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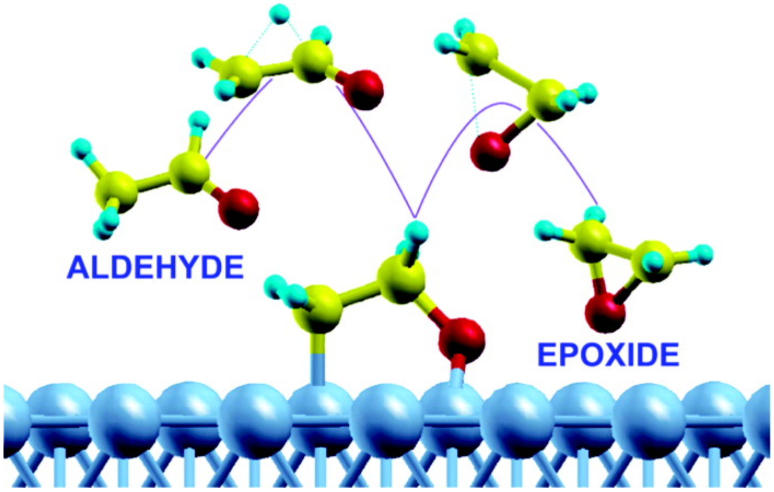

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Why Copper Is Intrinsically More Selective than Silver in Alkene Epoxidation: Ethylene Oxidation on Cu(111) versus Ag(111)

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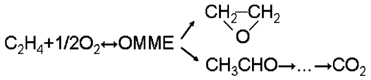
The heterogeneously catalyzed epoxidation of terminal alkenes is experimentally challenging, theoretically interesting, and technologically important. The epoxide products are versatile intermediates in chemical synthesis,[1] yet aspects of the reaction mechanism await clarification. In principle, studies carried out on well-defined surfaces under ultrahigh vacuum (UHV) conditions offer a means of examining mechanistic issues at a fundamental level. However, it is not possible to study the adsorption and subsequent oxidation of ethylene itself on metal single-crystal surfaces under UHV because its adsorption enthalpy is too low—the molecule desorbs before it can react. The strategy of using so-called model molecules that mimic the key functionalities in the actual target alkene has been validated,[2] and recent single-crystal studies demonstrate that oxygenated copper is intrinsically a much more selective epoxidizing agent than is oxygenated silver for both styrene (phenylethylene)[3,4] and trans-methyl styrene,[5] which are analogues for ethylene and propylene, respectively. It is therefore of interest to compare the catalytic epoxidation chemistry on these two metals by theoretical means.

Linic and Barteau have developed a model to examine ethylene epoxidation selectivity on Ag by analysis of the transition states of the competing reactions that drive the common oxametallocycle intermediate (OMME) to either epoxide or acetaldehyde, the latter being identified as the first step on the downhill path to combustion;[6] see Scheme 1. Here, we report a comparative study of ethylene epoxidation on the (111) surfaces of copper and silver with a view to elucidating the origin of the superior epoxidation selectivity that characterizes Cu.

The competing reaction pathways for aldehyde and epoxide formation have been studied by means of density functional theory. Periodic slabs consisting of four metallic layers interleaved with five equivalent empty layers (vacuum) were employed to determine adsorption energies and activation energies. The $p(2 \times 2)$ and $p(4 \times 4)$ adsorbate supercells corresponding to fractional coverages of 0.125 and 0.0625 monolayers,[7] respectively, were used to examine the effect of surface coverage. The energy was evaluated using the PW91 functional,[8] and the climbing image-nudged elastic band method was employed to locate the transition-state structures.[9] The PAW method[10] was used to represent the inner cores, and electron states were expanded in a plane wave basis with a kinetic cut-off energy of 315 eV. Calculations were performed using the VASP package.[11] A Monkhorst−Pack mesh with $2 \times 2 \times 1$ k-points was used with the larger supercells.[12] The adsorbate-induced dipole moment was eliminated in the vacuum region.[13]

Scheme 1. Competitive Reactions for Ethylene Oxidation



The following computational strategy was used. First, oxygen was adsorbed, and then ethylene was allowed to interact with the oxygenated surface, releasing 0.1 and 0.3 eV for Cu and Ag, respectively. Then, the OMME intermediate was formed via a relatively low energy barrier, ~0.7 eV for both Cu and Ag.

