Mechanism of ethylene oxychlorination over ruthenium oxide

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A B S T R A C T

The oxychlorination of ethylene is an industrially relevant process within the manufacture of polyvinyl chloride (PVC). Although RuO₂ is the best performing catalyst for the Deacon process ($4\text{HCl} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Cl}_2$), experiments demonstrate a modest activity in the selective oxychlorination to vinyl chloride, favouring oxidation and polychlorinated saturated products. From the computational modelling three main contributions are found to control the performance: (i) coverage effects that alter the configuration of intermediates; (ii) the monodimensional arrangement of the active sites, in which the reaction of coadsorbed species works on a “first-come, first-served” basis; and (iii) the high reactivity of the oxygen species. Competition between oxidation and chlorination processes results in variable selectivity, depending on the reaction conditions (particularly temperature and reactant partial pressures), which influence the surface composition. From the analysis of the complex reaction network, the essential requirements for a good oxychlorination catalyst are formulated.

1. Introduction

RuO₂ is an active catalytic material in a variety of processes, including catalytic CO [1–3], NH₃ [4], alcohol [5], and Hg oxidation [6], as well as in electrochemical phenolic wastewater oxidation [7], or as an anode in water splitting cells [8]. In addition to its electrochemical applications [9,10], one of the most significant industrial uses of RuO₂ is in HCl oxidation (Deacon process), where it is the best performing catalyst to produce molecular chlorine at low temperature [11–14]. Therefore, the chemistries of oxygen and chlorine on the RuO₂ surfaces are intertwined, as evidenced by the linear scaling relationships (Cl and O energies scale one with the other) [15,16] and thus the material is prone to exhibit a complex selectivity behaviour. In fact, when seawater is employed in a RuO₂-based electrochemical water splitting cell, the selectivity towards the O₂ evolution reaction is compromised as Cl₂ evolution emerges as a competitive path [10,15,17,18].

Given this ability to activate adsorbates such as HCl, O₂, and hydrocarbons [19], RuO₂ could potentially be a suitable catalyst for chlorination or oxychlorination reactions. This is especially relevant as polyvinyl chloride (PVC) production represented a market of 53 billion USD in 2015, still expected to grow at an annual rate of 5% in the coming years [20]. Therefore, vinyl chloride (VCM), the

monomer of PVC or its intermediate 1,2-dichloroethane (commonly known as ethylene dichloride, EDC) are target synthetic platform molecules. To date, VCM is either produced through hydrochlorination of acetylene [21,22], or derived from EDC through energy-intensive thermal cracking [23]. The latter process releases HCl in equimolar amounts to VCM, making HCl recovery crucial for sustainable large-scale PVC production. One way to recycle this HCl is by using it as a reactant together with O₂ in ethylene oxychlorination in order to produce EDC (or directly VCM) [13,23,24].

The current industrial catalyst for ethylene oxychlorination comprises cupric chloride (CuCl₂) as the active phase, impregnated on a porous support such as alumina, and promoted by numerous additives to reduce the metal loss and/or improve the activity and selectivity [25–28]. However, even though these cupric chloride catalysts are widely applied in industry due to their remarkable selectivity towards EDC (99%), they still suffer from active phase volatilisation or particle stickiness [29]. Previous efforts to describe the mechanism of ethylene oxychlorination on classical CuCl₂-based catalysts usually included *in situ* and *operando* characterisation by XAFS, XANES, and IR or EPR spectroscopies [30–35]. Briefly, the process follows a redox mechanism in three steps: chlorination of ethylene by reduction of CuCl₂ to CuCl, that then forms a cupric oxychloride, and finally CuCl₂ is recovered by re-chlorination of the oxychloride with HCl [24,26,27,30,31,33–43].

More recently, metal oxides like RuO₂, IrO₂, and CeO₂ were reported as active but very diverse in selectivity [44,45]. Whilst

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IrO_2 leads only to combustion of ethylene to CO and CO_2 , RuO_2 and CeO_2 exhibited formation of EDC and VCM (the combined selectivity at same conversion level of 10% is 10% and 98%, respectively) along with CO_x [44]. Alternatively, some catalysts based on lanthanide oxychlorides were found active for one-step VCM synthesis, of which EuOCl emerged as an excellent oxychlorination catalyst, achieving a VCM selectivity up to 100%, but at comparatively lower conversions [45]. Nevertheless, the mechanism of oxychlorination on these materials remains unknown, which hinders the catalyst design to overcome their specific drawbacks. A recent review highlights the challenges presented by catalytic oxyhalogenation processes [46].

In this study, we intend to shed light on the complex ethylene oxychlorination reaction network by combining state-of-the-art Density Functional Theory (DFT) calculations and a selected set of catalytic experiments to gain insight on the behaviour of RuO_2 in a broad range of operating conditions. Thus far, there is no mechanistic study of oxides in ethylene oxychlorination and RuO_2 presents a relatively uncomplicated electronic (conductive) and geometric (rutile) structure, allowing the extended investigation of the complete reaction network, which comprises (de-)chlorination, (de-)hydrogenation, and oxidation reactions (encompassing a total of 34 elementary steps). The main network characteristics could in the future be simplified when investigating other materials like CeO_2 or EuOCl , which are more appealing but present a more complex electronic structure. Furthermore, RuO_2 exhibits both oxychlorination and combustion activity, making it an ideal system to investigate the interplay between these two competing processes. Whilst recent theoretical studies suggest that surface uptake of Cl by RuO_2 is limited [47], previous combined experimental and theoretical investigations found that the Cl uptake is significant and does play some role in affecting HCl oxidation performance. Specifically, *operando* prompt gamma activation analysis (PGAA) studies show that under typical reaction conditions, Cl is present in considerable quantities in the catalyst sample [48,49]. Moreover, more recent theoretical *ab initio* thermodynamics studies suggest that the experimentally observed Cl uptake is limited to surface replacement of bridging oxygen atoms and the undercoordinated Ru positions and is present under typical reaction conditions [50]. Hence, whilst the kinetics of RuO_2 in oxychlorination are as yet unknown, it is reasonable to assume that the degree of chlorination may very well play an important role in oxychlorination activity, as much as it is believed to affect HCl oxidation performance [48]. Moreover, oxychlorination has profited once before from the inheritance of the original Deacon catalyst [25–28] and bears the potential to profit again from the recent major leap in HCl oxidation, i.e. the implementation of outstanding low-temperature catalysts $\text{RuO}_2/\text{TiO}_2$ -rutile and $\text{RuO}_2/\text{SnO}_2$ -cassiterite [14,51]. As such, this progress inspires the present work to develop a full understanding of ethylene oxychlorination on RuO_2 and derive intrinsic requirements for a good VCM production catalyst.

