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Priority Communication

Selectivity driven design of bimetallic ethylene epoxidation catalysts from first principles

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Abstract

The sequence of key elementary steps for ethylene epoxidation on silver was developed from surface science experiments and computational chemistry. This molecular-level mechanistic information was used as an input in computational screening of potential bimetallic alloy catalysts. The aim of the computational screening was to identify a catalyst that would offer higher selectivity to ethylene oxide (EO) than the traditional monometallic silver catalyst. Computational screening led to formulation of a new Cu/Ag alloy that is more selective than Ag to EO. These predictions were verified by steady-state experiments with monolith-supported catalysts.

Keywords: Ethylene oxide; Ag; DFT; High-throughput computation; Catalysis by alloys; Selective oxidation; Rational catalyst design

1. Introduction

In the commercial ethylene epoxidation process, ethylene and oxygen are converted into ethylene oxide (EO). The traditional catalyst uses silver as the active element [1]. The principal nonselective product is CO_2. The formation of CO_2 is highly exothermic; the process is run at low conversions to maintain high selectivity and to control excess heat released by combustion. Discovery of more selective catalysts can therefore improve economics, reduce heat load, and improve operability.

We have previously reported investigations of the mechanism of ethylene epoxidation [2–4]. We have used surface science and DFT first principles studies of well-defined model systems to isolate and identify a surface oxametallacycle as the common intermediate participating in both selective and unselective reaction pathways [4]. The identification of a common intermediate is consistent with earlier conclusions of Cant and Hall [5] and Campbell and co-workers [6,7] from reaction kinetics studies. This intermediate can react to form either EO or acetaldehyde, with both processes having similar activation barriers [4]. It has been shown previously that acetaldehyde is rapidly oxidized on Ag, ultimately forming combustion products [8,9]; i.e., acetaldehyde is a gateway for the production of undesired products. The relevant transition states for the respective reactions of the surface oxametallacycle to form EO (TS1) and acetaldehyde (TS2) were obtained from DFT-based quantum chemical calculations (see Methods for details), and are shown in Fig. 1a. The magnitude of the kinetic isotope effect was predicted from analysis of the changes in vibrational and entropy contributions to the Gibbs free energies of TS1, TS2, and the surface oxametallacycle for deuterated (C_2D_4) versus nonlabeled (C_2H_4) reactants [4]. The agreement of the predicted isotope effect as the reactant is changed from C_2H_4 to C_2D_4 with previous experimental measurements [5] provided additional support for the conclusion that competing reactions of the oxametallacycle control selectivity.

We have also developed a microkinetic model for ethylene epoxidation on unpromoted Ag [3]. The kinetic parameters for important elementary steps were either derived from DFT or measured in surface science studies. It was shown that the proposed model reproduced measured macroscopic parameters, e.g., the overall activation barrier and reaction orders, obtained in microreactor studies [10]. The partial

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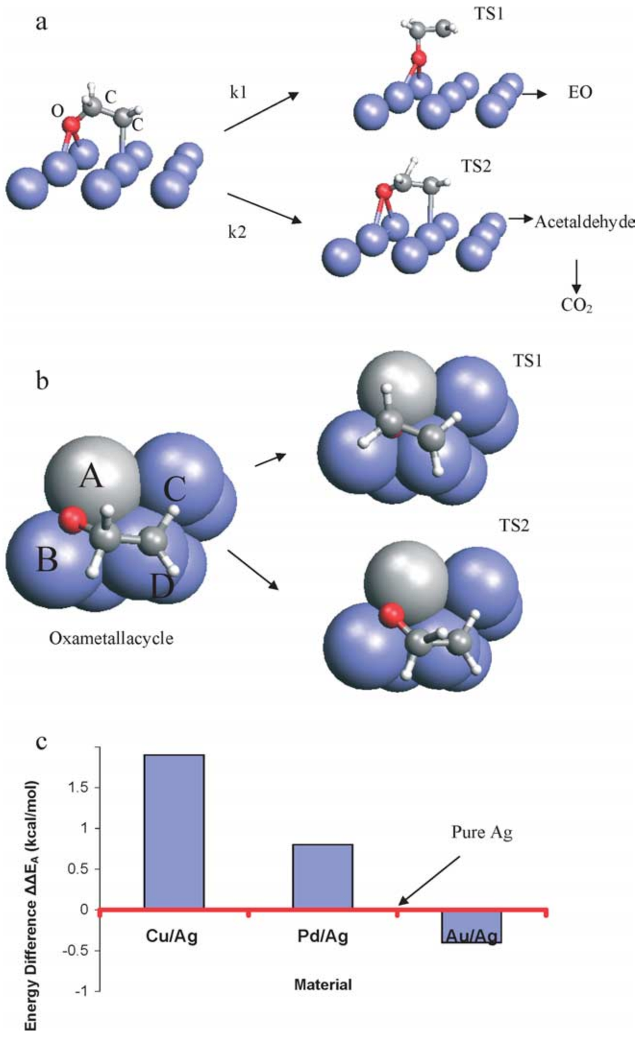

