



Research Note

Towards an understanding of promoter action in heterogeneously catalyzed ethene epoxidation: Why chlorine is the best halogen

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ABSTRACT

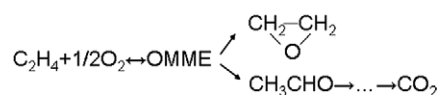
A detailed theoretical study is presented focusing on the role of halogens as promoters for the silver-catalyzed partial oxidation of ethylene to the epoxide (EO) and, in particular, aiming to understand why Cl is best. The study is based on periodic density functional theory calculations carried out for the reaction between ethene and atomic oxygen on the Ag(111) surface, taken as a model catalyst, in the presence of coadsorbed halogens. It is found that the presence of co-adsorbed halogens significantly decreases the energy barrier from the oxametallacycle intermediate (OMME) to EO relative to that from the same OMME intermediate to the undesired acetaldehyde (AC) product. However, co-adsorbed halogens are also found to increase the desorption energy of the reaction products. We present compelling evidence that the superior activity of Cl is due to the additional presence of subsurface Cl that favors EO formation with respect to AC but at the same time facilitates EO desorption, hampering further transformations. The results provide a signpost for the rational design of catalyst promoters.

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Trace amounts of foreign species are often incorporated into heterogeneous catalysts because they enhance activity, or selectivity, or both. Indeed, the viability of a number of strategically important large-scale processes is critically dependent on such so-called promoters. The silver-catalyzed partial oxidation of ethylene to the epoxide is a case in point. Here, the accidental discovery that chlorine greatly increases epoxidation selectivity from ~50% to ~80% has had a major impact on process economics; the associated substantial reduction in CO₂ emission is also of no small consequence. Thus in terms of global production of ethene epoxide, the superior selectivity of current generation catalysts is responsible for a reduction of CO₂ emission amounting to 10⁷ tons [1]. Nowadays, chlorine promotion is the universally and unquestioningly adopted industrially, and, until relatively recently, no attention appears to have been paid to the other halogens [2]. We found experimentally that all four halogens are selectivity promoters, with Cl markedly the most effective. Thus a scientific basis for technological practice was established, and a simple hypothesis proposed to account for the observed behavior. However, this behavior still awaits a detailed theoretical explanation, which is the subject of this Letter.

First we briefly review the generally accepted two step molecular mechanism for ethene epoxidation (Scheme 1).

According to both theory [3–7] and recent experiments carried out under highly controlled conditions [8], the first step involves formation of an oxametallacycle (OMME) intermediate which may further react *via* one of two competitive pathways to form either ethene oxide (EO) or acetaldehyde (AC), herein defined as *primary chemistry*. AC formation leads to combustion and this is the key process, defined as *secondary chemistry*, that limits epoxidation selectivity. The key role of the OMME was recently emphasized by Barteau [9] in a perspective article highlighting the recent work of Klust and Madix [8] which provides clear experimental evidence that an oxametallacycle is also the common intermediate in styrene oxidation. Recent theoretical work has also provided further evidence that this is the molecular mechanism for ethene epoxidation on Au(111) [10] and to play an important role in the epoxidation on propene on Cu(111) and Ag(111) [11]. However, one must realize that desorption of the products may also significantly affect the selectivity as already pointed out by Loffreda et al. [12] for the catalytic hydrogenation of unsaturated aldehydes on Pt(111). Therefore, the effect of co-adsorbed halogens on the elementary steps of the reaction mechanism in Scheme 1 as well as on the adsorption energies of reactants, intermediate and products needs to be investigated in detail. Note that desorption



Scheme 1. Molecular mechanism for ethene epoxidation.

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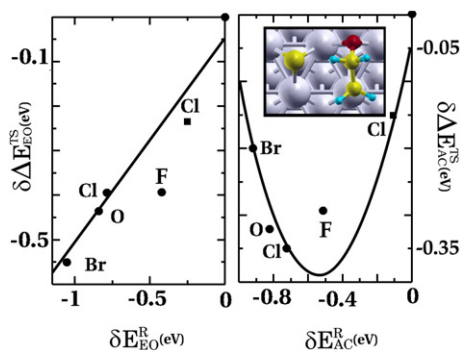