2. Materials and methods

2.1. Computational details

Density Functional Theory (DFT) as implemented in the Vienna *Ab initio* Simulation Package (VASP), version 5.3.3, was applied to bulk RuO_2 [52,53]. The ionic positions and cell volume were optimised for a cell containing two formula units, using a plane-wave cut-off of 600 eV and a k-point sampling mesh of $9 \times 9 \times 13$, employing the Monkhorst and Pack scheme [54]. The optimised bulk lattice parameters obtained ($a = b = 4.520$ Å, $c = 3.118$ Å) are in good agreement with experimental values

obtained from single-crystal X-ray diffraction; the difference between calculated lattice parameters and the experimental values is less than 0.7% [55]. From the optimised bulk structure, slabs representing the lowest energy rutile (1 1 0) facet of RuO_2 were constructed. Previous works have established that the (1 1 0) facet is the most stable, and hence it forms the largest contribution to the surface of polycrystalline RuO_2 , therefore being the most representative of the main component of surface activity [56]. A $p(4 \times 1)$ supercell was employed, with a k-point sampling of $2 \times 4 \times 1$. A slab consisting of five layers, interleaved by 15 Å of vacuum, was used. The top two layers of the slab were optimised, whilst the remaining bottom three were fixed. Two distinct surface environments were identified for both Ru and O (Fig. S1). Oxygen atoms are present as rows of 2-coordinate “bridging” oxygen atoms (O_b) on the surface, as well as 3-coordinate atoms lying within the plane of the surface. For Ru, 6-coordinate centres are present located beneath the O_b atoms, whilst 5-coordinate unsaturated sites (Ru_{cus}) provide the main adsorption sites for catalytic activity. Owing to their coordinatively unsaturated nature, the O_b and Ru_{cus} sites play the most important roles in catalysis. Forces were converged to within 0.015 eV Å^{-1} . In order to eliminate the spurious electrostatic interactions associated with asymmetric relaxation of the slab, a dipole correction was applied to the vacuum. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was employed throughout [57]. Inner electrons were replaced with projector augmented-wave (PAW) [58], and the valance states were expanded in plane-waves with a cut-off energy of 450 eV. The chosen functionals provide a reasonable reproduction of experimental results [48,59]. Transition states were identified using the climbing image nudged elastic band (CI-NEB) method [60], and vibrational analyses performed numerically with a step of 0.015 Å. Structures are available through the ioChem-BD repository [61,62].

To analyse the complete reaction network, a simple microkinetic (MK) model was set up based on our previous models for the Deacon reaction [49]. Rate coefficients of the elementary steps were determined using the thermodynamic and kinetic parameters obtained from the DFT calculations. The gas-phase entropies were taken from the NIST database [63], the attempt frequency for the rate calculations was set to 10^{13} for simplicity, and the Knudsen equation was taken for adsorption. Then MK simulations were performed using a batch-model reactor; further details can be found in Ref. [49]. In the MK simulations, the initial relative pressures and temperatures correspond to those employed experimentally, and the initial conditions are described in the text. The reaction order of HCl at the experimental 623 K conditions was derived from the MK models.

2.2. Experimental details

Commercial RuO_2 (Sigma-Aldrich, 99.9%) was calcined at 723 K in static air using a heating rate of 5 K min^{-1} and an isothermal step of 5 h prior to its catalytic evaluation. The gas-phase HCl oxidation and ethylene oxychlorination were investigated at ambient pressure in a continuous-flow fixed-bed reactor. The set-up consists of (i) mass flow controllers to feed C_2H_4 (PanGas, 20.15% in He), HCl (Air Liquide, purity 2.8, anhydrous), O_2 (Messer, 10.06% in He), He (PanGas, purity 5.0) as a carrier gas, and Ar (PanGas, purity 5.0) as an internal standard; (ii) an electrically heated oven hosting a quartz micro-reactor equipped with a K-type thermocouple whose tip reaches the centre of the catalyst bed; (iii) downstream heat tracing to avoid any condensation of the reactants and products; and (iv) a gas chromatograph coupled to a mass spectrometer (GC-MS) for on-line analysis. The effluent stream was neutralised by passing it through an impinging bottle containing an aqueous NaOH solution (1 M). The catalyst ($W_{\text{cat}} = 0.5 \text{ g}$,

particle size, $d_p = 0.4\text{--}0.6$ mm), diluted with quartz particles ($W_{\text{quartz}} = 2.5$ g, $d_p = 0.2\text{--}0.3$ mm, calcined at 1173 K) was loaded in the micro-reactor (10 mm inner diameter) and pretreated in He at 473 K for 30 min. Thereafter, a total flow (F_T) of $100\text{ cm}^3\text{ STP min}^{-1}$ containing 3 vol% C_2H_4 , 1–9 vol% HCl, 0–6 vol% O_2 , and 3 vol% Ar, balanced in He was fed to the reactor at a bed temperature (T) of 460–773 K and pressure (P) of 1 bar. Note that relatively low feed concentrations were selected to prevent corrosion, enable safe handling, and minimise the formation of hot spots in the catalyst bed due to the high reaction exothermicity. The standard conditions of 3 vol% C_2H_4 , 3 vol% HCl, and 1.5 vol% O_2 were chosen to reflect the reaction stoichiometry to form VCM (see Eq. (5), Table 1). Prior to the analysis of the reaction mixtures, the catalysts were equilibrated for at least 1 h under each condition. The gas composition at the reactor outlet containing reactants (C_2H_4 , O_2 , HCl) and products (EDC, VCM, CO, CO_2 , ethyl chloride (EC), 1,2-dichloroethene (1,2-DCE)) was analysed online using a gas chromatograph equipped with a GS-CarbonPLOT column coupled to a mass spectrometer (Agilent GC 7890B, Agilent MSD 5977A) with a triple-axis detector and an electron multiplier. In the oxidation tests, HCl (3 vol%) and O_2 were fed in a 1:2 volumetric ratio. The Cl_2 production was quantified by offline iodometric titration (using a Mettler Toledo G20 Compact Titrator) of triiodide, formed by purging the Cl_2 containing reactor outlet through an aqueous KI (Sigma-Aldrich, 99.5%) solution (0.1 M), with 0.01 M sodium thio-sulfate solution (Sigma-Aldrich, 99.99%). Further details on the calculation of conversions and selectivities are given in the [Supplementary Material](#).

