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Dipole effect on ethylene epoxidation: Influence of alkali metals and chlorine

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ABSTRACT

Ethylene epoxidation is one of the most important selective oxidation reactions in industry and is almost invariably carried out on silver catalysts. Empirically it is known that moderate selectivity of silver can be greatly enhanced with cesium and chlorine dopants, whereas a mechanistic understanding of the underlying reason remains elusive. In this work, we present a first-principles explanation of the dipole effect on reaction selectivity, which could, in principle, be effected by alkali metals. We show that, on a silver surface, alkali metals work in a similar fashion thanks to their low electronegative character. The selectivity is impacted by inducing electric dipoles on the catalytic surface, whereas the electronic properties of the catalyst remain largely unperturbed. Cesium, as the least electronegative metal, shows the most pronounced effect. This effect is shown to persist when alkali metals are treated as "naked" atoms or, more realistically, when oxidized. Additionally, alkali metals increase activity of the catalyst by favoring the rate-determining step of oxygen dissociation. Chlorine, which is strongly electronegative, acts differently. Subsurface chlorine would increase selectivity through the same mechanism, while surface chlorine stabilizes alkali metals and moderately increases selectivity. Interplay of both dopants is needed to precisely tailor the catalyst for the best performance.

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1. Introduction

Controlled oxidation of ethylene to ethylene epoxide (EO) is an important and experimentally challenging technological process. EO is a precursor to a plethora of chemicals. It is the basis for production of ethylene glycol, detergents, ethanolamines, and so forth. The principal challenge is to prevent the total oxidation of ethylene, which is thermodynamically the most favorable pathway, and instead steer the reaction towards epoxide.

Industrially, the reaction is carried out on silver catalysts, which are mostly doped with cesium and chlorine. By doing so, selectivity of pure silver catalyst, which ranges from 40% to 50%, is improved to over 90%. Despite having been thoroughly studied both experimentally [1–8] and theoretically [9–14], the promoter effect of these dopants is still not completely understood, and competing explanations (such as blocking oxygen vacant sites, influence on oxametallocycle formation, electric field, effects on surface reconstruction) have been put forth [12,15,16].

Silver is a commonly used catalyst. It is sufficiently mild not to break C–H bonds in the olefin but active enough to dissociate

oxygen [17]. There exist other competing catalysts; for instance, pure copper is also predicted to have high selectivity [18]. Interestingly, under reaction conditions, copper-silver alloy transforms into a copper oxide-like layer on top of silver and favorably influences the reaction [19,20]. However, under industrial reaction conditions pure metal co-exists in equilibrium with the oxide phase, where Ag₂O vastly outperforms Cu₂O and Au₂O [18].

Since the pioneering work of Linić and Barteau [9,10], it has been well known that epoxide and total combustion pathways proceed through the common intermediate oxametallocycle (OME) [21,22], which then converts either into EO or, when undergoing full combustion, initially into acetaldehyde (AA) and ultimately to CO₂. It is therefore understood that the difference in activation energies between their respective transition states determines the selectivity of the reaction. What is not known is how Cs and Cl influence the activation energies. Interestingly, the activity of the catalyst is determined earlier in the oxidation process. On pure silver, the rate-determining step is in fact oxygen dissociation [11]. When the catalyst gets doped and/or partially oxidized, this simple picture breaks down. As found by Greeley and Mavrikakis, oxygen might also be subsurface, where it adversely affects the selectivity [23]. On oxidized surfaces, oxide regeneration ceases to be the rate-controlling step [24]. Recently, ethylene epoxidation on silver has also been studied as a model reaction for enhancing activity





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with plasmonic excitations [25–27]. It has also been found that catalysts are more active near phase transitions [28].

Linić and Barteau [12] studied the effects of cesium on ethylene epoxidation on Ag(111) and tentatively argued that its promoter effect stems from the change in the *difference* between the EO and AA transition states owing to electric field effect. They argue that chlorine, which is strongly electronegative, might diffuse into Ag. Detailed theoretical calculations by Gava et al. cast some doubt on the possibility of interstitial subsurface chlorine [15], while a great deal of experimental data support the notion of subsurface chlorine even at lower temperatures and moderate coverages [5,29–31]. It has been shown, however, that chlorine might mitigate the diffusion of oxygen into the subsurface [32].

Ren et al. [33] showed computationally that cesium lowers the oxygen adsorption energy on pure Ag(111), effectively making oxygen bind less strongly to the silver surface. They do not consider oxygen binding directly to the cesium. At the same time, they showed that cesium doping lowers the activation barrier of epoxide formation in the selectivity-determining step and thus increases selectivity of the catalyst.

For $Ag_2O(001)$, Özbek et al. argue [16] that chlorine blocks oxygen vacant sites and prevents OME formation and surface reconstructions. Instead, it forces ethylene to react with surface oxygen in a one-step epoxidation [34]. Cesium acts as a copromoter and stabilizes the non-vacant $Ag_2O(001)$ surface. However, under industrial conditions, Ag_2O is less stable than pure Ag with a surface oxide [35]. This one-step mechanism, however, has been ruled out time and again for pure silver [36].