Fig. 1. (a) Schematic of the reaction coordinates for competing oxametallacycle reaction pathways calculated using the NEB (Nudged Elastic Band) algorithm [14,15]. The formation of EO is characterized by C–O ring closure, while acetaldehyde is formed via a 1,2-H shift from the central to the terminal C atom. Activation barriers for both processes are calculated to be approximately 17 kcal/mol. The surface is the close packed Ag(111) surface. (b) Structure of bimetallic model catalysts investigated in high-throughput computational screening. There is one adsorbate, the surface oxametallacycle, or one transition state per unit cell. The atoms labeled B, C, and D in the unit cell are Ag atoms while A represents an impurity element. (c) The results of the computational screening; $\Delta\Delta E_A$ is calculated as a function of catalyst composition. The higher energy difference means that the bimetallic is predicted to be a more selective catalyst than monometallic silver.

pressures used in the microkinetic modeling and the microreactor studies (up to 1 atm of O_2 and C_2H_4) were lower than those typical of industrial processes. Under higher reactant pressures, i.e., on crowded Ag surfaces, it is quite possible that additional adsorbate–adsorbate interactions may become important and will need to be included in the model. It is important to emphasize that the consistency of the microkinetic model and the macroscopic experimental observations, as well as kinetic isotope data analysis, suggest a window of operating conditions in which the mechanism of Fig. 1a controls the selectivity to EO.

In this contribution we utilize mechanistic molecular-level information representative of the low coverage/low conversion limit, illustrated schematically in Fig. 1a, to rationally design a catalyst that is more selective than the traditional monometallic Ag catalyst. We emphasize here the focus on *selectivity*-driven rational design of heterogeneous catalysts that emerged from systematic studies of the surface chemistry of the process. Previous successful examples of rational design of new metallic catalysts have focused primarily on the development of either more stable or more active catalysts [11,12].

2. Methods

Periodic DFT calculations were performed by using DACAPO (pseudopotential plane-wave code available at http://www.camp.dtu.dk). DFT is employed to calculate the geometries and binding energies of the relevant transition states and the surface oxametallacycle. The transition state geometries were calculated using a Nudged Elastic Band (NEB) algorithm [14,15]. NEB calculations were performed on a slab consisting of a 2×2 unit cell with 2 layers of Ag and 15 Å of vacuum in between, with one adsorbate per unit cell corresponding to coverage of 0.25 monolayers. Ionic cores are described by Vanderbilt ultrasoft pseudopotentials, and the Kohn–Sham one-electron valence states are expanded in a basis of plane waves with kinetic energy below 25 Ry. The surface Brillouin zone is sampled at 18 special **k** points. The exchange-correlation energy and potential are described by the generalized gradient approximation (GGA-PW91). The self-consistent PW91 density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density. All total energies have been extrapolated to $k_B T = 0$ eV. The transition states were considered to be optimized when the convergence threshold of 0.05 eV/Å force in the direction perpendicular to the reaction coordinate was reached for each structure along the reaction coordinate. All transition states presented here are subject to these constraints. Since transition state searches are computationally expensive, we use the geometries of transition states obtained from calculations for a 2×2 unit cell with 2 layers of Ag in calculations for unit cells with more layers of Ag and different (mainly lower) coverages. Nearly identical transition states have been identified previously in calculations involving 15-atom Ag clusters [4], which gives us confidence in the computed transition states.