3. Results

As shown in Table 1, the reactions above differ in the stoichiometry for O_2 and HCl. Among them, the most exothermic one is the irreversible oxidation of ethylene, thus this process represents a thermodynamic sink, whilst the formation of EDC, VCM, and 1,2-DCE are exothermic by a similar amount, much higher than HCl oxidation. In the following, we will analyse the reaction schemes that drive the selectivity of the reaction network, first by describing the experimental data for RuO_2 , making comparison with other well-known Deacon catalysts, and then by the detailed evaluation of the reaction profile through first-principles simulations.

In order to link HCl oxidation and ethylene oxychlorination behaviour, both processes were compared in a continuous-flow fixed-bed reactor at a temperature T_{20} , where the catalyst reaches 20% ($\pm 1\%$) conversion in the respective reactions (Fig. 1a). The T_{20} of ethylene oxychlorination over RuO_2 is 623 K, substantially higher than for the Deacon process (462 K). A stability test confirmed the catalyst stability of the discussed ethylene oxychlorination conditions at 623 K, exhibiting constant conversion and selectivities during 50 h (Fig. S2a). In addition, previous work showed that bulk RuO_2 continues to perform well as a HCl oxidation catalyst up to 673 K [56]. Comparatively, RuO_2 is more active than IrO_2 or CeO_2 for both processes, especially for HCl oxidation

Fig. 1. (a) T_{20} of HCl oxidation (white bar) and ethylene oxychlorination (grey bar) over RuO_2 . Conditions: $W_{\text{cat}} = 0.5$ g; $F_T = 100\text{ cm}^3\text{ STP min}^{-1}$ containing 3 vol% HCl and 6 vol% O_2 for HCl oxidation, 3 vol% C_2H_4 , 3 vol% HCl, and 1.5 vol% O_2 for oxychlorination at $P = 1$ bar, each point was stabilised for 2 h on stream. Conversion and selectivity versus (b) temperature with 3 vol% C_2H_4 , 3 vol% HCl, and 1.5 vol% O_2 , and (c) volumetric HCl and O_2 feed contents at $T = 623$ K with 3 vol% C_2H_4 , 1–9 vol% HCl, 1.5 vol% O_2 and 3 vol% C_2H_4 , 3 vol% HCl, 0–6 vol% O_2 . Other conditions as in (a).

[44,45,64]. In terms of selectivity, RuO_2 exhibits mostly combustion to CO_2 , but also shows some a limited degree of chlorinated hydrocarbon formation (Fig. 1b). By comparison, IrO_2 , the least active, exhibits purely combustion of C_2H_4 to CO, and CO_2 (the major product). CeO_2 , like RuO_2 , shows formation of both combustion products and chlorinated hydrocarbons, with selectivity towards EDC prevailing [44]. None of the three catalysts exhibit Cl_2 formation under oxychlorination conditions, but most likely for different reasons. On IrO_2 and RuO_2 , consumption of O_2 for combustion is strongly favoured over HCl oxidation, whilst on

Table 1

List of reactions that take place competitively on the surface of the catalyst and their enthalpies as obtained from the NIST database [63].

No.	Reaction	Equation	$\Delta H/\text{kJ mol}^{-1}$
1	HCl oxidation	$4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$	–114
2	Ethylene oxidation	$\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$	–1323
3	EC synthesis	$\text{C}_2\text{H}_4 + \text{HCl} \rightarrow \text{C}_2\text{H}_5\text{Cl}$	–69
4	EDC synthesis	$\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 + 2\text{HCl} \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 + \text{H}_2\text{O}$	–242
5	VCM synthesis	$\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 + \text{HCl} \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{H}_2\text{O}$	–180
6	1,2-DCE (Z/E) synthesis	$\text{C}_2\text{H}_4 + \text{O}_2 + 2\text{HCl} \rightarrow \text{C}_2\text{H}_2\text{Cl}_2 + 2\text{H}_2\text{O}$	–353
7	EDC dehydrochlorination	$\text{C}_2\text{H}_4\text{Cl}_2 \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$	+62

CeO₂ most of the Cl is consumed in the formation of EDC and VCM under these conditions (HCl is substoichiometric with respect to EDC). This result, in addition to previous works [19,44,45,64], suggests that contrary to expectations, a good Deacon catalyst may not necessarily be a good oxychlorination catalyst, but the reasons behind this were not investigated. Thus, we picked the best Deacon catalyst, RuO₂, which exhibits only moderate oxychlorination performance, for further investigation in order to identify the limitations.

A variation of temperature from 693 K to 473 K (Fig. 1b) revealed that the conversion stays constant at about 20% until 623 K before it significantly drops to 7% and less. At high temperatures, combustion products dominate, with CO only being formed at the highest investigated temperature, whilst at low temperature until 523 K only EDC is observed. Even though VCM formation is favoured at higher temperatures in ethylene oxychlorination (Fig. S2), it is formed only in the temperature window of 523–653 K, exhibiting a maximum at 573 K. Considering the temperature with still significant VCM formation and already about 20% conversion (623 K), the HCl feed content was varied from 1 to 9 vol%, in order to achieve a similar coverage history of the sample from low to high chlorine coverage as in the temperature variation.

Across the range of feed HCl concentrations, the conversion stays approximately constant, exhibiting a small minimum at 3 vol% HCl (Fig. 1c). With rising HCl content, the selectivity to CO₂ is decreased linearly (order –1 with respect to HCl) and the selectivity to EDC shows a first order dependence to HCl. VCM exhibits

a first order behaviour as well, although with a lower slope with respect to EDC. The formation of CO is not observed. In HCl oxidation the conversion was found to exhibit a 0.2 order on HCl [49].

In order to rationalise the experimentally observed temperature and input feed composition dependence of the catalyst selectivity, DFT calculations were performed simulating the surface under low Cl coverage conditions, probing the energetics of the relevant elementary processes. A large reaction network was studied, considering processes involving both chlorination and oxidation of C₂H₄, separately and in conjunction. Deacon-type processes take place under the reaction conditions, with HCl and O₂ dissociative adsorption being prerequisites for further reaction with C₂H₄, as well as HCl being oxidised by O₂ to Cl₂ and H₂O as in the standard Deacon process. A summary of the complete reaction network is presented in Fig. 2.

