

## Surface Science Perspectives

Surface science and the advancement of direct olefin epoxidation  
 A perspective on the article, “Partial oxidation of higher olefins on Ag(111) and Ag(110): Conversion of styrene to styrene oxide, benzene, and benzoic acid”, by Andreas Klust and Robert J. Madix

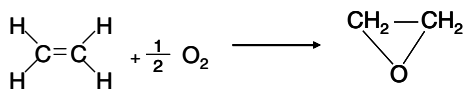
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Few reactions are as conceptually simple or as devilishly difficult as the epoxidation of ethylene to form ethylene oxide:



After all, the target ethylene has only two more electrons than the surface scientists favorite molecule, CO; the reaction involves only oxygen addition with no bond-breaking or rearrangement in the organic; and a wide variety of solids, metals and metal oxides included, are capable of activating oxygen and carrying out catalytic oxidations of some sort. Of course, as we know all too well, even the oxidation of CO is far from simple, exhibiting a rich variety of dynamic behavior and dependencies on the structure and composition of metal surfaces. Oxidation of organic molecules, even those with only a few more atoms and electrons than CO, introduces the additional complexity of reaction *selectivity*; CO<sub>2</sub> is only one of several possible carbon- and oxygen-containing products, and generally the least chemically or economically interesting.

Heterogeneous epoxidation of olefins continues to be an enticing subject for both scientific and practical reasons. Although the oxidation of ethylene to ethylene oxide by supported silver catalysts has been practiced commercially for more than one half century, it remains a singularity. Silver is the only metal that produces ethylene oxide with viable selectivities and, with the exception of a butadiene epoxidation process briefly practiced by Eastman Chemical, ethylene is the only olefin that is epoxidized commercially via a direct, heterogeneously catalyzed process. Such apparent uniqueness of catalyst and substrate invites explanation.

Surface science studies over the past three decades have made significant contributions to our understanding of this chemistry, and the paper by Klust and Madix [1] illustrates some of the important new insights and challenges emerging from epoxidation of more complex olefins on silver single crystal surfaces. It provides confirmation of key ideas about the mechanism of epoxidation, while pointing out the rich complexity of this chemistry. Much remains to be done if we are to understand the specific surface characteristics that lead to different competing reaction products, and to turn this knowledge into new catalytic processes.

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The first wave of surface science studies in the 1980s by the groups of Madix [2], Campbell [3], Lambert [4] and others focused primarily on the identity and chemistry of active oxygen species on silver surfaces. These efforts, along with catalyst reaction and characterization studies by van Santen and co-workers [5], largely resolved the longstanding question of whether molecular or atomic oxygen species are the active oxidant in favor of the latter. Understanding of the reaction mechanism and, in particular, what controls selectivity, has emerged only recently, and has benefited substantially from the combination of theoretical and experimental surface science.

The key concept driving this second wave is the recognition of surface oxametallacycles as the central intermediate in olefin epoxidation. These species, which incorporate an  $-O-C-C-$  unit attached to the metal surface at each end, were first associated with epoxide formation by Brainard and Madix in 1989 [6]. It took nearly a decade, however, before a stable oxametallacycle was synthesized and spectroscopically characterized [7], and even longer before the conversion of a spectroscopically confirmed oxametallacycle to an epoxide was demonstrated [8]. In the past few years, approximately 50 papers involving oxametallacycles on metal surfaces have appeared, and this species has dominated the discussion of olefin epoxidation mechanisms. Clear spectroscopic identifications of these species are much fewer, however. Indeed the situation is reminiscent of that once prevailing in the organometallic chemistry of the structurally analogous metallaoxetanes, which prompted one group to author a review with the title “Metallaoxetanes as intermediate in oxygen-transfer reactions – reality or fiction?” [9].

