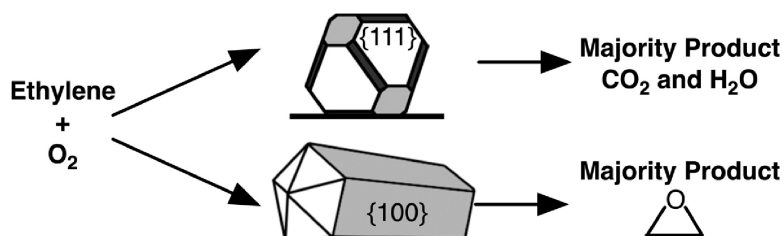


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Engineering Selectivity in Heterogeneous Catalysis: Ag Nanowires as Selective Ethylene Epoxidation Catalysts

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Controlling selectivity in heterogeneous catalysis is critical for the design of environmentally friendly processes that minimize the production of undesired byproducts and operate with high energy efficiency. In this communication we show an example where density functional theory (DFT) calculations have been utilized along with solution-based synthetic chemistry approaches to design heterogeneous silver (Ag) catalysts that are more selective in partial oxidation of ethylene to form ethylene oxide (EO) than conventional Ag catalysts. Our studies suggest that advances in synthetic chemistry, which have laid the groundwork for the controlled synthesis of uniform nanostructures with well-defined surface facets,² might provide an important platform for the design of highly selective heterogeneous catalytic materials.^{1,3}

Ethylene epoxidation is a process in which ethylene and oxygen react to form EO. EO is a gateway chemical used in the synthesis of ethylene glycol (antifreeze), ethanolamines, detergents, and many other chemicals. Silver is the only heterogeneous catalyst that can achieve reasonable selectivities to EO. The main byproduct in the reaction are combustion products, CO₂ and H₂O. Monometallic Ag catalysts, synthesized using standard incipient wetness methods and supported on α -Al₂O₃, achieve selectivities to EO of up to 20% for Ag particles with diameter less than 30 nm.^{4,5} The selectivity can be enhanced by increasing the particle diameter, reaching ~45% at differential conversions for an average diameter of 1 μ m.⁵

Recent DFT calculations, surface science experiments, and kinetic isotope studies have suggested that the selectivity to EO is controlled by a reaction network of competing elementary pathways where a surface oxametallacycle (OMC) intermediate undergoes isomerization reactions on Ag to form the selective product, EO, or acetaldehyde (AC), which subsequently reacts to form unselective combustion products.^{6,7} It was shown that on the Ag(111) surface the activation barriers for these elementary steps are comparable to each other, ultimately limiting the selectivity to EO on this surface.^{7b} The limited selectivity of Ag(111) has practical implications since catalytic particles that are synthesized using standard impregnations strategies are dominated by the Ag(111) facet.⁸ To enhance the selectivity of commercial catalysts—these reach the selectivity of over 80%—Ag is promoted with various additives including Cs, Cl, and Re. Another strategy to enhance the selectivity of Ag catalysts, explored in this contribution, relies on the identification of Ag surfaces that are inherently more selective than Ag(111) and synthesis of catalysts which are dominated by these surfaces.

In Figure 1 we show a DFT-calculated potential energy diagram associated with the transformation of the OMC intermediate to EO and AC on Ag(111) and Ag(100). The relevant transition states were identified using a climbing image-nudged elastic-band algorithm within the framework of DFT. Figure 1 shows that the difference in the activation barriers associated with the formation of AC and EO is by ~0.1 eV larger on Ag(100) than on Ag(111),

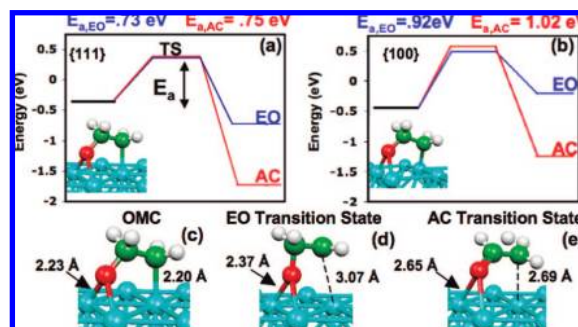


Figure 1. (a,b) Potential energy surfaces for transformation of OMC to AC and EO on Ag(111) (a) and Ag(100) (b). Energies are referenced to O(ads) and ethylene(g) (c) OMC on Ag(111), (d) EO transition state on Ag(111), (e) AC transition state on Ag(111).

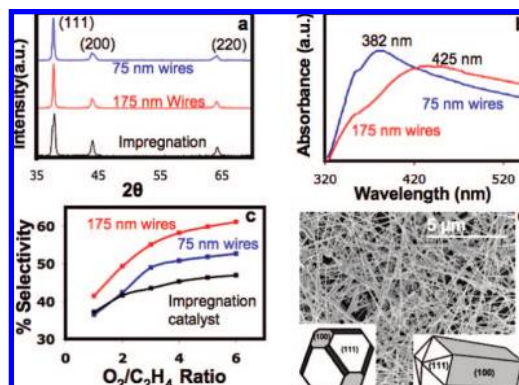


Figure 2. (a) XRD spectra for nanowire and particle catalysts, for relative peak intensities, see Table S1; (b) UV-vis absorbance spectra of 75 and 175 nm diameter Ag nanowires; (c) measured selectivity as a function of oxygen to ethylene ratio; (d) SEM image of 75 nm nanowires. Insets show models of nanowires and spherical particles

suggesting that the (100) surface should be intrinsically more selective to EO than the (111) surface.

To test this hypothesis we have synthesized two different catalysts containing monometallic Ag supported on α -Al₂O₃: (i) an Ag nanowire catalyst containing nanowires with mainly the Ag(100) surface facet exposed and (ii) a conventional Ag particle catalyst consisting of spherical particles with mainly the Ag(111) facet exposed.