Firstly, the processes that are common to both the Deacon and oxychlorination reactions are summarised in Table 2 and denoted by Roman numerals. Adsorption of O₂ is exothermic by –1.20 eV (process I, Table 2), with subsequent dissociation to 2O** also being exothermic by an extra –0.74 eV with an activation barrier of 0.28 eV (process II, Table 2). Dissociative adsorption of HCl is exothermic by –1.79 eV (process III, Table 2), with H being abstracted by bridging O atoms (O_b) present on the catalyst surface. In the Deacon process, Cl recombination yields the product Cl₂ which subsequently desorbs from the surface (process IV, Table 2). Surface H arising from HCl dissociative adsorption leaves the surface in the form of water, with H transferring from bridging O sites

Fig. 2. Reaction network for the processes investigated. Deacon-type processes, which are common to all of the reaction pathways, are omitted for clarity. Adsorption and desorption processes are omitted for similar reasons. Numbers refer to processes in Table 2. Possible end products are color-coded. The starting point (C₂H₄) and the observed products are also indicated with bold boxes.

Table 2Reaction and activation energies (ΔE and E_a in eV) for various elementary steps and imaginary frequencies (cm^{-1}) of the corresponding transition states.

No.	Reaction	ΔE	E_a	ν_i
<i>HCl oxidation</i>				
I	$\text{O}_2 + 2^* \rightarrow \text{O}_2^{**}$	−1.20	–	–
II	$\text{O}_2^* \rightarrow 2\text{O}^*$	−0.74	0.28	538
III	$\text{HCl} + \text{O}_b + ^* \rightarrow \text{Cl}^* + \text{O}_b\text{H}$	−1.79	–	–
IV	$\text{Cl}^* + \text{Cl}^* \rightarrow \text{Cl}_2 + 2^*$	+2.23	–	–
V	$\text{O}^* + \text{O}_b\text{H} \rightarrow \text{OH}^* + \text{O}_b$	−0.02	0.35	1073
VI	$\text{OH}^* + \text{O}_b\text{H} \rightarrow \text{H}_2\text{O}^* + \text{O}_b$	−0.11	0.18	845
VII	$\text{H}_2\text{O}^* \rightarrow \text{H}_2\text{O} + ^*$	+1.12	–	–
<i>C₂H₄ chlorination</i>				
A1	$\text{C}_2\text{H}_4 + ^* \rightarrow \text{C}_2\text{H}_4^*$	−0.66	–	–
1	$\text{C}_2\text{H}_4 + \text{Cl}^* \rightarrow \text{C}_2\text{H}_4\text{Cl}^* + ^*$	+0.14	0.26	201
2	$\text{C}_2\text{H}_4\text{Cl}^* + \text{O}_b\text{H} \rightarrow \text{C}_2\text{H}_5\text{Cl}^* + \text{O}_b$	+0.23	0.96	1345
A2	$\text{C}_2\text{H}_5\text{Cl}^* \rightarrow \text{C}_2\text{H}_5\text{Cl} + ^*$	+0.61	–	–
3	$\text{C}_2\text{H}_4\text{Cl}^* + \text{O}_b \rightarrow \text{VCM}^* + \text{O}_b\text{H}$	−0.21	1.07	1555
A3	$\text{VCM}^* \rightarrow \text{VCM} + ^*$	+0.88	–	–
4a	$\text{C}_2\text{H}_4\text{Cl}^* + \text{Cl}^* \rightarrow \text{EDC}^* + ^*$	+0.17	1.85	193
4b [†]	$\text{C}_2\text{H}_4\text{Cl}^* + \text{Cl}^* \rightarrow \text{EDC}^* + ^*$	−0.87	0.00	–
A4	$\text{EDC}^* \rightarrow \text{EDC} + ^*$	+0.71	–	–
<i>C₂H₄ oxidation</i>				
5	$\text{C}_2\text{H}_4 + \text{O}^* \rightarrow \text{OMME}^{**}$	−0.55	0.35	261
6	$\text{OMME}^{**} \rightarrow \text{CH}_3\text{CHO}^* + ^*$	−0.88	1.22	990
A5	$\text{CH}_3\text{CHO}^* \rightarrow \text{CH}_3\text{CHO} + ^*$	+0.90	–	–
7	$\text{OMME}^{**} \rightarrow \text{CH}_2^* + \text{H}_2\text{CO}^*$	+0.96	1.06	71
8	$\text{CH}_2^* + \text{O}^* \rightarrow \text{H}_2\text{CO}^* + ^*$	−1.30	0.02	71
9	$\text{H}_2\text{CO}^* + \text{O}^* \rightarrow \text{OCH}_2\text{O}^{**}$	−0.89	0.00	–
10	$\text{OCH}_2\text{O}^{**} + \text{O}_b \rightarrow \text{OCHO}^* + \text{O}_b\text{H} + ^*$	−2.30	0.54	1358
11a	$\text{OCHO}^* + \text{O}_b \rightarrow \text{CO}_2^* + \text{O}_b\text{H}$	−0.04	1.70	1169
11b [†]	$\text{OCHO}^* + \text{O}_b \rightarrow \text{CO}_2^* + \text{O}_b\text{H}$	−2.09	0.00	–
A6	$\text{CO}_2^* \rightarrow \text{CO}_2 + ^*$	0.20	–	–
<i>VCM chlorination</i>				
12	$\text{VCM}^* + \text{Cl}^* \rightarrow \text{ClCHCH}_2\text{Cl}^* + ^*$	+0.56	1.09	248
13	$\text{ClCHCH}_2\text{Cl}^* + \text{O}_b\text{H} \rightarrow \text{EDC}^* + \text{O}_b$	+0.47	1.18	1307
14	$\text{ClCHCH}_2\text{Cl}^* + \text{O}_b \rightarrow \text{Z-C}_2\text{H}_2\text{Cl}_2^* + \text{O}_b\text{H}$	−0.16	1.37	892
A7	$\text{Z-C}_2\text{H}_2\text{Cl}_2^* \rightarrow \text{Z-C}_2\text{H}_2\text{Cl}_2 + ^*$	+0.32	–	–
15	$\text{ClCHCH}_2\text{Cl}^* + \text{O}_b \rightarrow \text{E-C}_2\text{H}_2\text{Cl}_2^* + \text{O}_b\text{H}$	−0.15	0.97	1429
A8	$\text{E-C}_2\text{H}_2\text{Cl}_2^* \rightarrow \text{E-C}_2\text{H}_2\text{Cl}_2 + ^*$	+0.53	–	–
16	$\text{VCM}^* + \text{Cl}^* \rightarrow \text{CH}_2\text{CHCl}_2^* + ^*$	+0.72	0.99	207
17	$\text{CH}_2\text{CHCl}_2^* + \text{O}_b\text{H} \rightarrow \text{CH}_3\text{CHCl}_2^* + \text{O}_b$	+0.25	0.99	1314
A9	$\text{CH}_3\text{CHCl}_2^* \rightarrow \text{CH}_3\text{CHCl}_2 + ^*$	+0.53	–	–
18	$\text{CH}_2\text{CHCl}_2^* + \text{O}_b \rightarrow \text{CH}_2\text{CCl}_2^* + \text{O}_b\text{H}$	−0.25	1.39	1407
A10	$\text{CH}_2\text{CCl}_2^* \rightarrow \text{CH}_2\text{CCl}_2 + ^*$	+0.54	–	–
<i>VCM oxidation</i>				
19	$\text{VCM}^* + \text{O}^* \rightarrow \text{OCH}_2\text{CHCl}^{**}$	−0.04	0.98	323
20	$\text{OCH}_2\text{CHCl}^{**} \rightarrow \text{CH}_2\text{ClCHO}^* + ^*$	−1.05	1.10	946
A11	$\text{CH}_2\text{ClCHO}^* \rightarrow \text{CH}_2\text{ClCHO} + ^*$	+1.13	–	–
21	$\text{VCM}^* + \text{O}^* \rightarrow \text{CH}_2\text{CHClO}^{**}$	−0.27	0.73	272
22	$\text{CH}_2\text{CHClO}^{**} \rightarrow \text{CH}_3\text{COCl}^* + ^*$	−1.23	1.19	1118
A12	$\text{CH}_3\text{COCl}^* \rightarrow \text{CH}_3\text{COCl} + ^*$	+0.72	–	–

