ChemComm

COMMUNICATION



View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2014, 50, 7712

Received 17th March 2014, Accepted 9th May 2014

DOI: 10.1039/c4cc01992j

www.rsc.org/chemcomm

Room temperature spontaneous conversion of OCS to CO_2 on the anatase TiO₂ surface[†]

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High-resolution FT-IR spectroscopy combined with quantum chemical calculations was used to study the chemistry of OCSdisproportionation over the reduced surface of isotopically labelled, nanocrystalline TiO₂. 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 Ti³⁺ centres mediate the reaction of the adsorbed OCS molecules.

Titanium dioxide, TiO_2 , is one of the most versatile oxide materials and is used in a wide variety of applications.¹⁻¹³

The reactions of gaseous carbonyl sulphide (OCS) are of potential importance in atmospheric chemistry. OCS is a predominant sulphur-containing compound in the troposphere (a mixing ratio of 500 pptv).¹⁴ Approximately 0.64 Tg per year 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 less harmful species by reactions like catalytic dismutation is an on-going research challenge. In this paper we describe the conversion of OCS to CO₂ and CS₂ which is a model reaction of this kind. We show that the reaction occurs efficiently over the surface of partly reduced (n-doped) nanocrystalline TiO₂ (anatase) acting as a catalyst.

The partly reduced form of titania can be prepared by the thermal treatment of TiO_2 in a 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 Ti⁴⁺ to Ti³⁺. The resulting spin multiplicity can be a closed-shell singlet or an open-shell singlet and a 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.^{5–8,16–21}

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.^{21–23} For this purpose, we synthesised anatase isotopologues:^{2,24,25} Ti¹⁶O₂, Ti¹⁷O₂ and Ti¹⁸O₂. In the present study, we have extended this approach to examine the interaction of ¹⁶OCS with Ti¹⁸O₂ and describe the reactivity at the molecular level.

Similarly to our previous studies focused on the reactivity of reduced titania with CO_2 ,^{11,25–27} (which is a homologue of OCS), High resolution 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 ¹⁶OCS with nanocrystalline $Ti^{18}O_2$. They differed by the ratio of OCS/TiO₂, *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 ¹⁶OCS gas molecules – low pressure experiment (1.2 Torr of ¹⁶OCS).

One gram of vacuum-calcinated Ti¹⁸O₂ (450 °C) was placed in the IR optical cell with 1.2 Torr of ¹⁶OCS (99%). The spectra were obtained every 120 seconds using an InSb detector, in the spectral range of the main CO₂–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 ¹⁶OCS with solid Ti¹⁸O₂ (0.000146 mol OCS and 0.0125 mol Ti¹⁸O₂ respectively) is depicted in Fig. 1. During the reaction, the partial pressure of ¹⁶OCS significantly decreased, while new products appeared: C¹⁶O₂, C^{16,18}O₂ and C¹⁸O₂, with traces of ¹⁸OCS. After 5 days, the reaction gas mixture consisted of 45.8% C¹⁶O₂, 42.2% C¹⁸O₂, 3.2% C^{16,18}O₂ and 8.8% ¹⁶OCS, with traces of ¹⁸OCS. Gaseous CS₂ was not observed.

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4cc01992j

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

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

(I) Conversion of OCS to CO_2 with the involvement of ¹⁸O from titania:

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

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

$$2^{16} \text{OCS}(g) \xrightarrow{\text{Ti}^{18} \text{O}_2} \text{C}^{16} \text{O}_2(g) + \text{CS}_2$$
(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:

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

$$\mathrm{Ti}^{18}\mathrm{O}_2(s) + \mathrm{C}^{16,18}\mathrm{O}_2(g) \to \mathrm{Ti}^{16,18}\mathrm{O}_2 + \mathrm{C}^{18}\mathrm{O}_2(g) \tag{4}$$

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 (Ti¹⁸O₂) species was approximately 1:1000. According to our previous observations, C¹⁶O₂ immediately reacted at the active sites (surface oxygen vacancies) of Ti¹⁸O₂ and mutually exchanged the ¹⁸O atoms from the titania framework. The C^{16,18}O₂ 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}O₂ would rather be the primary product than an intermediate of the ¹⁶OCS conversion. In mechanism I, the pathway producing isotopologue C¹⁶O₂ is absent, because a subsequent isotopic exchange step would involve the formation of C18O2 from $C^{16,18}O_2$ according to reaction (4). This scheme is in obvious disagreement with the spectra depicted in Fig. 2, panel B, where all C16O2, C16,18O2 and C18O2 isotopologues have been identified. In contrast to mechanism I, in mechanism II, C¹⁶O₂ is characterized by a disproportionation reaction according to eqn (2). The $C^{16}O_2$ may subsequently undergo isotopic exchange reactions with the labelled titania via eqn (3) and (4), which leads to the formation of all possible CO₂ isotopologues. The latter scenario is in accordance with our observations.





