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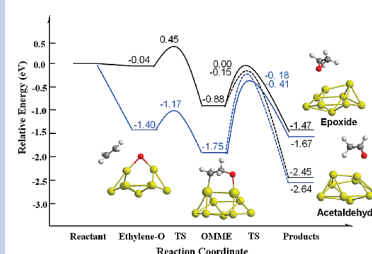
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ABSTRACT The heterogeneously catalyzed epoxidation of alkenes is experimentally challenging, theoretically interesting, and technologically of vital importance. Recent experimental studies show that small gold nanoparticles supported on inert materials are efficient and robust catalysts for the selective oxidation of alkenes. The reasons for the outstanding catalyst of Au nanoparticles have been investigated and compared with the Au(111) surface by means of density functional theory. The nanoparticle is intrinsically much more selective than the surface in the epoxidation. The fundamental cause is the inversion in the ordering of activation barriers for the competing pathways to epoxide formation versus acetaldehyde formation. On the nanoparticle, epoxide formation is less activated than acetaldehyde formation, whereas the opposite is true on the (111) surface. This behavior is associated with a late transition state to epoxidation on the nanoparticle (i.e., product-like) compared to an early (reactant-like) transition state to epoxidation on the (111) surface.

SECTION Surfaces, Interfaces, Catalysis



Nanosized gold particles have attracted much interest due to their unusual and unanticipated catalytic properties,^{1–5} although the origin catalyst of gold metal is noble. Many experimental studies have demonstrated that the reducible metal-oxide-supported Au nanoclusters showed high activity for CO¹ and alkene^{6,7} oxidation at low temperature. Very recently, Turner et al.⁴ reported that small gold clusters supported on inert materials are efficient and robust catalysts for the selective oxidation of styrene with oxygen, and even free gold clusters can be effective catalysts. The heterogeneously catalyzed epoxidation of terminal alkenes is experimentally challenging, theoretically interesting, and technologically of vital importance. The processes and the selective epoxidation of alkenes are pivotal in a wide range of chemistry industrial applications.² Theoretical studies of the gold nanocatalysis have mainly focused on the CO oxidation. Nonetheless, the theoretical study of the catalytic epoxidation of alkenes has been relatively unexplored.

Torres et al.⁸ have studied the epoxidation mechanism of ethylene on an oxygen-atom-covered Au(111) surface by density functional calculations. Their calculations showed that the predicted selectivity of ethylene epoxidation on Au(111) is ~40%, which is also very similar to that on Ag(111) reported by Barteau et al.⁹ Besides, they also showed that the origin of the superior selectivity of Cu(111) lies in the different character of the transition state leading to the epoxide, which is of early type for Ag and of late type for Cu.⁸ Linic et al.¹⁰ also showed that Cu/Ag alloy catalysts achieve higher selectivity to epoxidation than the respective pure Ag catalysts. In addition, the

selectivity is enhanced over ~80% by adding Cl and Cs on α -Al₂O₃-supported Ag catalysts.¹¹ Indeed, the remarkable catalytic behavior might in part arise from strong electronic interaction between the catalyst and adsorbate. It is therefore of interest to compare the catalytic epoxidation chemistry on the Au(111) surface and nanoparticle by theoretical means. In order to understand the catalytic properties of Au nanoparticles, the ethylene (smallest alkene) epoxidation is chosen as the modeling reaction.

Spin-polarized density functional theory (DFT) calculations with the generalized gradient approximation (GGA) and Perdew–Wang 1991 (PW91) formulation¹² are carried out to study the ethylene epoxidation on the Au(111) surface and Au nanoparticle. The climbing-image nudged elastic band (CI-NEB) method is employed to locate the transition state.¹³ Calculations are performed by the VASP package.¹⁴ In the present work, the Au₂₉ nanoparticle and Au p(2 × 2) (111) surface are chosen as the model catalysts for the ethylene oxidation. In our recent study, we have shown that the Au₂₉ has activity for CO oxidation.¹⁵ We propose that on this nanoparticle, the lower coordinated active sites are responsible for low-barrier ethylene oxidation.¹⁶ The computational details are given in the Supporting Information.

