The Effect of Ag Particle Shape and Surface Structure on Ethylene Epoxidation Selectivity

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Introduction

Approaching 100% selectivity in heterogeneous catalytic reactions is an ultimate objective of catalyst discovery and is critical for the design of efficient, environmentally friendly processes. This work focuses on an example where shape controlled synthesis of silver nano-particles has been utilized along with Density Functional Theory (DFT) calculations to design heterogeneous silver (Ag) catalysts that are more selective in partial oxidation of ethylene to form ethylene oxide (EO) than Ag catalysts prepared using conventional methods. These results indicate that advances in synthetic chemistry, which allow the synthesis of uniform metal particles of tunable shapes and sizes,[1] might play a crucial role in the development of highly selective heterogeneous catalysts.

Ethylene epoxidation involves the partial oxidation of ethylene to form ethylene epoxide and is an important industrial processes where catalytic performance is measured by selectivity to the epoxide. Silver is the only heterogeneous catalyst that can achieve reasonable selectivity to EO. The main by-products in the reaction are combustion products, CO_2 and H_2O. Ag catalysts synthesized using standard incipient wetness methods and supported on inert supports exhibit low selectivity, <20%, for small particle sizes, <20nm. It has been shown that pure Ag catalysts can achieve 40-50% selectivity when the particles are about 1 µm diameter and dominated by the (111) facet. Industrial Ag catalysts are further promoted with various additives including Cs, Cl, and Re to achieve a selectivity of ~80-85%. An alternative approach to enhance the selectivity of Ag catalysts, discussed in this work, 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.

Materials and Methods

A modified polyol synthesis method was used to synthesize Ag nanoparticle catalysts. In this process $AgNO_3$ is reduced in slightly acidic ethylene glycol at 150°C in the presence of poly(vinyl pyrrolidone).[2] Density Functional Theory (DFT) calculations were performed using the Dacapo code. Transition states (TS) were identified using Climbing-image nudged elastic band calculations. Surface enhanced Raman spectroscopy (SERS) measurements were performed in microscopy mode in an *in-situ* reaction cell.

Results and Discussion

Recent studies have suggested that selectivity to ethylene oxide is governed by a parallel reaction network in which a surface oxametallacycle (OMC) intermediate is isomerized on the catalyst surface to form selective epoxide product and unselective acetaldehyde (AC) intermediate, which then combusts on the catalyst surface.[2] The DFT calculated activation barriers for the formation of EO and AC from the OMC on Ag (111) are comparable to each other, see Figure 1a. This has practical implications since large catalytic particles synthesized using impregnation techniques are dominated by the Ag(111) facet. In Figure 1b we show DFT-calculated potential energies diagrams for the isomerization of the OMC intermediate to EO and AC on Ag(100). The difference in activation barriers associated with forming AC and EO is by ~ 0.1 eV larger on Ag(100) than on Ag(111), indicating that the (100) surface should be intrinsically more selective to EO that the (111) surface.[3]

This result was tested experimentally by comparing steady state selectivity to EO on pentagonal Ag nanowire and nanocube catalysts, both dominated by (100) facets, to conventional Ag catalysts dominated in the (111) surface. The selectivity to EO of the conventional catalyst reached 47%, while Ag nanowires were 65% selective and nanocubes were 75% selective, shown in Figure 1 (c). The nanocubes were found to be more stable then the nanowire catalyst, showing no decrease in selectivity for a week on stream. We attribute enhanced stability of the nanocubes to a removal of inherent strain the crystal structure of the nanostructure.

The Ag nanowires and nanocubes exhibit characteristic plasmon resonances in the visible region, which makes these materials SERS-active. We have utilized SERS to examine the formation of the oxametallacycle on the well-defined catalytic surfaces at atmospheric pressure and have found similarities with previous UHV studies.

Significance

This work represents a rare example where detailed understanding of the mechanisms of elementary steps that govern selectivity was employed to identify surface facets that are inherently more selective. Novel synthesis techniques, developed recently in the field of nano-technology, have allowed us to synthesize uniform catalytic particles that are dominated by the desired surface facect. Also, the use of Ag particles as SERS active catalysts for monitoring catalytic processes under relevant pressures and temperatures is identified as a powerful tool for obtaining mechanistic information.

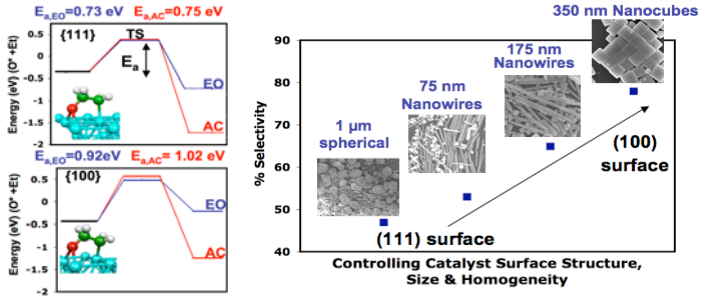

Figure 1. (a) & (b) DFT calculated potential energy surfaces for isomerization of OMC to EO and AC on Ag(111) and (100). (c) Measured steady-state EO selectivity for different catalysts.

References

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