[†] High coverage. Structures are available through the ioChem-BD repository [62].

(O_b) to coadsorbed O (O_{cus}) to generate $\text{O}_{\text{cus}}\text{H}$ (process V, Table 2), followed by a second H transfer to yield H_2O (process VI, Table 2) which then desorbs from the surface (process VII, Table 2). Both H transfer processes have mildly exothermic reaction energies (−0.02 eV and −0.11 eV for processes V and VI, respectively) and comparable low activation energies (0.35 eV and 0.18 eV for processes V and VI, respectively). Desorption of H_2O is endothermic by 1.12 eV (process VII, Table 2). Our results are thus in line with previous calculations [2,56,65–68]. A recent theoretical work identifies that water evolution is a key process in HCl oxidation, acting as an energetic bottleneck for the overall reaction [47]. However, with regards to ethylene oxychlorination, eventual evolution of water is a common process to all of the possible reactions, and hence will not have any appreciable impact on selectivity of the chlorinated products.

The addition of ethylene further expands the list of competitive reactions. Physisorption of C_2H_4 on the $\text{RuO}_2(110)$ slab was determined to be exothermic by −0.66 eV (process A1, Table 2).

Subsequently, addition across the $\text{C}=\text{C}$ bond can occur with either coadsorbed Cl or O occupying adjacent adsorption sites to C_2H_4 , yielding intermediates bound to the surface. The chlorination route (process 1, Table 2) is endothermic whilst the oxidation route (process 5, Table 2) is exothermic ($\Delta E_{\text{Cl}} = 0.14$ eV, compared to $\Delta E_{\text{O}} = -0.55$ eV). On the other hand, chlorination has a slightly lower activation barrier than oxidation ($E_{a,\text{Cl}} = 0.26$ eV compared to $E_{a,\text{O}} = 0.35$ eV). Hence, competition exists between the two processes, and the product distribution will vary depending on whether the system is under kinetic or thermodynamic control.

The chlorination pathway begins with the formation of a $\text{ClCH}_2\text{-CH}_2^*$ intermediate (process 1, Table 2). From here, a number of processes can take place. Firstly, direct protonation of the $\text{ClCH}_2\text{CH}_2^*$ intermediate from O_bH can occur (process 2, Table 2), yielding ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$); this process was found to possess a feasible activation barrier ($E_a = 0.96$ eV) but was also calculated to be slightly endothermic ($\Delta E = 0.26$ eV). Desorption of $\text{C}_2\text{H}_5\text{Cl}$ is endothermic by 0.61 eV (process A2, Table 2). A second alternative

is VCM generation by H abstraction from the $\text{ClCH}_2\text{CH}_2^*$ intermediate (process 3, Table 2); this process is both exothermic and kinetically feasible ($\Delta E = -0.21$ eV, $E_a = 1.07$ eV). Desorption of VCM from the surface is endothermic by 0.88 eV (process A3, Table 2). Finally, direct chlorination of the $\text{ClCH}_2\text{CH}_2^*$ intermediate yields the product EDC; the process was found to be slightly endothermic ($\Delta E = 0.17$ eV) but with a high activation barrier ($E_a = 1.85$ eV) (process 4a, Table 2).

Coverage effects are crucial in HCl oxidation [48] and thus are likely to be important also under oxychlorination conditions. Under high Cl coverage conditions, EDC formation from direct chlorination of $\text{ClCH}_2\text{CH}_2^*$ (process 4b[†], Table 2) yielded results more consistent with experimental observation; no activation barrier was observed for this process (thus it would be controlled by the Cl diffusion on the surface), and an exothermic reaction energy was determined ($\Delta E = -0.87$ eV). Under these conditions the $\text{ClCH}_2\text{CH}_2^*$ intermediate is destabilised by 1.42 eV, which is offset by the dissociative adsorption of HCl (-1.79 eV). In other words, the high coverage responsible for the induced destabilisation is a direct consequence of a high degree of HCl dissociative adsorption. Hence, HCl dissociation and the induced distortion are directly coupled with a net exothermic energy balance. Desorption of EDC is endothermic by 0.71 eV (process 15, Table 2).