Fig. 2 Spectra of the reaction mixture formed from 1.2 Torr ¹⁶OCS kept over solid Ti¹⁸O₂ are depicted in panel A at the beginning of the experiment (a) and after five days (b). All OCS has been completely exchanged to CO₂, and equilibrium has been achieved. Panel B shows details of the $v_1 + v_3$ and $2v_2 + v_3$ bands of all CO₂ isotopologues. For comparison, the spectrum of CO₂ isotopologues was simulated using the Winproof program and parameters of the absorption lines taken from the HITRAN database.²⁸

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

In parallel to the previous low pressure ¹⁶OCS experiment, a reference high pressure experiment was carried out using 0.0125 mol of Ti¹⁸O₂ and 0.017 mol of ¹⁶OCS. An identical cell was filled with 1 g of vacuum-calcined Ti¹⁸O₂ powder and blown with carbonyl sulphide until atmospheric pressure was reached. To achieve a higher detection limit, 1 ml of the reaction mixture was analysed in a 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 v_3 in Fig. 3, panel A, spectrum b). After the first month, the concentration of C¹⁶O₂ gradually grew to 2%, and after six months it reached 37% (Fig. 3, panel A, spectrum c). The ¹⁶OCS molecule was present at a high concentration and reacted at the surface of the Ti¹⁸O₂, where it filled the oxygen vacancies, according to reaction (2). The resulting CS₂ was adsorbed onto the Ti¹⁸O₂ 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 ¹⁶OCS remained in the mixture. The CS₂ was present in the gas phase at a 12% concentration (compare Fig. 3, panel A, CS₂ 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



Fig. 3 Spectra of the reaction mixture formed from 760 Torr of ¹⁶OCS kept over solid Ti¹⁸O₂ are depicted in panel A. The experimental spectra are compared with the spectrum of the CS₂ standard (a). The spectrum in the beginning of the experiment is marked (b). After one week, new bands of C¹⁶O₂ and CS₂ emerge (c). The most intense v_1 band of CS₂ and the fundamental ¹⁶OCS band^{29–31} are highlighted red and blue, respectively. The intensity of the CS₂ 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 CS₂ was achieved in the presence of 760 Torr of oxygen during the period of two days (f). A detailed view of the C¹⁶O₂ and CS₂ v_3 bands is presented in the panels B and C, respectively, which are shown in the ESI.†

6 months. This colour suggests the possible interaction of sulphur-containing species with TiO₂. However, no shifts of the characteristic Ti¹⁸O₂ vibration bands were found in the Raman spectrum of the exposed sample, which was directly measured several times in the glass cell that contained ¹⁶OCS. This confirms that the structure of titania remained essentially unchanged during the interaction with sulphur-containing species. The further exploration of the titania surface using XPS analysis is described in the ESI.[†]

To quantify the adsorbed CS_2 , we repeated the previous experiment. The cell was again filled with ¹⁶OCS until atmospheric pressure was reached. The gaseous mixture was measured after six months in a 30 m absorption cell using a HR FT spectrometer in the spectral range of the strong fundamental bands of CS_2 (see Fig. 3). The cell was then evacuated and re-filled with nitrogen until atmospheric pressure was reached. A small sample was analysed after four days, and several characteristic infrared bands (see Fig. 3, panel A, spectrum d) of desorbed CS₂ were observed. This four day desorption of nitrogen resulted in 22% CS₂ and 49% C¹⁶O₂ at the Ti¹⁸O₂ 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 Ti¹⁸O₂ was filled with pure oxygen. The high resolution spectra obtained after 1 and 2 days are depicted in Fig. 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 O₂ atmosphere), the gas sample only contained the mixture of CS₂ and CO₂: the concentration of CS₂ in the cell significantly increased to 36% after 1 day and to 50% after 2 days and the concentration of the isotopologue C¹⁶O₂ increased to 49 and 50%, respectively (see Fig. 3 and panel B in the ESI[†]). At this point, the reactant, ¹⁶OCS,

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	$\begin{array}{c} \mathrm{CS}_2 \ (\%) \end{array}$	Molecule ¹⁶ OCS (%)	$C^{16}O_2$ (%)	Spectrum (Fig. 4)
Gas phase after 6 months	12	52	37	с
Exposed for 4 days to	22	30	49	d
760 Torr of nitrogen				
Exposed for 1 day to	36	14	49	e
760 Torr of oxygen				
Exposed for 2 days to	50	0	50	f
760 Torr of oxygen				

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 ESI[†]) on a minimal model consisting of two coordinatively unsaturated Ti³⁺ centres, which may give rise to a triplet electronic configuration, in agreement with ref. 7, 12 and 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, is depicted in Fig. 4 (Cartesian coordinates of all optimized geometries are listed in the ESI[†]). 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, Fig. 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^{-1} (structure 2 shows the transition state of this reaction step) and leading to the formation of a thiocarbonatelike intermediate (structure 3) bound over two Ti³⁺ 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).



Fig. 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 ESI.[†] Colour coding: ¹⁶O light red, ¹⁸O dark red, S yellow, C grey, H white, Ti blue.

The relatively high activation energy of this reaction step, *i.e.*, 63.7 kcal mol⁻¹, 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**.

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⁻¹) 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⁻¹. This explains why the reaction proceeds despite the low reaction rates, practically without external heat administration.‡

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 chemical calculations suggest a reaction pathway, in which a pair of Ti³⁺ 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.

This work was supported by the Grant Agency of the Czech Republic (No. P108/12/0814) and by the Ministry of Education, Youth and Sports of the Czech Republic (Nos LD14115 and LD13060, COST CM1104).

Notes and references

[‡] 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.

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