Silver catalysts were prepared using standard wet impregnation techniques, with $AgNO_3$ used as the silver salt and water as the solvent. The volume of the aqueous solution was in slight excess of the volume required for incipient wetness of the support. The support was dried at 80 °C. The dried precursor was then thermally reduced at 400 °C in a calcination furnace for approximately 12 h. The silver weight loadings for these catalysts ranged from 11 to 13%. For the copper-promoted catalysts, copper was added in the form of aqueous $Cu(NO_3)_2$ to the reduced silver catalyst via wet impregnation. Following addition of the $Cu(NO_3)_2$, the catalysts were exposed to a flowing H_2/He stream for 12 h at 300 °C, allowing for reduction of the copper.

The supports employed for these experiments consisted of low surface area, fused α-Al_2O_3 monoliths. The monoliths were 18 mm in diameter and 10 mm in length. Surface areas of the monoliths were on the order of 0.2 m^2/g, with pore volumes on the order of 0.1 cc/g. All catalysts were evaluated under steady-state conditions in a 5 psig reactor using gas flows of N_2, C_2H_4, and O_2, each of which was delivered through a mass-flow controller. For all experiments, the feed consisted of 10% C_2H_4, 10% O_2, and 80% N_2. The reactor consisted of a 20 mm i.d. quartz tube encased in a horizontal tube furnace. Analysis of the product gas stream was performed by in-line gas chromatography. The gas chromatograph utilized both thermal conductivity and flame ionization detectors to give quantitative analysis of all gaseous products.

3. DFT studies

We first identify a productive method that takes advantage of molecular-level mechanistic information in order to provide directions for the synthesis of more selective catalysts. The approach taken in these studies is partially inspired by the recent impact of combinatorial methods on the search for new catalysts. In combinatorial approaches a large number of different materials are created and screened by high-throughput methods to identify promising catalysts. In this study we also rely on the idea of combinatorial screening, but rather than physically making and testing a large number of potential catalysts, we employ thermodynamic and computational tools to screen a number of possible catalysts and search for those that are predicted to exhibit higher selectivity to ethylene oxide. This approach identifies potential catalysts which are then synthesized and tested experimentally.

We focus on bimetallic alloys with Ag as the main component. Bimetallic alloys have demonstrated superior performance for a number of catalytic processes [12,13]. We are interested in those materials in which an Ag catalyst is only slightly perturbed by the introduction of another metal, i.e., alloys in which the added component is highly diluted. In focusing on dilute alloys we assume that the surface chemistry of the process, i.e., the nature of the relevant pathways and the configurations of surface intermediates and transition states, will not change dramatically compared to pure Ag.

In order to find an optimum catalyst that will enhance selectivity to EO and suppress the production of combustion products, we search computationally for a bimetallic alloy that accentuates the difference between the activation barrier for the production of acetaldehyde and the activation barrier for the production of ethylene oxide (ΔE_A), and therefore increases the production of EO and decreases the production of combustion products compared to a monometallic Ag catalyst.

$$\Delta E_A = E_A(\text{acetaldehyde}) - E_A(\text{EO}), \qquad (1)$$

here E_A(acetaldehyde) is the activation barrier for the formation of acetaldehyde; i.e., the activation barrier for the formation of combustion products and E_A(EO) is the activation barrier for the formation of EO on the same catalyst. ΔE_A represents the difference in the energies of TS2 and TS1 (see Fig. 1) for a given catalyst.

After ruling out those Ag-containing bimetallic materials that either do not form bulk alloys or do not mix at the surface, i.e, do not form surface alloys, we performed DFT calculations on a number of model bimetallic catalysts. Selected results from these calculations are contained in Fig. 1c which depicts the difference, $\Delta\Delta E_A$, between ΔE_A calculated on bimetallic catalysts and ΔE_A calculated on a pure Ag(111) surface. A higher value of this difference implies that a particular catalyst might offer improved selectivity to EO. Fig. 1b also shows a top view of the 2 × 2 unit cell of model catalysts for which periodic DFT calculations were performed. The unit cell is modeled with this surface layer and 3 layers of Ag below it, in addition to 6 layers (~15 Å) of vacuum. Fig. 1c suggests that Cu/Ag alloy catalysts with a small concentration of Cu should offer a higher selectivity to EO than a pure Ag catalyst.