The OMME structure involves the interaction of three metal atoms with the O−C−C skeleton, and the energy profiles for the competing reaction channels are shown in Figure 1. Oxygen (not shown) and OMME interact more strongly with Cu than with Ag, with the additional stabilization induced by Cu amounting to 1.22 and ~1.19 eV, respectively. The products, however, interact with the two metals to the same degree (Figure 1). On Cu(111), OMME formation is almost thermoneutral, whereas on Ag(111), it is exothermic by ~0.4 eV, with respect to coadsorbed oxygen and ethylene. The system may then evolve to yield either epoxide or aldehyde—which the latter is the precursor to combustion.[7] On Cu(111), epoxide formation from OMME is *endothermic* by 0.54 eV, whereas acetaldehyde formation is *exothermic* by −0.49 eV. On Ag(111) *both* pathways are exothermic: −0.32 and −1.32 eV for epoxide and aldehyde, respectively. In every case, the reaction product is weakly bonded to the surface by ~0.1 eV.

Clearly, the four activation barriers that characterize the competing reaction pathways on Cu and Ag play a key role in determining reaction selectivities and selectivity differences. The activation barriers on silver are 0.80 and 0.73 eV for epoxidation and acetaldehyde formation, respectively, in good agreement with earlier studies.[6,7] For Cu, both barriers are significantly higher, 0.98 and 1.23 eV for epoxide and aldehyde, respectively. *Most importantly, the critical difference between the two* metals is that, on copper, epoxide formation is less activated than aldehyde formation, whereas, on silver, the opposite is true. When thermal effects are taken into account, the differences in Gibbs energy barriers for the two reaction pathways starting from OMME ($\Delta G^{\ddagger}$(aldehyde) − $\Delta G^{\ddagger}$(epoxide)) are 0.06 eV for Ag and −0.20 eV for Cu, at 500 K (typical reaction temperature). That is, on Cu, epoxidation is substantially favored relative to Ag.

The relatively low activation barrier toward epoxide formation on Cu as compared to that on Ag is an important factor in determining the intrinsically superior epoxidation selectivity exhibited by copper. The structures of the four transition states that lead to epoxide and acetaldehyde on both metals are illustrated in Figure 2. We find that whereas, on Ag, both channels are characterized by early transition states (that resemble the reactants), on Cu, aldehyde formation involves an early transition state whereas epoxidation is via a late transition state. This suggests that the stronger the metal−OMME interaction, the more favorable the barrier difference. It explains why copper wins over silver—the relative size of the epoxidation and aldehyde formation barriers is inverted in going from Ag to Cu.

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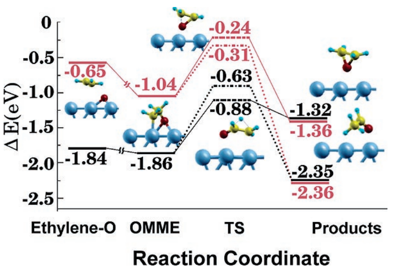

Figure 1. Reaction profiles and structures for epoxide and acetaldehyde formation starting from coadsorbed ethylene and oxygen on Cu (black) and Ag (red). Note inversion of the energy barriers for OMME reactions. Energy is referred to gaseous $1/2O_2$ and ethylene. Only barriers relevant to selectivity are shown.

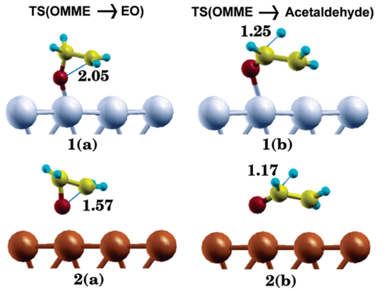

Figure 2. Comparison between the transition states from OMME to (a) epoxide and (b) acetaldehyde on both Ag (1, gray) and Cu (2, red) (111) surfaces. Relevant distances are given in angstroms.