The competing oxidation route, the oxametallacycle intermediate (OMME) formed by the addition of coadsorbed O to C_2H_4 (process 5, Table 2), can undergo a variety of processes. Formation of acetaldehyde (by 1,2-H shift, process 6, Table 2) is a possibility, as discussed in previous works [69]. Acetaldehyde formation is exothermic by -0.88 eV and has an activation barrier of $E_a = 1.22$ eV; desorption of acetaldehyde is endothermic by 0.90 eV (process A5, Table 2). Under thermodynamic control, it is likely that this species will ultimately undergo combustion to CO_2 and H_2O . It is found that cleavage of the C–C bond in OMME, resulting in fragmentation, has a lower activation barrier of 1.06 eV, making this the more feasible route (process 7, Table 2). The fragmentation yields formaldehyde and a CH_2^* species bound to the surface. The CH_2^* fragment can then react with coadsorbed O to generate a second equivalent of formaldehyde (process 8, Table 2); this step is highly exothermic ($\Delta E = -1.30$ eV) and has a negligible activation barrier ($E_a = 0.02$ eV) owing to the instability of the CH_2^* fragment. Subsequently, formaldehyde can re-adsorb to the surface, forming an intermediate bridging the coordinatively unsaturated Ru site (Ru_{cus}) and another O_{cus} , adding across the C=O carbonyl bond in the process (process 9, Table 2). The formation of the bridging intermediate is exothermic ($\Delta E = -0.89$ eV) and was determined to have a negligible activation barrier. CO_2 is then generated by two consecutive H abstractions from the intermediate. The first H abstraction (process 10, Table 2) is highly exothermic ($\Delta E = -2.30$ eV) and has a low activation barrier ($E_a = 0.54$ eV). The second H abstraction (process 11a, Table 2), on the other hand, was determined to have a high activation barrier of 1.70 eV and was found to be thermoneutral ($\Delta E = -0.04$ eV) under the low coverage model applied. Further calculations using a high Cl coverage model (process 11b[†], Table 2) yielded a much more exothermic reaction energy ($\Delta E = -2.09$ eV), and a negligible activation barrier. The intermediate was calculated to have been destabilised by 1.66 eV, again this energy can be compensated for by the exothermicity of HCl dissociative adsorption. Desorption of CO_2 is endothermic by 0.20 eV (process A6, Table 2). Finally, the H abstracted from the intermediates by vicinal O_b will ultimately be transferred to coadsorbed O_{cus} , thus evolving water and preserving the surface O_b atoms, as in the case of the Deacon reaction (processes V, VI and VII, Table 2).

Since VCM, like C_2H_4 , possesses a C=C bond, the same processes (both chlorination and oxidation) that apply to C_2H_4 may also apply to VCM, at least in theory, resulting potentially in products

containing both O and Cl. Several pathways were investigated. Addition of either Cl or O across the C=C results in two possible intermediates, since there are two approach trajectories (as opposed to only one for C_2H_4 , owing to the fact that in the latter molecule the two C atoms are equivalent). Considering first VCM chlorination, it is noted that there are two possibilities arising from Cl addition to VCM; either a vicinal dichloride ($\text{ClCH}_2\text{ClCH}^*$) or a geminal dichloride ($\text{Cl}_2\text{CHCH}_2^*$). Formation of the geminal dichloride (process 16, Table 2) is endothermic by 0.72 eV and has an activation barrier of 0.99 eV. The $\text{Cl}_2\text{CHCH}_2^*$ intermediate can then either gain H from O_bH , originating from HCl dissociative adsorption, yielding CH_3CHCl_2 ($\Delta E = 0.25$ eV, $E_a = 0.99$ eV, process 17, Table 2), or alternatively O_b can abstract H from the intermediate to give an unsaturated product, CH_2CCl_2 ($\Delta E = -0.25$ eV, $E_a = 1.39$ eV, process 18, Table 2). Both CH_3CHCl_2 and CH_2CCl_2 have similar adsorption energies (-0.53 eV and -0.54 eV, processes A9 and A10 respectively, Table 2). Formation of the vicinal dichloride is endothermic by 0.56 eV and has an activation barrier of 1.09 eV (process 12, Table 2). As with the geminal dichloride intermediate, potential products can be evolved by either gaining H from O_b , or by H abstraction by O_b . Addition of H leads to an alternative route to obtain EDC ($\Delta E = 0.47$ eV, $E_a = 1.18$ eV, process 13, Table 2). H abstraction can yield two unsaturated products, Z- $\text{C}_2\text{H}_2\text{Cl}_2$ and E- $\text{C}_2\text{H}_2\text{Cl}_2$, which form a pair of geometrical isomers depending on the conformation of the intermediate. The reaction energies for the two processes are very similar ($\Delta E = -0.16$ eV, $\Delta E = -0.15$ eV, for Z- $\text{C}_2\text{H}_2\text{Cl}_2$ and E- $\text{C}_2\text{H}_2\text{Cl}_2$ respectively, processes 14 and 15, Table 2). However the activation barrier for the formation of Z- $\text{C}_2\text{H}_2\text{Cl}_2$ is significantly higher than that of E- $\text{C}_2\text{H}_2\text{Cl}_2$ ($E_a = 1.37$ eV, c.f. $E_a = 0.97$ eV), likely due to steric repulsion between Cl on the same side of the molecule in the case of Z- $\text{C}_2\text{H}_2\text{Cl}_2$. Additionally, the E- $\text{C}_2\text{H}_2\text{Cl}_2$ desorption energy is more endothermic at 0.53 eV (process A8, Table 2) compared to 0.32 eV for Z- $\text{C}_2\text{H}_2\text{Cl}_2$ (process A7, Table 2). Indeed, it is possible that the unsaturated products from VCM chlorination could in turn undergo further reaction in an analogous manner. However, since all the reaction energies associated with the formation of VCM chlorination products are endothermic, and all of these processes have high activation barriers, further reactions beyond this point have not been examined.

Turning to VCM oxidation, similarly two distinct intermediates can be formed, $\text{CH}_2\text{CHClO}^{**}$ ($\Delta E = -0.27$ eV, $E_a = 0.73$ eV, process 21, Table 2), and $\text{OCH}_2\text{CHCl}^{**}$ ($\Delta E = -0.04$ eV, $E_a = 0.98$ eV, process 19, Table 2), depending on the side of the VCM molecule from which O approaches. As with OMME, H transfer can yield an aldehyde, CH_2ClCHO , from $\text{OCH}_2\text{CHCl}^{**}$ ($\Delta E = -1.05$ eV, $E_a = 1.10$ eV, process 20, Table 2), and in the case of $\text{CH}_2\text{CHCl}^{**}$ an acid chloride, CH_3COCl , is formed ($\Delta E = -1.23$ eV, $E_a = 1.19$ eV, process 22, Table 2). Desorption of the aldehyde is considerably more endothermic at 1.13 eV (process A11, Table 2), compared to 0.72 eV for the acid chloride (process A12, Table 2).