Before experimentally testing Cu/Ag alloy catalysts we established that the Cu/Ag surface alloy is thermodynamically stable under the chosen conditions, i.e., that the predicted catalyst is feasible. The phase diagram of the Cu/Ag system suggests that, for low concentrations of Cu and temperatures at which ethylene epoxidation takes place ($T =$ 500–600 K), there exists a stable, Ag-rich primary Cu/Ag alloy phase [16]. DFT calculations were also utilized to compute the propensity of Cu to be located in the bulk versus its tendency to segregate to the surface layer. The quantitative measure of the tendency of an impurity atom to segregate to the surface layer is the surface segregation energy. This is defined as the difference of the total energy of the system with the impurity element in the surface layer minus the energy of the system with the impurity element in the bulk. Surface segregation energies for many binary alloys have previously been computed and are readily available [17,18].

Since ethylene epoxidation involves oxygen adsorption and dissociation, the surface segregation energy, as defined above, must be corrected for the energy difference due to the presence of adsorbed oxygen. For example, in the Cu/Ag system without oxygen, Cu prefers slightly to reside in the bulk; however, in the presence of oxygen, Cu tends to be pulled up toward the top layer. The reason for this is that the O–Cu bond is stronger than the O–Ag bond. The corrected surface segregation energy is calculated as

$$E'_{\text{seg.}} = E(\text{imp\_s}) - E(\text{imp\_b}) + E(\text{O\_imp\_s}) - E(\text{O\_imp\_b}), \quad (2)$$

where $E(\text{imp\_s})$ is the energy of a structure in which the impurity atom (copper in this case) is placed in the surface layer while $E(\text{imp\_b})$ is the energy of the same structure but with the impurity atom in the bulk. $E(\text{O\_imp\_s})$ and $E(\text{O\_imp\_b})$ are the same energies but with an O atom adsorbed on the top layer. A negative value of $E'_{\text{seg.}}$ implies that surface layer alloying is thermodynamically favorable compared to bulk alloying. We computed $E'_{\text{seg.}}$ for Cu in Ag to be -0.15 eV, indicating that in the presence of oxygen, Cu prefers thermodynamically to be alloyed into the surface layer, which was confirmed in the XPS experiments.

4. Steady-state reactor and XPS studies

To test the predictions above for Cu/Ag alloys, we synthesized and tested a number of Cu/Ag catalysts. These catalysts contained metal supported on porous α-Al_2O_3 monoliths. All catalysts contained 11–13 wt% Ag with Cu concentrations ranging from 0 to 535 ppm Cu by weight of active catalyst. All catalysts were prepared following identical preparation procedures. The Ag catalysts were first prepared on the α-Al_2O_3 support and then thermally reduced. Subsequently, Cu salt was added and the whole system (support with Ag and Cu) was reduced by exposure to hydrogen at 573 K. The results of catalytic studies are shown in Table 1.

We have divided catalysts into batches A and B since these batches were prepared with different lots of Ag and Cu precursors as well as with different lots of α-Al_2O_3 monoliths. While the performance of base-case Ag catalysts for the two batches was unfortunately not the same, it is clear that Cu/Ag alloy catalysts achieve higher selectivities to EO than the respective pure Ag catalysts for all catalysts and conditions examined. Fig. 2 summarizes the results displayed in Table 1 as normalized selectivities of alloy catalysts. The normalized selectivity of various catalysts in batches A and B is obtained by dividing the selectivity of an alloy catalyst by the selectivity of the pure Ag catalyst corresponding to the respective batch. The normalized selectivity to EO changes as a function of Cu loading. It is observed that the selectivity to EO increases rapidly up to a Cu content of 0.2 mol% per mole of Ag. The optimal selectivity obtained with a Cu/Ag alloy is about 1.5 times the selectivity of pure Ag catalyst under identical conditions (528 K and 2% conversion with equal partial pressures of ethylene and oxygen). These observations clearly support the prediction that Cu/Ag alloys will achieve higher selectivities to EO.