The paper by Klust and Madix provides valuable spectroscopic confirmation, by both RAIRS and XPS, of the formation of oxametallacycle intermediates in the oxidation of styrene to styrene oxide on silver single crystal surfaces. It also goes beyond earlier work on this chemistry by Lambert and co-workers [10,11] and by Enever et al. [12,13] in several important ways. The former workers were unable to identify side products in TPD studies of the reaction of styrene with adsorbed oxygen on Ag(111) and (100) surfaces. Klust and Madix have done so, demonstrating the formation of products such as benzoic acid, benzene, and ultimately  $CO_2$ , via a surface oxametallacycle. This is a critical point. Although the existence of a “common intermediate” leading to both epoxides and combustion products in olefin epoxidation was proposed by Cant and Hall in 1978 [14], only recently has it been shown that the oxametallacycle is this common intermediate, and that its competing reaction channels control the selectivity of the catalytic epoxidation process [15]. This concept has led to the demonstration of new bimetallic ethylene epoxidation catalyst designed to inhibit side reactions of oxametallacycles [16], but it remains controversial. Alternative schemes for selectivity control involving different oxygen species on the catalyst also find support [17]. The paper by Klust and Madix provides experimental evidence for the extension of the “oxametallacycle as common intermediate” hypothesis beyond ethylene to styrene oxidation.

What is the optimum state of the surface to facilitate olefin epoxidation? As Klust and Madix point out, this is an open issue. While the literature has long been filled with speculation about the surface oxidation state of working silver catalysts, the development of surface oxametallacycle chemistry via surface science studies has sharpened the focus considerably. DFT calculations have indicated that ethylene epoxidation can proceed via surface oxametallacycles on Ag(111) at low oxygen coverages [18,19], and on the oxidized Ag(111)-p(4×4)-O surface [19]. A recent calculation [20] suggests that this reaction is inhibited on the highly oxidized surface, and the results of Klust and Madix provide experimental evidence that isolated oxygen adatoms exhibit a higher selectivity toward partial oxidation than do oxygen atoms incorporated in the p(4×4)-O structure.

Finally, this paper provides a glimpse of the challenges ahead in controlling the selectivity of olefin epoxidation by controlling the speciation and reactivity of surface oxametallacycle intermediates. As the authors point out, there are two possible oxametallacycles that can be formed by oxygen addition to the  $C=C$  bond of styrene: a “linear” structure formed via oxygen attachment to the terminal carbon, and a “branched” structure formed via oxygen addition at the second carbon. Results for styrene oxide ring opening on clean silver surfaces have provided evidence only for the linear oxametallacycle to date [12], but Klust and Madix suggest that both isomers may be required in the epoxidation process to account for all the observed side products. For di-olefins with a  $C_4$  backbone such as butadiene and isoprene, the situation may be even more complicated; one may also need to consider *cis* and *trans* oxametallacycle isomers depending on the configuration of substituents around the interior  $C-C$  bond. Can one rationally manipulate the state of the surface or catalyst to select one oxametallacycle isomer and thereby control product selectivity? Today we are far from that goal. As this paper demonstrates, the stability of oxametallacycle intermediates may be strongly dependent on surface structure and reactant coverages. Styrene oxide is formed at 330 K in the reaction of styrene with oxygen atoms on the Ag(111) surface. Ring closure of linear oxametallacycles formed by ring opening of styrene oxide occurs at 485–505 K on clean (111) and (110) surfaces in the absence of adsorbed oxygen [12,21]. We have also observed significant differences in ring-closure kinetics for oxametallacycles formed from epoxybutene on Ag(110) vs. (111) surfaces [22]. The connections between surface structure and the reactivity of these new intermediates remain to be established. The potential payoff is large however. Imagine being able to carry out direct, chiral epoxidations of olefins on surfaces with enantioselectivities that rival those in homogeneous catalysis. Styrene oxide has two enantiomers after all, and the understanding that this paper adds to the mechanism, kinetics, and selectivity of its synthesis on silver surfaces is a first step toward such goals.

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