_2$ vibration bands were found in the Raman spectrum of the exposed sample, which was directly measured several times in the glass cell that contained ^{16}OCS. This confirms that the structure of titania remained essentially unchanged during the interaction with sulphur-containing species. The further exploration of titania surface using XPS analysis is described in the ESI supplementary material.

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Table 1: The concentrations of the individual gases of the samples formed in the cell containing ^{16}OCS and $Ti^{16}O_2$ (A450) at the beginning of the experiment.

Sample Description	CS_2	Molecule ^{16}OCS	$C^{16}O_2$	Spectrum (Figure 4)
Gas phase after 6 months	12%	52%	37%	c
Exposed for 4 days to 760 Torr of nitrogen	22%	30%	49%	d
Exposed for 1 day to 760 Torr of oxygen	36%	14%	49%	e
Exposed for 2 days to 760 Torr of oxygen	50%	0%	50%	f

To quantify the adsorbed CS_2, we repeated the previous experiment. The cell was again filled with ^{16}OCS until atmospheric pressure was reached. The gaseous mixture was measured after six months in a 30 m absorption cell using HR FT spectrometer in the spectral range of the strong fundamental bands of the CS_2 (see Figure 3). The cell was then evacuated and re-filled with nitrogen until atmospheric pressure. A small sample was analysed after four days, and several characteristic infrared bands (see Figure 3, panel A, spectrum d) of desorbed CS_2 were observed. This four day desorption of nitrogen resulted in 22 % CS_2 and 49 % $C^{16}O_2$ at the $Ti^{18}O_2$ surface. The quantitative data are summarised in Table 1. The colour of the $Ti^{16}O_2$ (A450) powder sample remained yellow-brown. The evacuation procedure was repeated, and the cell containing the still yellow-brown $Ti^{18}O_2$ was filled with pure oxygen. The high resolution spectra obtained after 1 and 2 days are depicted in Figure 3, panel A, spectra (e) and (f). A significant increase in the intensity of the CS_2 band near 1500 cm^{-1} is apparent. After 2 days (in an O_2 atmosphere), the gas sample only contained the mixture of CS_2 and CO_2: The concentration of CS_2 in the cell significantly increased to 36 % after 1 day and to 50 % after 2 days and the concentration of the isotopologue $C^{16}O_2$ increased to 49 and 50 %, respectively (see Figure 3, panel B). At this point, the reactant, ^{16}OCS, was no longer detected. Moreover, the TiO_2 sample returned to white. The results from the quantitative analysis of the reaction mixture are summarised in Table 1.

We propose a plausible mechanism for the disproportionation reaction using quantum chemical calculations (for details see the Supporting information) on a minimal model consisting of two coordinatively unsaturated Ti^{3+} centres, which may give rise to a triplet electronic configuration, in agreement with Refs. [7,12,13] Note that we also made numerous unsuccessful attempts to find a possible reaction pathway assuming singlet electronic configuration. The computed free energy profile of the reaction, along with the optimized geometries, are depicted in Figure 4 (Cartesian coordinates of all optimized geometries are listed in the Supporting Information). The reaction starts with the activation of the first OCS molecule upon binding to two adjacent Ti^{3+} surface sites in the fashion shown in structure 1, Figure 4. This is followed by the attack of a second gas-phase OCS molecule at the activated carbon of OCS, requiring an activation energy of 43.2 kcal/mol (structure 2 shows the transition state of this reaction step) and leading to the formation of a thiocarbonate-like intermediate (structure 3) bound over two Ti^{3+} centres. In the rate determining step, this intermediate isomerises via a four-centred transition state, shown in structure 4, which leads to the formation of a dithiocarbonate-like intermediate (structure 5). The relatively high activation energy of this reaction step, i.e., 63.7 kcal/mol, concurs with the experimentally observed low reaction rates. In the next reaction step, this intermediate decomposes to CS_2 and CO_2 bound to two adjacent Ti^{3+} centres (structure 7) in a quick reaction step via a transition state shown in structure 6.