In this work, we employ density functional theory (DFT) calculations to shed light on the effects of dipoles on the selectivity of the reaction on Ag(111). We show how alkali metals on Ag(111) can bring about surface dipoles and increase selectivity. We show that this effect persists even in oxidizing conditions when Cs is oxidized. Activity is also increased through more favorable oxygen dissociation. The effect of chlorine is less pronounced on Ag (111), because it mostly serves to stabilize alkali metals and speed up the conversion of OME, but is more important on oxides [16].

2. Computational details

For electronic structure computations with periodic boundary conditions, the VASP package was used [37-40]. The Perdew-Burk e-Ernzerhof formula [41,42] was used for evaluating the semilocal exchange and correlation contribution, while the projector augmented wave method [43,44] was used to describe the interaction between valence electrons and the core. Criteria for relaxation were 0.01 eV/Å for stable structures and 0.03 eV/Å for transition states. The latter were preconverged with nudge elastic band [45,46] and subsequently refined by using the dimer method [47–50]. By calculating the Hessian matrix with the finite difference approach with a step size of 0.01 Å, vibrational analysis was performed to check for the imaginary vibrational frequencies and to obtain zero-point energy corrections. Spin-polarized calculations were carried out as necessary (triplet gaseous oxygen, oxygen dissociative adsorption). On Ag(111), magnetic moments were quenched as expected.

Ag(111) was modeled as four layers of silver atoms with the bottom two layers being fixed in their bulk positions. The top two layers along with adsorbates and dopants were fully relaxed. The bulk calculation of the silver fcc lattice with $16 \times 16 \times 16$ Monkhorst–Pack mesh of *k* points gave a cell constant of 4.17 Å, which is within 2% of the experimental value (4.08 Å). Because rather large $p(4 \times 4)$ supercells were used for slab calculations, using a $2 \times 2 \times 1$ mesh sufficed for well-converged results. In the perpendicular direction, slabs were separated by 16 Å of vacuum.

To account for spurious dipole interactions because of asymmetric slabs, dipole corrections in vacuum were employed [51,52]. For gaseous species, Γ -point calculations with 20 Å of vacuum in all directions were carried out.

Ab initio calculations were performed by using the Gaussian software [53]. As a gold standard in computational chemistry, coupled-cluster singles and doubles theory with perturbative triples corrections [CSSD(T)] was used [54–57]. Dunning's correlation-consistent polarized triple-zeta basis (aug-cc-pVTZ) set with added diffused functions was used [58]. Zero-point energy correction and translational, vibrational, and rotational contributions to partition functions were considered for thermodynamics. Equilibrium constants are obtained from $\Delta G^0 = -RT \ln K_p$.

3. Results and discussion

3.1. Thermodynamics

Partial oxidation of ethylene to epoxide is exothermic with an *ab initio* [CCSD(T)] computed reaction energy of $\Delta E_{\rm EO}^{298 \text{ K}} = -101 \text{ kJ mol}^{-1}$ and a standard Gibbs free energy of $\Delta G_{\rm EO}^{298 \text{ K}} = -77 \text{ kJ mol}^{-1}$ at 298 K and 1 atm. At the PBE level, which was used for slab calculations throughout this paper, this value is $\Delta E_{\rm EO}^{298 \text{ K}} = -105 \text{ kJ mol}^{-1}$, which justifies its use. For further justification, see the comparison with previous work in Table 1.

Thus, successfully producing epoxide is a matter of kinetics. However, a competing oxidation reaction to acetaldehyde, which then quickly transforms into CO₂ and water, is thermodynamically even more favorable ($\Delta G_{AA}^{298 \text{ K}} = -194 \text{ kJ mol}^{-1}$). Catalyst preparation is therefore crucial to steer the reaction towards the desirable product. See Table 2 for the full thermodynamics with industrially relevant parameters. We see that *ab initio* results are in good agreement with experimental values.

3.2. Active surface

The stable form of silver depends on the oxygen chemical potential, which is a function of temperature and oxygen partial pressure. As shown by Li [62], Michaelides [63], Martin [35], and Jones [64], under industrial operating conditions (550–600 K, 0.2–1.0 bar O_2), the formation of Ag_2O is not favorable. Instead, bulk silver is covered with adsorbed oxygen atoms (1/16 ML) and some surface oxide starts forming only if the oxygen chemical potential increases. A simple Ag_2O -like $p(4 \times 4)$ overlayer was proposed more than 40 years ago [65], but the exact structure of the surface oxide remains elusive [66]. Since many different possible surface oxide structures and adsorbed oxygen adatoms have very similar chemical potential, it is likely that the exact structure is determined by kinetics on a given catalyst particle [35].

We reconstructed a simplified phase diagram (Fig. 1) by using standard methods to check that our setup predicts accurate energetics and that we study relevant structures. This, however, is by no means a comprehensive study of possible surface structures, which has been done before [35]. Under a given oxygen chemical potential μ_0 , the surface free energy of a particular coverage with oxygen is minimized:

$$\gamma(T,p) = \frac{1}{A} \Big[G^{\text{surf}}(T,p) - N_{\text{M}}\mu_{\text{M}} - N_{\text{O}}\mu_{\text{O}} \Big].$$
(1)

As shown by Reuter [67], entropy and enthalpy contributions for solids can be safely ignored, substituting the Gibbs free energy with simple total energies. The formation of Ag₂O becomes thermody-namically preferred when its Gibbs free energy is more favorable (negative) than an equivalent amount of bulk metal and oxygen in the gas phase:

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