4. Discussion

4.1. Origin of selectivity

Selectivity between oxidation and chlorination of C_2H_4 is governed by the interplay between thermodynamic and kinetic factors. Thermodynamic selectivity can originate from differing adsorption energies between species. Products with highly exothermic adsorption energies are more likely to undergo further reaction than to be desorbed as an observed product, thus dictating selectivity [70].

Fig. 3 depicts the adsorption energies for a variety of chlorination products as well as C_2H_4 as a function of surface coverage

Fig. 3. Adsorption energies of ethylene, EC, EDC, VCM, and Z-DCE for a variety of surface compositions. (a) Adsorption energy as a function of Cl coverage on the RuO_2 surface where half of the bridging oxygen atoms were replaced with Cl. (b) Adsorption energy as a function of Cl coverage. (c) Adsorption energy as a function of O coverage.

(by O or Cl). In general, higher coverages lead to destabilised adsorbed species. It is notable that VCM is more strongly adsorbed than other species at all but the highest of coverages, owing to its compact size and its ability to interact with Ru active sites through either Cl or the C=C bond, or indeed both (occupying two active sites) at lower coverages. Therefore, if formed, VCM is likely to stay on the surface, as it is the most stable product at low coverages. It is also important to note that the C_2H_4 adsorption energy remains relatively unchanged at high O coverage, compared to the adsorption energy for a clean surface. Since C_2H_4 is the precursor for combustion products, the stronger C_2H_4 adsorption further supports oxidation to CO_2 and H_2O . However, at high coverages, VCM shows a lower adsorption energy than C_2H_4 , thus favouring the thermodynamic selectivity. This phenomena has been reported for the gold-catalysed selective hydrogenation of C—C triple bonds in

alkynes, to the exclusion of hydrogenation of C=C bonds in the resulting alkenes, since competitive adsorption between the reactants and products ensure that the products do not undergo further reaction, being displaced in favour of the adsorption of the reactant [69]. The lower adsorption energy for VCM compared to C_2H_4 means that under high coverage conditions, the two species compete for the remaining adsorption sites, with C_2H_4 being preferentially adsorbed. Consequently, VCM desorbs from the catalyst surface once it is generated in favour of adsorption of C_2H_4 , rather than undergoing further reaction and thus leading to an enhanced selectivity.

As for the kinetic aspects of the reaction, the first step in the reaction is crucial, i.e. whether chlorination (process 1) or oxidation (process 5) of C_2H_4 takes place. The activation barrier for addition of Cl to C_2H_4 is lower than for the addition of O, however the chlorination process is endothermic compared to the exothermic oxidation route. Whilst it is very likely that the initial and final states for Cl addition to C_2H_4 exist in equilibrium, the higher activation barrier for oxidation cannot be breached. Thus, at lower temperatures, the system is more prone to kinetic control and only chlorinated products are observed, as the intermediate $\text{C}_2\text{H}_4\text{Cl}^*$ is consumed to form chlorinated products over time. On the other hand, at higher temperatures, thermodynamic control prevails, and since the oxidation process is much more exothermic, it is more likely that the formation of OMME is irreversible, and hence at higher temperatures more combustion products are observed to the exclusion of chlorination products.

Fig. 4 depicts the reaction profile for the oxidation and chlorination of C_2H_4 , with chlorination progressing ultimately to EDC formation, at high and low Cl coverage. At low coverage, the activation barrier towards EDC is prohibitively high, whereas at high Cl coverage (process 4b, Table 2), the same process yielded results more consistent with experimental observation. It was calculated that the $\text{ClCH}_2\text{CH}_2^*$ intermediate is destabilised by 1.42 eV, which can be easily offset by the dissociative adsorption of HCl (−1.79 eV). At high Cl coverage, however, adsorbed species are somewhat destabilised by the coadsorbed chlorine atoms, thus diminishing the activation barrier of the processes as the energetic gap is closed between the initial and transition states of each

Fig. 4. (a) Reaction profiles for oxidation and chlorination of C_2H_4 at low (LC) and high (HC) chlorine coverage. The chlorination route depicts the eventual formation of EDC. The white background region indicates where the oxidation and chlorination processes compete at the specific coverage, whilst the green background region indicates that additional HCl has been dissociatively adsorbed to allow the reaction to continue to the formation of EDC, at high and low Cl coverages. (b) Diagrams depicting the considered configurations, where green circles indicate chlorine atoms, green/white circles indicate either a chlorine or no atom, and green/red circles indicate either chlorine or oxygen atoms.

process. This is reflected in differences in the atomic distances at high Cl coverage compared to low Cl coverage. At low Cl coverage, the distance between a Cl atom and the C atom of a coadsorbed $\text{C}_2\text{H}_5\text{Cl}^*$ intermediate (Table 2, process 4a Fig. 5b) is 3.53 Å. However, at high coverage (Table 2, process 4b†), the corresponding distance is only 3.08 Å, reflecting the crowding on the surface responsible for the destabilisation of the $\text{C}_2\text{H}_5\text{Cl}^*$ intermediate. It is also notable that whilst the activation barrier for C_2H_4 chlorination is lower than that of oxidation under low coverage conditions, at high coverages the pattern is reversed and the activation barriers are comparable. This implies that at high coverage, the competition between oxidation and chlorination of C_2H_4 is enhanced, leading to reduced selectivity.

Under kinetic control, it is important to consider why EDC, and not $\text{C}_2\text{H}_5\text{Cl}$ or VCM, is produced. The key to this again is the surface coverage, which can confine and destabilise intermediates. For EDC generation under high Cl coverage, the additional coadsorbed Cl destabilises the $\text{C}_2\text{H}_4\text{Cl}^*$ intermediate, with the destabilisation being compensated for by the exothermicity of HCl dissociative adsorption. Hence, the energetic barrier between the intermediate and the transition state is eliminated by the destabilisation of the intermediate. Formation of EDC takes place *via* the intermediate reacting with one of the adjacent coadsorbed Cl, thus relieving the species of its confinement, and as such, the process is highly exothermic. On the other hand, gaining (losing) H from (to) O_bH (O_b) to generate $\text{C}_2\text{H}_5\text{Cl}$ (VCM) does not involve the coadsorbed Cl responsible for the destabilisation and hence, the confinement is not relieved, therefore rendering it very likely that the thermodynamics and kinetics of these processes at high coverage would be largely unchanged from their low coverage values. As such, the experimental observation that the main chlorination product is EDC, rather than VCM, is justified theoretically.