Fig. 1. $\delta\Delta E^{\text{TS}}$ changes induced by the presence of 0.25 ML of co-adsorbed Cl(a), Br(a) and O(a) with respect to δE^{R} for the OMME to EO or AC pathways. For Cl, a situation with 0.06 ML coverage (square) has also been considered. The derived linear-regression line, excluding F(a), for the EO pathway is $\delta\Delta E_{\text{EO}}^{\text{TS}} = 0.48\delta E^{\text{R}} - 0.03$ with $R^2 = 0.97$ and the quadratic-regression equation for the AC pathway is $\delta\Delta E_{\text{AC}}^{\text{TS}} = 1.25(\delta E^{\text{R}})^2 + 1.37\delta E^{\text{R}}$ with $R^2 = 0.97$. Inset in right panel shows the relative atomic positions of the OMME initial state and the co-adsorbed halogen (or oxygen) atom.

strongly controls the secondary chemistry since EO on the surface can eventually react backwards to OMME thus increasing the AC yield and its subsequent combustion.

In order to investigate the effect of co-adsorbed halogens on the ethane partial oxidation catalyzed by silver, the Ag(111) surface has been chosen as a model catalyst and periodic density functional (DF) calculations have been carried out, using the PW91 functional [13] on slab surface models. The effect of adsorbed F, Cl and Br—hereafter referred to as F(a), Cl(a) and Br(a)—on the reaction selectivity has been investigated by making use of a large enough supercell. The effect of adsorbed oxygen—O(a)—is also considered as it is known from experiment [14], and confirmed by theory [15], that epoxidation selectivity increases with oxygen coverage. We employed small $p(2 \times 2)$ and large $p(4 \times 4)$ slabs consisting of 4 atomic layers interleaved by a 12 Å vacuum gap. Note that for the small unit cell there are two possible adsorption sites for halogen adsorption but one of them is too close to the OMME intermediate and results in a large repulsion. This is not the case for the larger unit cell where different sites are possible. These have been considered and found to induce qualitatively the same effect. However, to properly compare the different coverage situations only the most stable site for the coadsorbed halogen has been considered. The CI-NEB method [16] was used to locate the transition state (TS) structures which were characterized by means of vibrational analysis. The effect of core electrons on the valence density, expanded in a plane wave basis with a kinetic cut off energy of 315 eV, was taken into account through the PAW method [17]. Monkhorst–Pack meshes with $5 \times 5 \times 1$ or $2 \times 2 \times 1$ k-points were used for small and large cells [18]. Extensive test calculations on several systems ensured that with this setup relative energies are converged within 0.01 eV, see for instance recent work concerning oxygen adsorption on the surface of coinage metals [19]. Nevertheless, to further test the accuracy of the present computational setup, key calculations on the small cell for the reaction pathway from OMME to EO carried out using a cutoff of 500 eV imply a change in the reaction and energy barrier toward EO of 20 and 7 meV, respectively. Similarly, the use of a denser k-point grid leads to changes of 30 and 13 meV, for reaction and energy barrier, respectively. Therefore, these changes will hence imply only a small shift in the lines of Fig. 1 thus providing confidence on the numerical accuracy of the present density functional calculations. Zero point vibration energies were explicitly computed but are not included in the numerical results because the main trends are not affected. In this sense, note that the main goal of the present work is to analyze the changes induced by co-adsorbed halogen on the reaction en-

ergy profile corresponding to Scheme 1 above and, therefore, the resulting relative energies are much less affected by the GGA inherent errors (see Refs. [20–23] and references therein) and hence the present study provides meaningful results. All calculations were carried out using the VASP package [24].