A standard incipient wetness technique was used to synthesize the Ag particle catalyst. The self-seeding polyol synthesis was used to synthesize pentagonal Ag nanowires.⁹ The nanowires have been characterized previously using electron diffraction and STM measurements, showing that these are terminated on all sides by the (100) planes.^{8,10} This is further supported by the results of X-ray diffraction (XRD) studies in Figure 2a indicating that the Ag nanowire catalysts have reduced quantities of high-index Miller

planes as compared to the impregnation catalyst; that is, the nanowires grow in the longitudinal direction (also see Supporting Information Table S1). We have also established that the diameter of nanowires can be systematically manipulated by controlling the concentration and rate of addition of the Ag salt and the stabilizer molecules. Figure 2b shows UV-vis absorbance spectra for two different nanowire solutions. The measured spectra are characteristic of nanowires with approximate diameters of 75 and 175 nm (also see Figures S1 and S2).

The particle and nanowire catalysts were tested in the ethylene epoxidation reaction in a continuous flow reactor at constant total flow rate, differential conversion, temperature $T = 510$ K, and atmospheric pressure. The nanowire catalysts contained Ag nanowires with an average diameter of ~ 75 and 175 nm. The impregnation catalyst contained spherical particles with average diameter of ~ 1 μm . Figure 2c shows measured selectivities to EO, defined as the amount of EO produced divided by the amount of ethylene consumed, as a function of oxygen to ethylene feed ratio. The conversion for different catalysts, defined as the amount of ethylene consumed divided by the amount of ethylene entering the reactor, was kept constant ($\sim 3\%$) by adjusting the mass of active Ag material.

The measurements in Figure 2c show that the nanowire catalysts are more selective than the particle catalyst over a wide range of external conditions. For example, the highest measured selectivity for a nanowire catalyst was 65%, while the Ag particle catalysts reached the selectivity of 47%. It is important to point out that the measured turn over frequencies (TOF) per surface site for nanowire catalysts were similar to the TOF for the particle catalyst. Since the nanowires had larger surface to volume ratio than the particles, the EO yield on per catalyst mass basis was significantly higher for the nanowire catalyst. Figure 2c also shows that the selectivity to EO of the nanowire catalyst increased as the average diameter of Ag nanowires was increased. It is believed that this enhancement in the EO selectivity is a result of an increased ratio of well-coordinated Ag sites to under-coordinated step and kink sites for larger nanowires. The reactor tests were performed over a period of 5 days without significant loss of selectivity and conversion. The selectivity dropped by $\sim 3\%$ after additional 3 days on stream.

To understand the origin of the selectivity increase for the nanowire catalyst, the calculated geometries of the transition states (TSs) for the formation of AC and EO were analyzed. The analysis showed that on both surfaces, Ag(111) and Ag(100), the TS leading to AC requires significant elongation of the O-Ag and C-Ag bonds in the oxametallacycle. On the other hand, for the EO TS, the O-Ag bond distance in the oxametallacycle is only slightly changed while the C-Ag bond is substantially elongated.¹¹ We have used DFT to calculate adsorption energies for two saturated functional groups, OCH₃ and CH₃, that form the surface oxametallacycle on the Ag surfaces. The analysis showed that the adsorption energy of the OCH₃ fragment is by 0.35 eV more exothermic on Ag(100) compared to Ag(111), indicating that it is energetically more demanding to elongate the O-Ag bond on Ag(100) than on Ag(111). This ultimately results in the high activation barrier for the formation of AC on Ag(100). The adsorption of the CH₃ group is more exothermic on Ag(100) by only 0.1 eV.

In light of the results presented herein it is important to revisit the concept of structure sensitivity in ethylene epoxidation on Ag and generally in heterogeneous catalysis. Structure sensitivity has classically been defined in terms of the variation in TOF as a function of the size of catalytic particles. The reactions for which there is a small change in TOF as the average size of active catalytic

particles is changed are termed structure insensitive.¹² It has been shown previously that for conventional Ag particle catalysts, ethylene epoxidation is structure insensitive.⁴ The results presented in this Communication suggest that TOFs for ethylene epoxidation on Ag are similar for the nanowire and particle catalysts; that is, the reaction is structure insensitive irrespective of the shape of active catalytic structures. We note that this does not mean that the activation barriers for individual elementary steps are not affected by Ag surface structure, but rather it suggests that complex interplay of the elementary steps yields macroscopic TOFs that are similar for different Ag surfaces. The concept of structure sensitivity as defined above reflects only on the TOFs (i.e., the rate of ethylene consumption). More importantly, our results show that the selectivity to EO is affected significantly by the nature of the dominant Ag surface facet. This would suggest that this reaction is highly structure sensitive with respect to the selectivity to EO. The structure sensitivity of the selectivity to EO is a consequence of significantly different activation barriers associated with the isomerization of the OMC intermediate to form EO and AC on Ag(111) and Ag(100).

In conclusion, we show that the Ag nanowire catalysts exhibit higher selectivity to EO than conventional particle catalysts in the ethylene epoxidation reaction. The higher selectivity of the nanowire catalysts was attributed to a higher concentration of the Ag(100) surface facets in the nanowire catalysts compared to the particle catalysts. DFT calculations showed that the transformation of the surface oxametallacycle intermediate to form the selective product, EO, is more favorable on the Ag(100) than on Ag(111). The studies showed that recent advances in the controlled synthesis of uniform nanostructures with well-defined surface facets might provide an important platform for the design of highly selective heterogeneous catalysts.

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Supporting Information Available: Detailed synthesis, computational, and experimental methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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