Previous studies [44] suggest that EDC dehydrochlorination, generating VCM and HCl, requires sufficiently acidic sites on the catalyst surface, which $\text{RuO}_2(110)$ lacks, hence *in situ* dehydrochlorination does not occur and VCM is not a major product. Furthermore, it was suggested that at high partial HCl pressures, a significant proportion of O_b atoms are replaced by Cl, thus limiting the number of O_b sites able to abstract hydrogen from intermediates, or indeed provide hydrogen to intermediates having deprotonated HCl during dissociative adsorption [37]. This would also hinder any processes that require such sites, thus further favouring the generation of EDC which does not depend on H transfers to or from O_b . Under thermodynamic control, it is evident that oxidation dominates, and it is clear why combustion to CO_2 is preferred over intramolecular formation of CH_3CHO . The activation barrier for fragmentation of OMME to CH_3^* and H_2CO is consider-

ably lower than that of the alternative H transfer processes. Additionally, all of the subsequent steps under low coverage (except for the final H abstraction) are strongly exothermic and possess either small or negligible activation barriers.

4.2. Requirements for a good VCM catalyst

From the description above, we have identified three main requirements needed for a successful ethylene-to-VCM catalyst. Firstly, we consider the thermodynamic term. The adsorption energy for ethylene must fall in the same range as at least one of the other reactants (fulfilled by O_2 in this case). Moreover, it has to be more strongly bound than the desired product. For RuO_2 , this is only achieved for high coverages where the bonding energy of VCM is lower than that of ethylene. Hence, competition for active sites on the catalyst surface between adsorbates means that VCM is displaced in preference of C_2H_4 , limiting the extent to which VCM undergoes subsequent reactions. These persistent active oxygen atoms are a severe threat to the production of VCM. The C—O bond is stronger than the C—Cl bond (3.71 vs. 3.39 eV). This is an indication for the calculated effect that chlorination is reversible on the surface, whilst C—O formation is exothermic and thus irreversible. Energetically, this restriction implies that oxygen cannot diffuse across Ru_{cus} positions close to adsorbed ethylene. Secondly, the geometry of the (110) surface poses also the additional problem of dimensional confinement, shared by the other lowest energy surfaces: (101) and (001) [71]. Transport of the active Cl and O atoms takes place only along the [001] Ru_{cus} direction. This implies that once ethylene is adsorbed, the first atom in the neighbouring sites is the first one to be incorporated on the surface. As chlorination is reversible, the presence of a single O atom in the neighbouring site precipitates the production of CO_2 . Therefore, confined transport along a single direction is detrimental to the formation of VCM, with the constrained diffusion of ethylene across the surface limiting the number of coadsorbed species it can react with, making it more difficult for the kinetically preferred chlorination to occur.

The final point concerns the effective abstraction of the H atoms from the chlorinated fragments or even EDC. Basic sites are needed for stripping H atoms from the intermediates leading to VCM. As the presence of O_{cus} limits selectivity by favouring combustion, the basicity of the geometrically reachable O_b needs to be strong enough to allow effective H abstraction. On the RuO_2 surface, HCl- O_2 mixtures produce surfaces where O_b are partially replaced by Cl atoms (~50% replacement) [56]. Whilst this limit is crucial to ensure the stability of the catalyst under Deacon conditions, it impedes an effective dehydrogenation of the intermediates, most

Fig. 5. (a) Side view of the optimised geometry of $\text{C}_2\text{H}_4\text{Cl}^*$ at high coverage. (b) $\text{C}_2\text{H}_4\text{Cl}^*$ under low Cl coverage. (c) CHO_2^* under high Cl coverage. (d) CHO_2^* under low Cl coverage. Colour legend: blue (Ru), pale red (surface O), bright red (adsorbed O), green (Cl), dark grey (C), and light grey (H).

likely leading to enhanced EDC production. Therefore, a successful VCM catalyst needs to maintain effective O centres able to strip hydrogen from the intermediates.

Additionally, in order to further validate our approach, we set up a microkinetic model. The model is built on our previous results on Deacon reaction [49] and thus is only briefly commented on here. Notice that since the surface presents strong anisotropy and monodimensional character [59], mean-field approaches can be biased and thus they can only be taken as qualitative. Still, the reaction order for HCl in the Deacon is found to be 0.3, in reasonable agreement with the experimental values. In contrast, the reaction orders of HCl for EDC and VCM production over RuO₂ are 0.89 and -0.14, respectively. Thus, ethylene oxychlorination to EDC shows a remarkable difference compared to the Deacon reaction, in terms of the dependence on HCl. The kinetic similarities between reaction orders close to zero for Cl₂ and VCM can also represent a challenge in improving VCM production on RuO₂. Finally, it is noted that the production of Cl₂ was negligible under the conditions at which EDC was observed, in excellent agreement with experiments.

5. Conclusions

Under the conditions required for catalytic oxychlorination of ethylene over RuO₂(1 1 0), a variety of chemical reactions are possible, with competing oxidation and chlorination processes. Whilst oxidation, and ultimately combustion to CO₂ and H₂O, is favoured thermodynamically, conversion to the desired oxychlorination products is possible at lower temperatures through kinetic control. The coverage and composition of the surface is crucial to the behaviour of the system. Under high Cl coverages, competitive adsorption between C₂H₄ and VCM ensures that VCM is displaced by C₂H₄, owing to its less exothermic adsorption energy, preventing the excessive formation of products derived from VCM. The effect of dimensional confinement of C₂H₄ means that coadsorbed species react on a “first-come, first-served” basis, thus resulting in a potentially considerable degree of combustion where coadsorbed O is involved. The effect of substitution of bridging O sites by Cl, is key to understanding the prevalence of EDC over VCM under kinetic control, since the O_b sites required to abstract H from intermediates are essential to VCM formation. Therefore, the surface composition of the catalyst has a major impact on activity and selectivity and is an important consideration in the development of new catalysts. It is intended that this study will inform future work in developing highly selective, robust and active catalysts for ethylene oxychlorination, defining the basic requirements for a good catalyst by offering mechanistic insights at the molecular level.

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Appendix A. Supplementary material

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