The calculated activation barriers may be used to estimate the relative rates of epoxide versus aldehyde production at 500 K via conventional transition state theory. If we assume that this is the dominant factor in determining selectivity, one arrives at crude estimates for selectivity toward epoxidation of ~99% (Cu) and ~50% (Ag). These estimates may be compared with results obtained with temperature-programmed reaction measurements for the epoxidation of styrene on single-crystal surfaces of Cu and Ag under UHV conditions, where secondary reactions are negligible. On Cu(111)[5] and Ag(100)[3], epoxidation selectivities of 100 and ~50% (maximum), respectively, are found—in qualitative accord with the above theoretical estimate.

The effect of increased adsorbate coverage, as indicated by the results for the $p(2 \times 2)$ supercell versus the $p(4 \times 4)$ supercell, is interesting; these two structures correspond to (equal) coverages of O_a and ethylene of 0.25 and 0.0625 monolayers, respectively. On copper, the activation barrier to epoxidation increases by 0.12 eV when O_a coverage is increased from 0.0625 to 0.25 monolayers. In contrast, the activation barrier to 1,2-H shift (aldehyde formation) is essentially unaffected (within <0.01 eV). This is qualitatively consistent with the experimentally observed 10-fold reduction in butadiene epoxidation yield, at fixed alkene coverage, when the oxygen coverage was increased from 0.05 to 0.25 monolayers on Cu(111).[14] The origin of this coverage-dependent barrier to epoxidation on Cu resides in differences in adsorption-induced metal surface relaxation, an important effect first reported in connection with the dissociative adsorption of methane on Ir.[15] Here, ethylene epoxide adsorption on Cu(111) at high coverage results in a significant average contraction of the first metal interlayer layer by −0.03 Å, whereas the elastic relaxation is close to zero for the large supercell. On Ag, there is no such effect. Interestingly, this is in qualitative agreement with recent experimental results for styrene epoxidation on Ag, where, in contrast to Cu, epoxide production is observed over the whole range of oxygen coverage.[3] The present results also provide insight into experimental findings regarding epoxidation catalysis by the bimetallic Cu/Ag system.[16] From a theoretical standpoint, it has been shown that, in such cases, interpolation of the properties of the separate metals provides an approximation to the catalytic behavior of the bimetallic system.[17] Here, for the case of a $p(2 \times 2)$ supercell of Cu atoms substitutionally embedded in a Ag matrix, interpolation of the relevant activation barriers from the values pertinent to Cu and Ag predicts a modest increase in epoxidation selectivity from ~50 to ~56% at 500 K. This is in agreement with the ~58% selectivity observed by Barteau et al. for a $p(2 \times 2)$ dispersion of copper atoms in a matrix of silver.[16]

A possible practical limitation to the use of Cu as an epoxidation catalyst is related to the stability of the epoxide. As is apparent from Figure 1, ethylene oxide is thermodynamically unstable with respect the adsorbed reactants (the opposite is true of Ag). This implies that short contact times might be necessary in order to limit decomposition of the product. Very recent work[18] on the Cu-catalyzed epoxidation of propene at atmospheric pressure demonstrates that steady-state selectivities toward propene epoxide of ~40% are achievable at low reactant conversion—comparable to the performance of the Au/TiO_2 catalytic system discovered by Haruta and co-workers,[19] but without the need for co-fed hydrogen. Furthermore, the epoxidation selectivity increases with decreased contact time.[20]

In summary, Cu is predicted to be intrinsically much more selective than Ag for ethylene epoxidation, especially at low oxygen coverage. The superiority of Cu is due to inversion of the activation energy barriers for cyclization to epoxide versus H-shift to aldehyde, relative to Ag.

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Supporting Information Available: Supporting Information concerning structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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