



Mechanism of ethylene oxychlorination over ruthenium oxide



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ABSTRACT

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 (4HCl + O₂ → 2H₂O + 2Cl₂), 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.

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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 ($a = b = 4.520 \text{ \AA}$, $c = 3.118 \text{ \AA}$) 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 \AA 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 $0.015 \text{ eV \AA}^{-1}$. 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 valence 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 \AA . 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 ($W_{\text{cat}} = 0.5 \text{ g}$,

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