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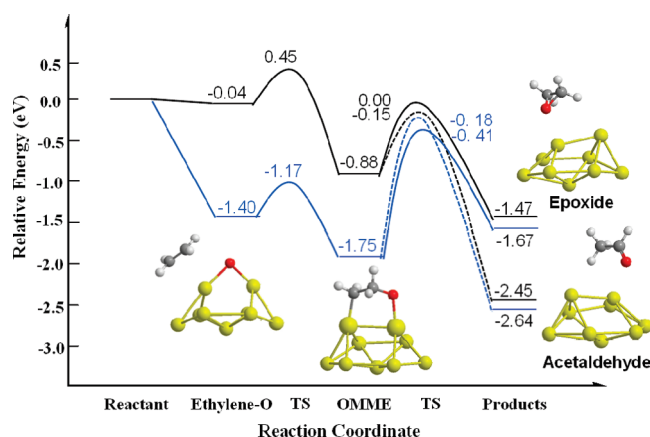


Figure 1. Potential energy diagram for the epoxide and acetaldehyde formation from ethylene and atomic oxygen adsorbed on a Au(111) surface (black line) and nanoparticle (blue line).

The O_2 is weakly adsorbed on the Au(111) surface (0.02 eV), whereas a stronger adsorption of O_2 on the Au nanoparticle is obtained (0.60 eV). However, the dissociation barriers of O_2 on both catalysts are very high, 2.23 eV for the (111) surface and 1.31 eV for the nanoparticle, which indicates that the molecular O_2 does not dissociate on the Au(111) and Au nanoparticle over a wide range of temperatures. However, atomic oxygen is known to be readily and preferably adsorbed on the fcc three-fold hollow site of Au(111)¹⁷ and the bridge site of Au nanoparticle¹⁵ (an adsorption energy of 2.54 eV for the (111) surface and 3.26 eV for nanoparticle, which are in agreement with previous studies^{15,17}). This explains the strategy reported by the Deng et al.,¹⁸ who successfully prepared to dose atomic oxygen on Au(111) in their experimental study. They also pointed out that there will be significant enhancement of O_2 dissociation as the Au(111) surface is mainly precovered by oxygen atom. On the basis of aforementioned observations, we therefore chose oxygen-atom-precovered Au(111) and a Au nanoparticle as our two hypothetical substrates. As shown in Figure 1, the ethylene initially interacts with the oxygenated surface and nanoparticle to form an oxametallacycle (OMME) intermediate via a relatively low barrier, 0.49 and 0.23 eV, for the Au(111) surface and the Au nanoparticle, respectively. The ethylene moiety of OMME interacts more strongly with the Au nanoparticle than with the Au(111) surface, with the additional stabilization energy induced by the Au nanoparticle amounting to 0.87 eV. On the Au nanoparticle, the epoxide formation through the OMME intermediate is endothermic by 0.08 eV, whereas the acetaldehyde formation is exothermic by 0.89 eV. On the Au(111) surface, both pathways are exothermic, 0.43 and 1.57 eV for epoxide and acetaldehyde formation, respectively. The leading product is weakly bonded to the surface by ~ 0.1 eV and the nanoparticle by ~ 0.4 eV. The activation barriers on the Au(111) surface are 0.88 and 0.73 eV for epoxide and acetaldehyde formation, respectively. For the Au nanoparticle, the energy barriers are significantly higher, 1.34 and 1.57 eV for epoxide and acetaldehyde, respectively. Most importantly, the critical difference is that, on the Au nanoparticle, epoxide formation is more competitive than

Table 1. Reaction Mechanisms and Barriers with ZPE-Corrected (E_a) Used for Microkinetic Modeling

	process	E_a (eV)	
		surface	nanoparticle
R1	$O(g) + * \leftrightarrow O^*$		
R2	$C_2H_4(g) + O^* \leftrightarrow C_2H_4^* + O^*$		
R3	$O_2(g) + 2^* \leftrightarrow O^* + O^*$	2.19	1.27
R4	$C_2H_4^* + O^* \rightarrow OMME^*$	0.46	0.21
R5	$OMME^* \rightarrow epoxide^*$	0.85	1.31
R6	$OMME^* \rightarrow acetaldehyde^*$	0.76	1.59

acetaldehyde formation, whereas on the Au(111) counterpart, it is less competitive. That is, on the Au nanoparticle, epoxidation is substantially favored as compared to the Au(111) surface.

