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Heterogeneous Catalysis

Low-Basicity Oxygen Atoms: A Key in the Search for Propylene Epoxidation Catalysts[**]

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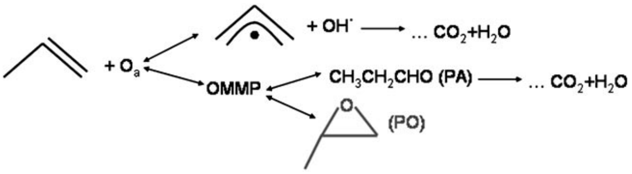
Epoxides are versatile intermediates of great value to the chemical industry. Ethylene oxide is produced on a very large scale (global annual production ca. 5000 million pounds) by the direct silver-catalyzed heterogeneous partial oxidation of ethylene with oxygen. In this process, selectivity towards epoxide production (vs. CO_2 and H_2O formation) is about 85%.[1] However, propylene oxide (PO), a product with much higher added value used extensively for the production of polyether polyols, propylene glycol, and propylene glycol ethers,[2] cannot be obtained by this route: silver-catalyzed oxidation yields very low selectivity towards epoxide formation (ca. 5%) because of the competing very rapid combustion of propylene. As a result, industrial production of PO is carried out either by the chlorohydrin process, which is costly and environmentally problematic, or by the hydroperoxide process, which produces equal amounts of styrene or *tert*-butyl alcohol as by-products.[3] Therefore, a direct heterogeneously catalyzed oxidation that uses molecular oxygen is highly desirable. Recently, it was shown that Cu/SiO_2 catalysts are active for propylene epoxidation under practical conditions where Cu^0 survives,[4] and these catalysts are about 55% selective towards epoxide at around 1% conversion of the reactant.[5] This finding was significant because the performance of the catalyst is comparable to that originally reported for Au/TiO_2 catalysts discovered by Haruta and co-workers.[6] However, unlike Au/TiO_2 propylene-epoxidation catalysts, the copper catalysts do not require hydrogen cofeeding, which leads to extensive coproduction of water. Herein, we describe theoretical studies that address the fundamental question: why is copper much more selective that silver? To date, only a few attempts to theoretically describe the oxidation of propylene have been published,[7] which is in contrast to the very detailed knowledge of the production of ethylene oxide.[8]

Density functional theory (DFT) has been used to determine the thermochemistry and activation-energy barriers for the competing reactions of combustion and selective oxidation that determine selectivity in propylene epoxidation. Periodic slab calculations were carried out to explore oxidation reaction mechanisms on Cu(111) and Ag(111) surfaces to determine the energy profiles and kinetic parameters for the processes illustrated in Scheme 1, which are in agreement with the generally accepted mechanism given by Linic and Barteau.[8b]



Scheme 1. Reaction mechanism for propylene oxidation.

The reaction between oxygen and propylene on the metal surface can either lead to dehydrogenation of the latter (to yield hydroxyl and allyl species, which are precursors to combustion) or to an intermediary propylene oxametallacycle (OMMP;[9] Figure 1). This intermediate is analogous to the intermediate proposed for ethylene epoxidation (OMME).[8a]

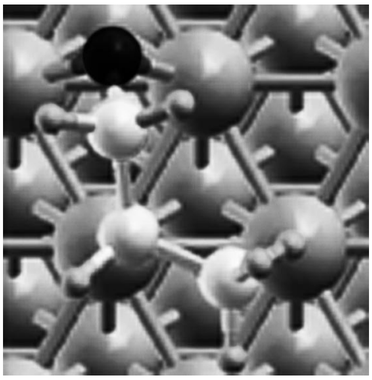


Figure 1. A propylene oxametallacycle (OMMP) on a (111) metal surface (C white, H small gray, O black, metal large gray).

We shall refer to the formation of the intermediate as the "primary chemistry". The OMMP intermediate then undergoes rearrangement to either PO or propanal (PA), the latter eventually leading to combustion. We shall refer to this second process as the "secondary chemistry".

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Oxygen adatoms (O_a) are preferentially located at threefold sites.[10] Propylene adsorption occurs at neighboring vacant sites with the C=C bond across a face-centered cubic (fcc) site, in analogy to ethylene.[8d] There are four nonequivalent adsorption atomic configurations for coadsorbed propylene and oxygen (Figure 2). These configurations differ in the relative position of the methyl group with respect to O_a. From configuration I, a search for the minimum-energy path leads to the stripping of hydrogen atoms to yield allyl and hydroxyl radicals, whereas configurations II, III, and IV (Figure 2) lead to the formation of OMMP intermediates.

