

On the Mechanism of Cs Promotion in Ethylene Epoxidation on Ag

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The outcome of many catalytic processes can be altered dramatically by an introduction of a small amount of various promoters that speed up certain reaction steps or various poisons that can either slow particular reaction steps or neutralize catalyst sites that lead to undesired products.^{1,2} For example, alkali metals are used as promoters in Fe- and Ru-based ammonia synthesis,³ Fischer–Tropsch synthesis,⁴ ethylene epoxidation on Ag,^{5,6} and many other heterogeneous reactions.^{1,2} In ethylene epoxidation, the catalyst is α -Al₂O₃-supported Ag with Cs and Cl as common additives.^{5,6} Various roles have been suggested for both species, including Cs promotion of the desired epoxidation channel,⁷ Cs poisoning of acid sites on the support,⁸ Cl poisoning of sites for combustion,⁹ and Cl promotion of favorable states of surface oxygen.¹⁰ Even though ethylene epoxidation has been practiced commercially for decades, the molecular level mechanisms of promotion are not well understood. The difficulty in understanding mechanisms of promotion stem from the decisive importance of complex adsorbate–adsorbate interactions, which are not well understood.

In this study the mechanism by which Cs impacts the selectivity of ethylene epoxidation on pure silver is examined. Support effects are not considered. The main focus of our investigation is analysis of promoter–intermediate and promoter–transition state interactions. We show that Cs can enhance selectivity to EO by stabilizing the transition state for formation of EO with respect to the transition state involved in combustion.

Our recent work and contributions of others have suggested that the formation of EO on Ag proceeds through a surface oxametallacycle.^{11–13} We have also demonstrated that the chemistry of the oxametallacycle can explain the selectivity of silver epoxidation catalysis.¹⁴ Our analysis of the relevant transition states and kinetic isotope effect data showed that there exists an important competing reaction pathway leading to acetaldehyde and thence to complete combustion. This pathway branches off from the selective reaction pathway at the oxametallacycle; see Figure 1. Subsequent microkinetic modeling of a complete catalytic cycle has yielded macroscopic parameters, i.e., overall activation barriers and selectivity and activity dependences on temperature and pressure, that are consistent with experimental results obtained under steady-state catalytic conditions.^{15,16} The proposed molecular level mechanism was further utilized in a first principles catalyst design that produced a qualitative description of a Cu/Ag alloy that is more selective than a monometallic Ag catalyst.¹⁷ Subsequent experiments confirmed these predictions.¹⁷

To understand the role of Cs in ethylene epoxidation, we have performed DFT calculations on model systems where Cs is adsorbed on Ag(111) and its impact on the energies of the surface oxametallacycle and TS1 (which forms EO) and TS2 (which leads to combustion) is examined. We caution that it is possible that, under process conditions, formation of cesium oxide or hydroxide

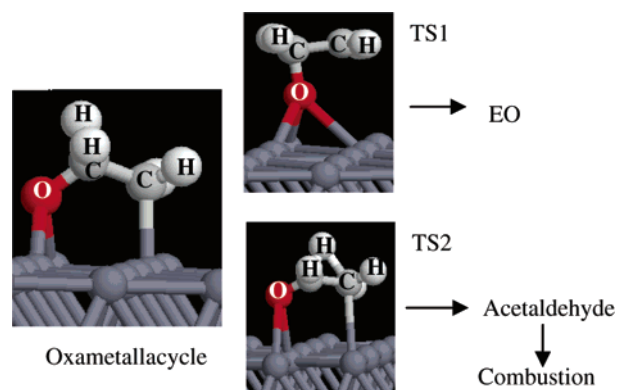


Figure 1. Competing oxametallacycle pathways. The surface oxametallacycle, formed by reaction of ethylene and oxygen, reacts via TS1 to form EO, while it reacts via TS2 to form acetaldehyde, which is further oxidized.

complexes may occur.¹⁸ We did not investigate these complexes, but rather we have focused on a qualitative understanding of promoter action that should not be altered by the stoichiometry of such complexes, since they do not change the *direction* of the surface dipole moment.¹⁸

The quantity that is central to the discussion, $\Delta\Delta E_a$, is the difference in the activation barrier for acetaldehyde vs EO formation calculated on Cs-promoted Ag(111), less the same difference calculated on unpromoted Ag(111). This quantity is calculated by comparing the energies of TS1 and TS2 on promoted and unpromoted Ag(111). A higher value of $\Delta\Delta E_a$ implies a higher selectivity to EO.

$$\Delta E_a = E(\text{TS2}) - E(\text{TS1})$$

$$\Delta\Delta E_a = \Delta E_a(\text{Cs/Ag(111)}) - \Delta E_a(\text{pureAg(111)})$$