We have also performed XPS studies of a few catalysts, catalysts labeled I, II, and III in Fig. 2, used in our reactor studies. XPS is a surface-sensitive technique that determines the concentration of various elements in the top few layers of the catalyst. These results suggest that the concentration of Cu in the top few layers is much greater than the overall concentration of Cu. For example, the catalyst with 0.1 mol% of Cu overall (catalyst II) is measured to have ∼ 9 Cu surface atoms per 100 (Ag + Cu) surface atoms, while the catalyst with 1 mol% Cu overall concentration (catalyst III) is measured to have ∼ 43 Cu surface atoms per 100 (Cu + Ag) surface atoms. These values will be a strong function of operating conditions, mainly partial pressure of oxygen and temperature. The enrichment of the catalysts' surfaces with Cu is not surprising considering that ethylene epoxidation was carried out with an equimolar O_2 and ethylene feed, and that oxygen binds to Cu more strongly than to Ag. These results validate our strategy, both with respect to predicted selectivity enhancements and with respect to the ability to prepare and operate catalysts that correspond to the model.

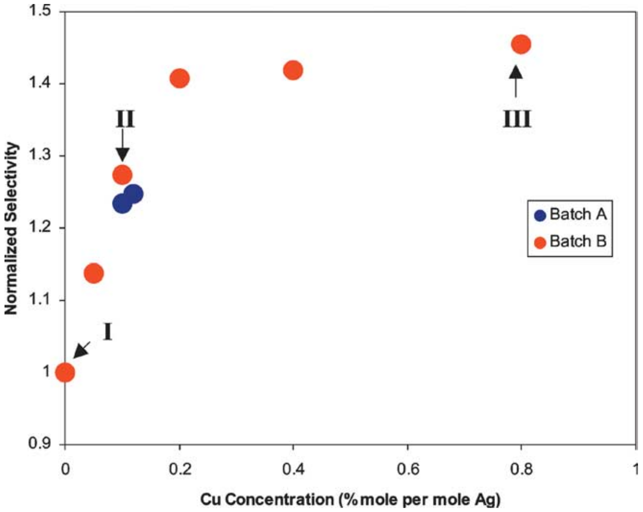

Fig. 2. Normalized catalyst selectivities to EO, i.e., the measured selectivity divided by the selectivity of pure Ag under the same conditions as a function of bulk Cu content. For catalysts labeled I, II, and III we have performed XPS studies to measure the amount of Cu in the top layers of a catalyst. For catalyst I there is no Cu present, catalyst II has ∼9 Cu atoms per 100 surface metal atoms, while catalyst III has ∼43 Cu per 100 Cu + Ag atoms in the surface layers. It is observed that Cu is enriched at the surface, as predicted.

Table 1
Results of reactor studies

Cu loading (ppm)	Cu atomic loading per 1000 Ag atoms	C_2H_4 conversion (%)	EO selectivity (%)
Batch A			
0	0	0.8	49.2
0	0	2.0	46.5
78	1	0.8	60.2
100	1.2	2.0	57.4
Batch B			
0	0	2.0	24.8
40	0.5	2.0	28.2
83	1	2.0	31.6
141	2	2.0	34.9
303	4	2.0	35.2
535	8	2.0	36.1

Selectivity to EO is reported as a function of Cu atomic loading in Cu/Ag bimetallic catalysts. The partial pressures of O_2 and C_2H_4 were set at 0.1 atm each.

It is also important to note that if more Cu is deposited onto an Ag catalyst, it is expected that a phase separation would take place with Ag- and Cu-rich phases forming. This would inevitably diminish the performance of the catalyst, since the Cu-rich phase would oxidize and become inert to ethylene epoxidation, i.e., a large number of sites on this catalyst would become spectator sites.

This example shows that first principles studies can be extremely valuable in catalyst design. The quantitative results of fundamental studies have been implemented to specify a *new* alloy catalyst that is more *selective* than the corresponding monometallic catalyst. The method advanced here takes advantage of computational screening of potential catalysts based on molecular-level understanding of the reaction mechanism in order to make testable predictions of superior catalyst formulations.

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