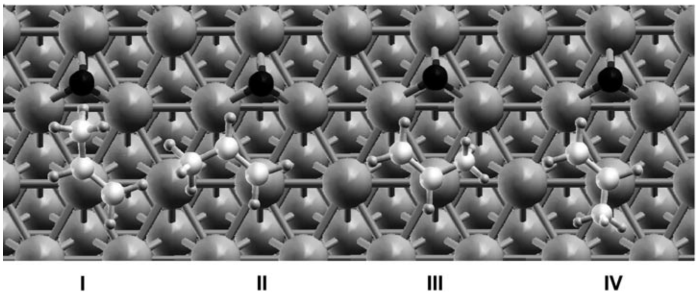

Figure 2. Structures for coadsorbed oxygen atoms and propylene molecules (C white, H small gray, O black, metal large gray).

On Ag(111), the adsorption energies of coadsorbed propylene and O_a lie in the range of 0.55–0.63 eV with respect to gas-phase reactants. This range corresponds to an appreciable surface coverage of propene under practical conditions, namely, around 1 bar of O_2 at 500 K. As a result, all four configurations shown in Figure 2 will be present under reaction conditions (ca. 500 K). Configuration I is distinguished by having the shortest O–H distance (1.841 Å), which results from a hydrogen bond between O_a and the methyl group. This interaction is strong enough to rotate the methyl group towards the surface. In its absence (configurations II–IV), the methyl group points away from the surface. For both copper and silver, the calculated energy profiles for the primary and secondary chemistry are shown in Figures 3 and 4; the relevant structures are also shown.

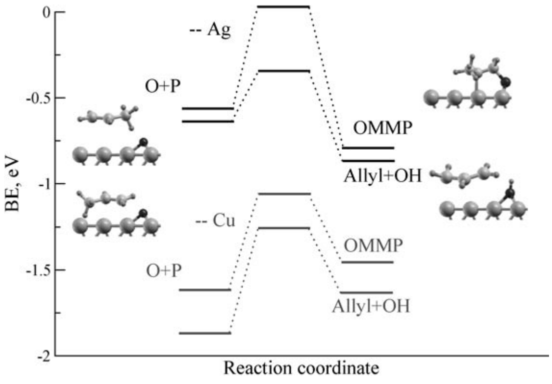

Figure 3. Primary chemistry: reaction profiles for allylic hydrogen abstraction and OMMP formation. BE = bond energy. See text for details.

On the silver surface, hydrogen stripping from configuration I is associated with a small energy barrier (0.30 eV). Configurations III and IV lead to OMMP formation with the oxygen atom linked to the terminal carbon atom: the resulting species are enantiomers and the corresponding energy barrier is 0.60 eV. Configuration II leads to a different OMMP intermediate (OMMP-2) in which the C–O bond involves the secondary carbon atom. The associated energy barrier (1.21 eV) is much larger than that for OMMP formation; indeed, it lies high above the zero level corresponding to the gas-phase reactants. Therefore, this reaction path can be neglected. This result agrees with the observation that secondary OMM intermediates are only formed upon epoxide product adsorption and not as the result of a reaction between propylene and oxygen.[11] Moreover, OMMP is 0.4 eV less stable than the corresponding intermediate for ethylene epoxidation.[8d] Thus, configuration I is the critical one that triggers allylic hydrogen abstraction and combustion. This conclusion is in agreement with experimental results for the copper-catalyzed epoxidation of structural isomers of phenylpropylene for which it was found that orientation of the adsorbed alkene with respect to the oxygenated surface is the key factor that determines selectivity towards epoxide formation.[12]

For silver, the secondary chemistry is shown in Figure 4. Cyclization of OMMP to epoxide is hindered by an energy barrier of 0.62 eV. Aldehyde formation involves a 1,2-hydrogen shift and a barrier of 0.56 eV. These barriers are lower than those in ethylene epoxidation: 0.80 and 0.73 eV for epoxide and aldehyde, respectively.[8d] The differences may be traced back to the lower stability of OMMP compared to OMME. However, the difference in energy barriers is very similar in both cases: 0.06 and 0.07 eV for propylene and ethylene, respectively. As the structures for the OMMP and OMME are very similar, we may conclude that in the secondary chemistry the propylene methyl group is essentially a spectator.