Figure 2 shows $\Delta\Delta E_a$ calculated for various coverages of Cs and the relevant oxametallacycle intermediates or transition states. The DFT calculations clearly suggest that Cs should promote selectivity to EO. Cs stabilizes TS1, leading to EO, with respect to TS2, leading to combustion products. It is also observed that the positive impact of Cs on the selectivity drops off as the distance between Cs and the organics increases. Cs can affect adsorbate energies either by interacting with the adsorbates directly through space or indirectly via the substrate.¹⁹ We attempt to separate these interactions by decomposing the substrate electronic density of states (DOS) into atomic contributions. Figure 3a suggests that the only Ag atoms that are electronically perturbed by the presence of Cs are the ones to which Cs is bonded directly. Ag atoms farther away are not impacted at all; the DOS of these atoms overlaps the DOS of unpromoted Ag, Figure 3a. The perturbed Ag atoms, i.e., those that are directly bonded to Cs, are not expected to participate in catalytic reactions. Since Cs is fairly large, its electron density spreads over these sites, and any additional adsorbates would be repelled by Pauli repulsion. We have also calculated (not shown

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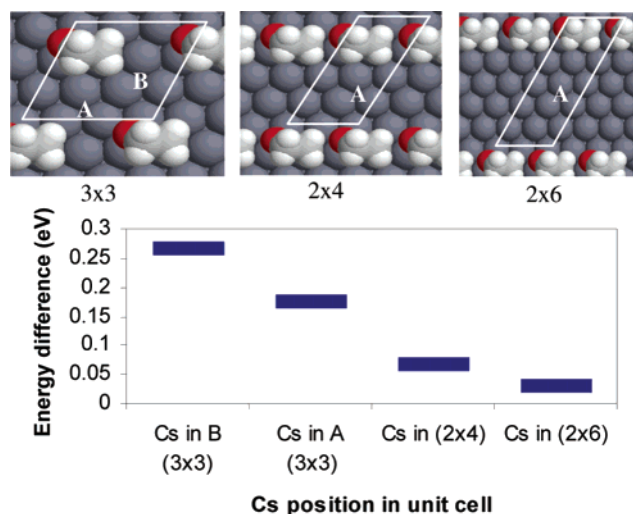


Figure 2. Calculated energy difference $\Delta\Delta E_a$ for various coverages of Cs and various distances between the Cs and a relevant adsorbate. Different configurations with unit cells are also shown; A and B indicate different Cs adsorption sites.

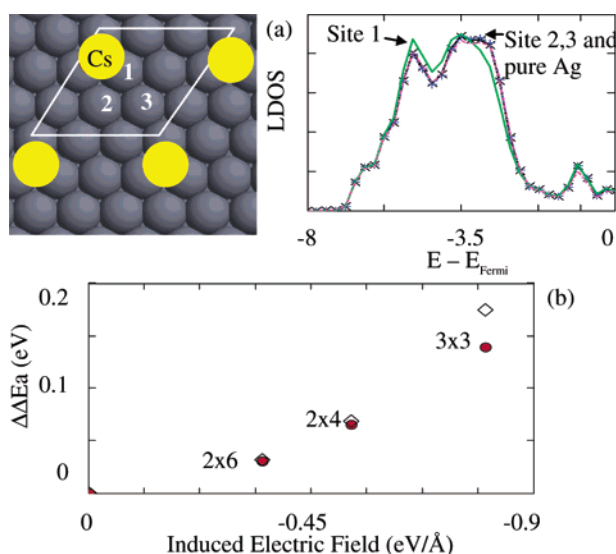


Figure 3. (a) Density of states (DOS) projected on atoms labeled 1–3 is shown and compared to DOS projected onto a Ag atom of pure, unpromoted Ag(111). (b) Calculated energy difference $\Delta\Delta E_a$ for Cs-promoted Ag(111) (empty squares) and $\Delta\Delta E_a$ calculated for unpromoted Ag(111) with artificially induced electric fields (filled circles). Labels reflect the unit cells; Cs is located in position A (see Figure 2) of each respective unit cell.

here) that adsorbates that share common Ag atoms with Cs are much less stable on the surface than those adsorbates that do not share common Ag atoms with Cs. These observations suggest that Cs, since it perturbs electronically only those Ag atoms to which it is directly bonded, does not act through the substrate but rather through space. This conclusion is consistent with experimental studies of Cs-induced changes in surface–adsorbate interactions on silver.²⁰