The relatively low activation barrier toward epoxide formation on the nanoparticle as compared to that on the surface is an important factor in determining the intrinsically superior epoxidation selectivity exhibited by the nanoparticle. The configurations of the four transition states that lead to epoxide and acetaldehyde are depicted in the Supporting Information. It is found that both channels are characterized by early transition states (that resemble the reactants) on the Au(111) surface. However, on the nanoparticle, 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 the Au nanoparticle wins over the surface; the relative size of the epoxidation and aldehyde formation barriers is inverted in going from the Au surface to the nanoparticle.

Once the atomic oxygen is adsorbed on the surface and nanoparticle, the formation of epoxide and acetaldehyde from the OMME is straightforward. We assume that this elementary step is the dominant factor in determining selectivity. To identify the selectivity-controlling factor, we carry out a microkinetic analysis. The calculated activation barriers are used to estimate the relative rates of epoxide versus acetaldehyde production by using the conventional transition-state theory (TST).¹⁹ Zero-point energy (ZPE) corrections are included for microkinetic modeling. All elementary steps involved for microkinetic modeling are listed in Table 1. One should note that the acetaldehyde can be further and easily oxidized to form acetates which are readily oxidized to produce CO_2 .^{20,21} However, in this Letter, we do not consider the selectivity of the byproduct, CO_2 , which will be our future work.

The adsorption processes (R1 and R2) are assumed to be in equilibrium. The slowest step among R4–R6 is considered as the rate-determining step in the present microkinetic model. A detailed description of microkinetic modeling is given in the Supporting Information. The relative selectivity of the products at different temperatures is shown in Figure 2. The estimated selectivity toward epoxide on the Au(111) surface in the temperature range of 500–550 K is around 40–46% (see Figure 2), which is in good agreement with the experimental results²² for the styrene oxidation on Au surface. Similar selectivity is found for a silver surface.⁹ The similarity between the two metals is related to the energy difference

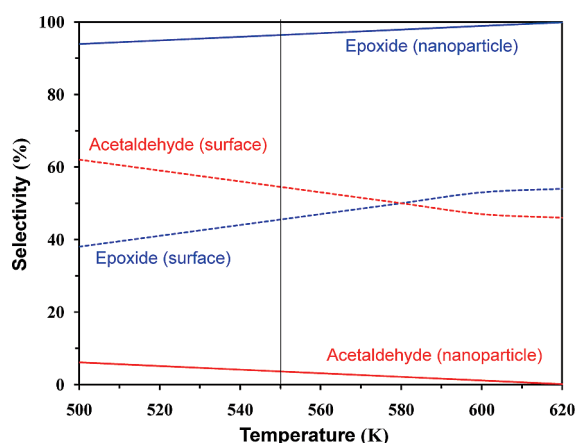


Figure 2. Temperature dependence of the relative selectivity of epoxide (blue line) and acetaldehyde (red line) on the surface (dashed line) and nanoparticle (solid line) using the microkinetic modeling technique.

between both TS structures leading to epoxide and acetaldehyde, respectively, which is evident in the complete energy profile. The selectivity toward epoxide on the Au nanoparticle is indeed enhanced by 95–99%. The high activity for epoxidation is also found on a Cu(111) surface with ~100% selectivity.⁸ The similarity between the Au nanoparticle and Cu(111) surface is also supported by the energy profile. A possible practical limitation to the use of a Au nanoparticle as an epoxidation catalyst is related to the stability of the epoxide. As it is apparent from Figure 1, ethylene oxide is thermodynamically unstable with respect to the adsorbed reactants. This implies that short contact times might be necessary in order to limit decomposition of the product. Furthermore, the epoxidation selectivity may increase with decreased contact time.

In summary, the Au nanoparticle is predicted to be intrinsically much more selective for ethylene epoxidation than the Au(111) surface. The high catalytic activity of the Au nanoparticle is due to inversion of the activation energy barriers for cyclization to epoxide versus the H-shift to aldehyde, relative to the Au(111) surface. The validity of our DFT calculations is provided by a simple study to understand the promoting effect of selectivity toward epoxidation on the Au nanoparticle. In addition, Lee et al.²³ pointed out that the support metal oxide of Au_n/oxide plays a significant role in the selective propene epoxidation. Therefore, a framework for the epoxidation of alkenes on the Au/oxide based on the DFT calculations will be carried out, which might aid in rationally designing the improved catalytic nanoparticles/oxide catalysts for the important practical applications.

SUPPORTING INFORMATION AVAILABLE Detailed information on the computational method and microkinetic modeling. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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