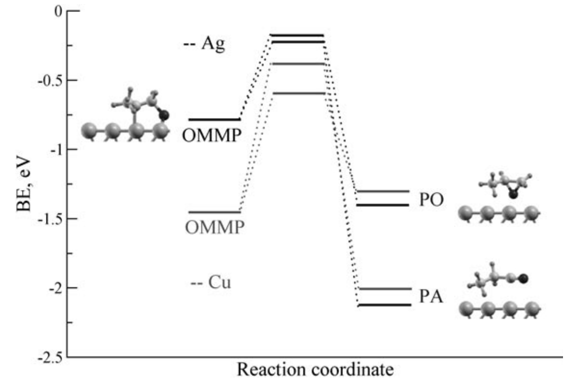

Figure 4. Secondary chemistry: reaction profiles for epoxide and aldehyde formation by rearrangement of OMMP. BE = bond energy. See text for details.

On Cu(111), the starting point again is O_a on hollow sites with coadsorbed propylene in configurations I to IV as discussed above. As with the case of silver, the binding energies for coadsorbed propylene and O_a lie in the range of 1.60–1.83 eV with respect to gas-phase reactants. The O–H distance in configuration I is 2.012 Å, which is slightly longer than that on silver. For configurations I and III, the competing reactions that lead to abstraction of an allylic hydrogen atom or OMMP formation have barriers of 0.60 and 0.54 eV, respectively. Again, an OMMP-2 species may be formed from configuration II, but the process is hindered by 1.28 eV and, therefore, can be neglected. As for the secondary chemistry, the barriers to PO and PA formation are 0.96 and 1.10 eV, respectively.

With these results, we can estimate the selectivity for silver- and copper-catalyzed production of PO by using rate constants derived from transition-state theory for the two branching reactions given in Scheme 1 and possible back reactions can be neglected. These estimates do not take into account vibrational and tunnel-effect contributions; however, they are qualitatively meaningful because of the large differences found in the barriers when going from silver to copper. On Ag(111), the difference in the barrier height between the two competing paths in the primary chemistry is around 0.3 eV. An estimate based on a straightforward application of transition-state theory indicates that at about 500 K around 99 % of the adsorbed propylene molecules will undergo allylic hydrogen-atom stripping then combustion. The situation is strikingly different on Cu(111); in the primary chemistry, OMMP formation is actually favored over abstraction of a hydrogen atom and at about 500 K selectivity towards OMMP is predicted to be around 60 %. In the secondary chemistry, the barrier heights imply that around 99 % of the OMMP should undergo cyclization to PO. The net result is that the overall PO selectivity should be more than 50 %, which is of the same order as the best value obtained in catalytic experiments.[5] In passing, we note that although detailed microkinetic modeling has been used to rationalize alkene epoxidation, the large number of parameters and approximations involved allows a fit to experimental data to be obtained by using different models so that the resulting physical insight can be limited.[13]

Our message is simple. The theoretical results imply that the key difference between silver and copper resides in the primary chemistry: silver favors allylic hydrogen stripping, copper favors metallacycle formation. This difference suggests that attempts to further improve the selectivity of copper catalysts should focus on the primary chemical processes, possibly by altering the structure and/or composition of the metal surface.

It is of interest to ask how this difference between the two metals arises. The propensity to strip hydrogen atoms is driven by the basic character of O_a. This may be evaluated by adsorption of chemical probes that measure the availability of the electrons in the valence band of the O_a atom.[14] Accordingly, to obtain an indication of the relative basicity of O_a in the two cases, we examined the adsorption of a Lewis acid, SO_2, on the oxygen-covered metal surfaces to form SO_3. The binding energies of SO_2 to O_a on copper and silver are 1.45 and 2.48 eV, respectively. Thus, the fundamental reason for the superior performance of copper is its low Lewis basicity relative to silver—this conclusion provides a clear signpost for further work. It also points to practical experimental means for screening candidate systems.

In summary, propylene epoxidation on silver is strongly disfavored by the markedly basic character of O_a, which leads to allylic hydrogen stripping and combustion. In contrast, the lower basicity of copper favors metallacycle formation then epoxide production. Theoretical estimates of epoxidation selectivity are in good agreement with experimental data for both silver and copper catalysts.

Experimental Section

DFT calculations applied to slabs were carried out to investigate the reaction between coadsorbed oxygen and propylene on the (111) surfaces of copper and silver. Periodic slabs comprised four metallic layers separated by a vacuum width corresponding to five equivalent empty layers. The reactants and products were adsorbed only on one side of the slab. p(3×3) supercells that corresponded to an equal fractional coverage of 0.11 monolayers were used. The energy was evaluated by using the PW91 functional[15] and the climbing image-nudged elastic band (CI-NEB)[16] method was employed to locate the transition-state structures that were characterized by vibrational analysis. The PAW method[17] was used to represent the inner cores and one-electron states were expanded in a plane-wave basis with a kinetic cut-off energy of 315 eV. Calculations were performed by using the VASP program.[18] A Monkhorst–Pack mesh with 5 × 5 × 1 *k* points was used.[19]

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