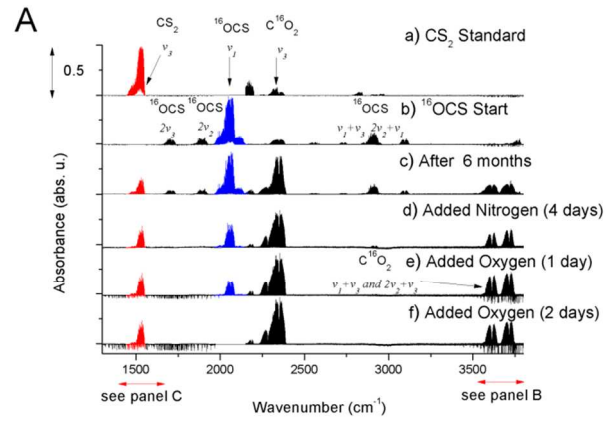

Figure 3: Spectra of the reaction mixture formed from 760 Torr of ^{16}OCS kept over solid $Ti^{18}O_2$ are depicted in panel A. The experimental spectra are compared with the spectrum of CS_2 standard (a). The spectrum in the beginning of the experiment is marked (b). After one week, new bands of $C^{16}O_2$ and CS_2 emerge (c). The most intense ν_1 band of CS_2 and the fundamental ^{16}OCS band[29,30] are highlighted red and blue, respectively. The intensity of the CS_2 band increases due to desorption of this molecule into the gas phase in the presence of nitrogen (d) and oxygen (e). The maximum desorption of CS_2 was achieved in the presence of 760 Torr of oxygen during the period of two days (f). A detailed view of the $C^{16}O_2$ and CS_2 ν_3 bands is presented ESI.

Finally, the high-energy intermediate 7 releases a CO_2 molecule, which leads to the final product of the reaction, i.e., CS_2 adsorbed over two Ti^{3+} catalytic centres. Whereas the high (63.7 kcal/mol) activation energy of the rate-determining step indicates slow kinetics of the entire conversion process, the total free energy change is only 6.5 kcal/mol. This explains why the reaction proceeds despite the low reaction rates, practically without external heat administration.[†]

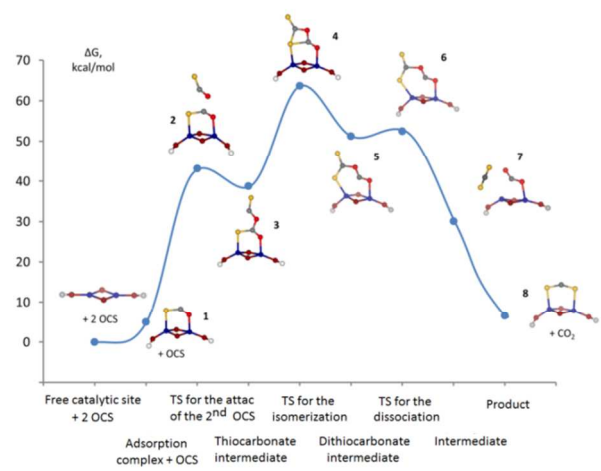

Figure 4: The calculated free energy profile of the disproportionation reaction. Computations were carried out at the B3LYP level of theory using the aug−cc−pVTZ basis set on all atoms except Ti, which was described with the Stuttgart small core relativistic pseudo-potential.[30] For computational details, see the Supporting information. Colour coding: ^{16}O light red, ^{18}O dark red, S yellow, C grey, H white, Ti blue.

Conclusions

In summary, we describe the conversion of OCS to CO_2 and CS_2 over the surface of partly reduced titania. The experiments indicate that the reaction does not involve lattice oxygen atoms. Quantum

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chemical calculations suggest a reaction pathway, in which a pair of Ti^{3+} centres catalyses the disproportionation of two OCS molecules. The main advantage of the chemistry presented here is that it proceeds spontaneously, albeit on longer timescales.

Notes and references

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† The B3LYP-calculations for this system are of a rather qualitative character. However, none of the currently available multireference codes are able to treat these systems at a higher level.

Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

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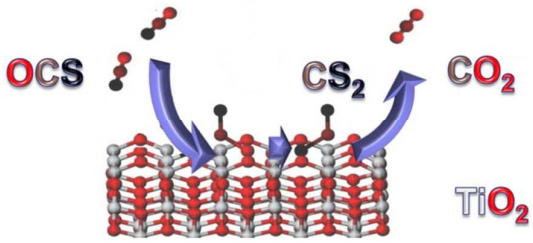
Spontaneous OCS disproportionation on the anatase surface has been observed and the mechanism has been explained using quantum chemical calculations.



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