The quantities designated E_{EO}^{R} and E_{AC}^{R} are the energies of EO and AC relative to OMME; this is the energy difference between the product (EO or EA) and the common OMME metallacycle intermediate ($E_{\text{EO}}^{\text{R}} = E_{\text{EO}} - E_{\text{OMME}}$ and $E_{\text{AC}}^{\text{R}} = E_{\text{AC}} - E_{\text{OMME}}$). The corresponding change in adsorbate energies induced by the presence of the halogen (denoted $\delta E_{\text{EO}}^{\text{R}}$ or $\delta E_{\text{AC}}^{\text{R}}$) is given by the difference in E^{R} between the promoted and clean surfaces. The energy barriers for the EO and AC are defined as $\Delta E_{\text{EO}}^{\text{TS}}$ and $\Delta E_{\text{AC}}^{\text{TS}}$ and, hence, the energy barrier variations induced by the presence of the co-adsorbed halogen ($\delta\Delta E_{\text{EO}}^{\text{TS}}$ or $\delta\Delta E_{\text{AC}}^{\text{TS}}$) can be defined in a similar way. Within this framework, promoter-induced changes in adsorbed EO formation rate with respect to AC may be ascribed to relative changes in the activation energy barriers ($\delta\Delta\Delta E^{\text{TS}} = \delta\Delta E_{\text{EO}}^{\text{TS}} - \delta\Delta E_{\text{AC}}^{\text{TS}}$). Thus, $\delta\Delta\Delta E^{\text{TS}}$ controls the promoter effectiveness; a selectivity enhancement in adsorbed EO formation rate with respect to AC is achieved when this descriptor is a large negative number. For a Cl coverage of 0.25 monolayer (ML; $1 \text{ ML} \sim 3 \times 10^{18} \text{ atoms m}^{-2}$), we found that the presence of Cl decreases E_{EO}^{R} and E_{AC}^{R} with respect to the unpromoted surface. Similarly, the presence of Cl decreases $\delta\Delta E_{\text{EO}}^{\text{TS}}$ and $\delta\Delta E_{\text{AC}}^{\text{TS}}$. The calculated values for $\delta E_{\text{EO}}^{\text{R}}$, $\delta E_{\text{AC}}^{\text{R}}$, $\delta\Delta E_{\text{EO}}^{\text{TS}}$ and $\delta\Delta E_{\text{AC}}^{\text{TS}}$ are -0.78 , -0.72 , -0.39 and -0.32 eV. The corresponding value for $\delta\Delta\Delta E^{\text{TS}}$ is hence -60 meV; which means that Cl(a) enhances adsorbed EO formation with respect to AC.

We propose that the two principal chlorine-adsorbate interactions that affect $\delta\Delta E_{\text{EO}}^{\text{TS}}$, $\delta\Delta E_{\text{AC}}^{\text{TS}}$ and thus $\delta\Delta\Delta E^{\text{TS}}$ are (i) long range interaction of the promoter-induced electric field (F) with the two transition states and (ii) direct electronic modifications of δE^{R} due to electronic charge redistribution [25–27]. Thus, for a given reaction pathway and for relatively small changes in F and δE^{R} , we may expand $\delta\Delta E^{\text{TS}}$ as a linear Taylor series as in Eq. (1):

$$\delta\Delta E^{\text{TS}} \approx \left(\frac{\partial \delta\Delta E^{\text{TS}}}{\partial F} \right)_{\delta E^{\text{R}}} F + \left(\frac{\partial \delta\Delta E^{\text{TS}}}{\partial \delta E^{\text{R}}} \right)_{F} \delta E^{\text{R}}. \quad (1)$$

In a similar way, $\delta\Delta\Delta E^{\text{TS}}$ can be obtained as in Eq. (2), including the contribution of both EO and AC reaction pathways

$$\delta\Delta\Delta E^{\text{TS}}(F, \delta E^{\text{R}}) \approx \alpha F + \beta \delta E^{\text{R}} \quad (2)$$

with α and β parameters, defined as in Eqs. (3) and (4):

$$\alpha = \left(\frac{\partial \delta\Delta E_{\text{EO}}^{\text{TS}}}{\partial F} \right)_{\delta E^{\text{R}}} - \left(\frac{\partial \delta\Delta E_{\text{AC}}^{\text{TS}}}{\partial \delta E^{\text{R}}} \right)_{\delta E^{\text{R}}}, \quad (3)$$

$$\beta = \left(\frac{\partial \delta\Delta E_{\text{EO}}^{\text{TS}}}{\partial \delta E_{\text{EO}}^{\text{R}}} \right)_{F} - \left(\frac{\partial \delta\Delta E_{\text{AC}}^{\text{TS}}}{\partial \delta E_{\text{AC}}^{\text{R}}} \right)_{F}, \quad (4)$$

describing the response of $\delta\Delta\Delta E^{\text{TS}}$ towards the perturbation of F and δE^{R} , respectively. These parameters determine the relative response of the primary chemistry reaction pathways towards the promoter-induced perturbations, and hence EO formation rate with respect to AC. Their sign determines whether F and δE^{R} act to increase or decrease the formation rate towards the desired reaction product.