Previous investigations of Cs adsorption on various transition metals have shown that Cs adsorption is accompanied by charge donation to the metal substrate.²¹ This charge donation results in Cs-induced variations in electrostatic potential along the surface normal and, therefore, in the electric field. We have calculated this Cs-induced electric field on Ag(111) to range from -0.5 (at the farthest point) to -1.5 eV/Å (close to Cs) for Cs adsorbed in a 3×3 unit cell at the distance of 2 \AA above the surface, i.e., where organic adsorbates reside. It is important to note that these electric

fields are significant even for adsorption sites that are far away from the Cs site. The question that we address is whether these Cs-induced electric fields can be responsible for Cs-induced selectivity enhancement. We have calculated $\Delta\Delta E_a$ on unpromoted Ag(111) but with artificially induced electric fields that are equivalent to those induced by Cs. The results of these calculations are shown in Figure 3c. It is observed that the Cs-induced increase in the selectivity to EO can be almost completely reproduced by artificially inducing electrostatic fields that are equivalent to the Cs-induced fields. This leads us to conclude that the Cs-induced electric field acts to stabilize TS1, leading to EO, as compared to the TS2. Further analysis has shown that the effect of the Cs-induced electric field can be understood in terms of simple dipole/dipole interactions where the field stabilizes TS1, which has a favorable dipole orientation as compared to TS2.

Cl is also a promoter in this process. If one considers electro-negativity arguments only, one would expect Cl to have an effect opposite to that of Cs. However, Cl is much smaller than Cs, and has been observed to diffuse into Ag at moderate temperatures.²²

Subsurface Cl (or subsurface oxygen, also claimed to be important⁶) would enhance Cs-created fields and accentuate rather than diminish the effect of Cs, i.e., we would predict a cooperative Cl and Cs effect mutually amplifying the electric field.

To conclude, Cs acts via electric field/dipole interactions to stabilize TS1, which is involved in EO formation, compared to TS2, which is involved in combustion. We also note that in order to understand the role of various additives in catalytic processes, it is important to analyze interactions of these additives not only with stable intermediates, reactants, and products but also with relevant transition states.

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Supporting Information Available: Computational methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Ertl, G.; Knözinger, H.; Weitkamp, J., Eds. *Handbook of Heterogeneous Catalysis*; VCH: Weinheim, 1997.
- (2) King, D. A.; Woodruff, D. P., Eds. *Chem. Phys. Sol. Surf. Heterog. Catal.* **1993**, 6.
- (3) Mortensen, J. J.; Hammer, B.; Norskov, J. K. *Phys. Rev. Lett.* **1998**, 80, 4333.
- (4) Dry, M. E.; Hoogendoorn, J. C. *Catal. Rev., Sci. Eng.* **1981**, 23, 265.
- (5) Serafin, J. G.; Liu, A. C.; Seyedmonir, S. R. *J. Mol. Catal.* **1998**, 131, 157.
- (6) van Santen, R. A.; Kuipers, H. P. C. *Adv. Catal.* **1987**, 35, 265.
- (7) Campbell, C. T. *J. Phys. Chem.* **1985**, 89, 5789.
- (8) Minahan, D. M.; Hoflund, G. B.; Epling, W. S.; Schoenfeld, D. W. *J. Catal.* **1997**, 168, 393.
- (9) Campbell, C. T.; Koel, B. E. *J. Catal.* **1985**, 92, 272.
- (10) Grant, R. B.; Harbach, C. A. J.; Lambert, R. M.; Tan, J. *J. Chem. Soc., Faraday Trans. 1* **1987**, 83, 2035.
- (11) Linic, S.; Barteau, M. A. *J. Am. Chem. Soc.* **2002**, 124, 310.
- (12) Linic, S.; Piao, H.; Adib, K.; Barteau, M. A. *Angew. Chem., Int. Ed.* **2004**, 43, 2918.
- (13) Bocquet, M. L.; Michaelides, A.; Loffreda, D.; Sautet, P.; Alavi, A.; King, D. A. *J. Am. Chem. Soc.* **2003**, 125, 5620.
- (14) Linic, S.; Barteau, M. A. *J. Am. Chem. Soc.* **2003**, 125, 4034.
- (15) Linic, S.; Barteau, M. A. *J. Catal.* **2003**, 214, 200.
- (16) Stegelmann, C.; Schiödt, N. C.; Campbell, C. T.; Stoltze, P. *J. Catal.* **2004**, 221, 630.
- (17) Linic, S.; Jankowiak, J.; Barteau, M. A. *J. Catal.* **2004**, 224, 489.
- (18) Campbell, C. T. *J. Phys. Chem.* **1985**, 89, 5789.
- (19) Mortensen, J. J.; Hammer, B.; Norskov, J. K. *Surf. Sci.* **1998**, 414, 315.
- (20) Campbell, C. T.; Daube, K. A. *J. Catal.* **1987**, 106, 301.
- (21) Scheffler, M.; Stampfl, C. In *Handbook of Surface Science*; Horn, K., Scheffler, M., Eds.; Elsevier: Amsterdam 1999; Vol. 2, p 285.
- (22) Piao, H.; Adib, K.; Barteau, M. A. *Surf. Sci.* **2004**, 557, 13.

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