We will first focus on the electric field effects. For small F values, α was previously estimated to be $\sim 0.08 \text{ \AA}$ [25]. Following Mortensen et al. [26], we estimate a maximum value of 0.22 eV Å⁻¹ for the electric field induced by Cl at 0.25 ML. Therefore, the electrostatic contribution to the selectivity descriptor would be of the order of only ~ 10 meV. In fact, for the coadsorbed species considered here, the F values lie in the range $0\text{--}0.3 \text{ eV \AA}^{-1}$ with αF making only a small contribution to $\delta\Delta\Delta E^{\text{TS}}$. Thus, one may

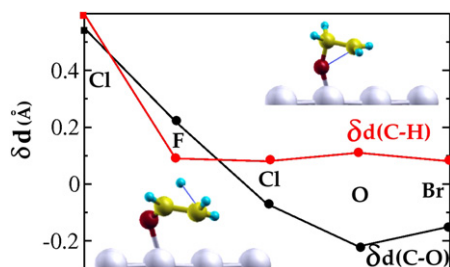


Fig. 2. Effect of halogen and atomic oxygen co-adsorption on the geometries of the TS involved in the competitive pathways. Variations are given with respect to the corresponding structure on clean Ag(111).

conclude that promoter-induced electrostatic effects have only a minor effect on the reaction energy profile and, consequently, on catalytic selectivity.

Accordingly, $\delta\Delta\Delta E^{\text{TS}}$ is controlled by the bonding modifications (δE^{R}) induced by co-adsorbed promoter atoms. We now consider the effects of 0.25 ML of each of F(a), Cl(a) and Br(a) on $\delta\Delta\Delta E^{\text{TS}}$. Fig. 1 reports $\delta\Delta E_{\text{EO}}^{\text{TS}}$ (left panel) and $\delta\Delta E_{\text{AC}}^{\text{TS}}$ (right panel) induced by the various coadsorbed species as a function of the corresponding induced variation in δE^{R} . We found that different adsorbates induce different bonding modifications. To cover a δE^{R} range of ~ 1 eV we consider Cl(a) at 0.06 ML and also investigate the effect of 0.25 ML of O(a). Precisely the promoter effect of coadsorbed O has recently been described in detail for the reaction taking place on Cu(111) [15]. It is clear that the bonding effect response for the two pathways is very different. For EO formation, a Brønsted–Evans–Polanyi trend is followed. This implies that the energy profile for this pathway responds linearly and in the same direction as do changes in the OMME/EO energy difference: coadsorbates stabilize both the transition state and the product with respect to the reactant. In this case, favoring the thermodynamics also favors the kinetics. In contrast, the reaction pathway from OMME to AC responds very differently to the identity of the co-adsorbed species. In this case (Fig. 1, right panel) there are two distinct regimes. For small (negative) variations in δE^{R} , $\delta\Delta E_{\text{AC}}^{\text{TS}}$ decreases: the opposite trend is found for larger δE^{R} values once a certain critical value for δE^{R} is exceeded. This trend can be understood from a change in the curvature of the potential energy surface connecting the OMME with AC, once a certain critical value for δE^{R} is achieved. It is possible to get a deep insight on this effect by analyzing the geometry of the TS for the different cases. In Fig. 2 we report the most important geometrical parameters associated with the TS of each competitive pathway. One can see that for small changes on δE^{R} , both TS resemble the reactant even more than for the clean Ag(111) surface. When δE^{R} is decreasing the TS leading to EO progressively resembles the product, in agreement with the progressive change in the energy barrier due to changes in reaction energy. Differently, for the TS leading to AC, there is a clear discontinuity in the geometry for low δE^{R} changes. This effect has important implications regarding the overall effect of these coadsorbates on reaction selectivity. Specifically, the response of $\delta\Delta\Delta E^{\text{TS}}$ to variations in δE^{R} for the two different pathways controls, through the β parameter in Eq. (2), the promoter character of a given coadsorbed species.

Fig. 3 (left panel) shows β as a function of δE^{R} . Regarding the derived linear-regression for Fig. 1 (left panel) and the quadratic-regression for Fig. 1 (right panel), β , defined as in Eq. (4), should depend linearly on δE^{R} being the slope of $\beta(\delta E^{\text{R}})$ directly related to the curvature of $\delta\Delta E_{\text{AC}}^{\text{TS}}$ with respect to δE^{R} . Note in Fig. 3 (left panel) that beyond a certain critical δE^{R} value, β changes sign. Negative β values, which correspond to small changes in δE^{R} , act to decrease the kinetic rate towards EO production with respect to AC. Correspondingly, for positive β values, which correspond to

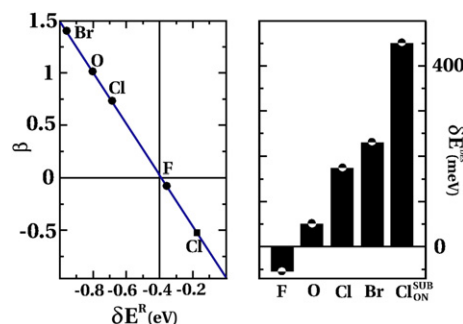


Fig. 3. (Left) Change of β with respect to the average modifications in δE^{R} due to the effect of various coadsorbed species. (Right) δE^{Des} values for the different coadsorbates including Cl(sub).

sufficiently large changes in δE^{R} , the co-adsorbed species act to promote the EO formation with respect to AC. $\delta E^{\text{R}} \sim -0.4$ eV is the predicted pivotal value at which a co-adsorbate switches from poison to promoter.

Whilst the present results provide a detailed explanation of the origin of selectivity promotion by coadsorbed halogens, they predict Br to be better than Cl whereas experiment shows that in practice Cl is the most effective promoter of all [2]. The explanation for this apparent discrepancy lies in the secondary chemistry that determines the fate of newly-formed EO, i.e. desorption versus further conversion to $\text{CO}_2 + \text{H}_2\text{O}$. Two facts are germane here. Under industrial conditions continuous feeding of the chlorinating agent is necessary. Also, adsorbed Cl readily diffuses into Ag and accumulates beneath the surface in substantial amounts [28,29]. Subsurface bromine is very unlikely to be formed as accommodating the large Br atom would require major substrate relaxation with a concomitant excessively high energy cost. Accordingly, to analyze the role of subsurface chlorine—Cl(sub)—we carried out calculations for a system with 0.25 ML of Cl(a) and 1 ML of Cl(sub) occupying all *fcc* subsurface sites between the first and second Ag layer; Cl on *hcp* sites has not been considered because recent work [29] has shown that *fcc* and *hcp* adsorption sites are, within the accuracy of the present DFT techniques, energetically equivalent. The purpose of these new series of calculations is to investigate the combined effect of surface and subsurface Cl on the secondary chemistry although has to accept that the precise conditions in this series of calculations may differ from those employed in industrial production. Note, however, that recent DFT calculations have also shown that at low coverage ($\theta_{\text{Cl}} < 0.2$ ML) on-surface adsorption is favored over Cl penetration while at higher coverage on-surface and subsurface adsorption become both thermodynamically and kinetically favored [29]. Subsurface penetration of Ag by Cl has long been known from experiment (see for example Ref. [30]) so our calculations provide important insight into how and why Cl is the most effective promoter. In fact, the presence of Cl(sub) has a noticeable effect on the EO and AC energy barriers as previously found for other subsurface impurities, [31] leading to a value of -80 meV for $\delta\Delta\Delta E^{\text{TS}}$, very similar to the value obtained for the case of 0.25 ML Cl(a) alone. The key point, however, is that halogens also decrease the EO desorption energy relative to the clean surface value ($\delta E_{\text{EO}}^{\text{Des}}$) and this effect is strongest for Cl(sub). Thus Cl(a) and Br(a) decrease the EO desorption energy by 183 meV and 350 meV, respectively, whereas the decrease induced by Cl(a) + Cl(sub) is 446 meV. This strongly suggests that the observed superior performance of Cl is due to its additional favorable effect on the secondary chemistry: subsurface Cl in combination with Cl(a) is most effective in promoting EO desorption, thus minimizing its further conversion to CO_2 and H_2O .

Fig. 3 (right panel) shows δE^{Des} values for the various coadsorbates. In particular, δE^{Des} is greater for Cl(sub) than for Cl(a),

implying a maximum enhancement in EO desorption rate when subsurface Cl is present along with Cl(a). For other coadsorbates, particularly O(a) and F(a), a large change in $\delta\Delta E^{\text{TS}}$ is accompanied by a small change in δE^{Des} , resulting in reduced selectivity enhancement. Thus F(a) actually increases the EO residence time, increasing the probability for its further conversion before desorption occurs.

In summary, density functional calculations provide detailed insight into the mode of selectivity promotion by co-adsorbed halogens in the silver-catalyzed epoxidation of ethene. All of them affect the primary chemistry favorably, promoting EO formation. Overall, however, Cl is best of all because adsorbed and subsurface chlorine also act to minimize unfavorable secondary chemistry, namely the unwanted further conversion of EO.

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