Journal of Catalysis 321 (2015) 1–6

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Ab initio prediction of the equilibrium shape of supported Ag nanoparticles on α-$Al_2O_3(0001)$

Mónica García-Mota [a,*], Michael Rieger [a], Karsten Reuter [b]

[a] BASF SE, Scientific Computing (GVM/S), Carl-Bosch-Str 38, 67056 Ludwigshafen, Germany
[b] Technische Universität München, Chair for Theoretical Chemistry and Catalysis Research Center, Lichtenbergstr. 4, 85747 Garching, Germany

ARTICLE INFO

Article history:
Received 11 August 2014
Revised 29 September 2014
Accepted 19 October 2014
Available online 18 November 2014

Keywords:
Ethylene epoxidation
Silver/alumina catalyst
DFT
Wulff–Kaichew construction
Thermodynamics
Surface energy
Oxygen adsorption

ABSTRACT

We combine first-principles atomistic thermodynamics with a Wulff–Kaichew construction to determine the equilibrium shape of Ag particles supported on α-$Al_2O_3(0001)$ under gas-phase conditions representative for ethylene epoxidation. The formation of three-dimensional truncated octahedra is predicted for both the Al-terminated (AlO_3Al-R) and the fully hydroxylated O-terminated (H_3O_3Al-R) alumina surface, albeit with largely different contact angles. Overall, this is fully consistent with the common description of hemispherical Ag microcrystals on this support, but at variance with the cubic Ag nanoparticles reported recently by Christopher and Linic (2008). This result suggests the latter particles to be stabilized kinetically. We establish a framework from which strategies to thermodynamically stabilize cubic particles can be explored. The Wulff–Kaichew construction is proposed to provide a straightforward criterion that may be used as a suitable descriptor in the computational screening of surface additives that would stabilize the arguably highly selective Ag(100) facets.

1. Introduction

Ethylene epoxidation is a process in which ethylene and oxygen react to form ethylene oxide (EO). EO serves as a very useful chemical intermediate from which other macroscopic materials such as plastics, detergents, and many other chemicals can be derived [1,2]. The main undesired by-products in the reaction are the combustion products, CO_2 and H_2O. Industrially, the traditional catalyst employed for the ethylene epoxidation reaction contains silver particles dispersed on alumina. Corundum α-Al_2O_3 is one of the many possible allotropic forms of alumina. Over the years, considerable experimental and theoretical efforts have been devoted to characterize the corundum surface [3–12]. The majority of these investigations have focused on the geometrically most simple (0001) basal plane, with non-basal surfaces only recently receiving attention [10,12]. Whereas early studies predicted the $Al_2O_3(0001)$ surface to be terminated with a layer of Al atoms [3], it is nowadays generally accepted that surface hydroxyl groups may form since water is a by-product of the unselective combustion of ethylene [4,5]. Furthermore, it is discussed that hydroxyl groups may be present in patches and that the surface likely has multiple termination regions [6–9].

Silver displays unique catalytic properties and selectivity toward ethylene epoxidation [13]. In the context of EO, the complex morphology of Ag particles on alumina supports has already been extensively investigated [14–16]. Despite these efforts, the structure of the catalyst surface in corresponding oxygen-rich environments is still controversial, and there is no consensus on its active state at reaction conditions [17–22]. It is almost clear that this state does not correspond to mere metallic silver and is more than a simple oxygen adsorption system. Since the interaction between oxygen and silver is believed to play an essential role in understanding ethylene epoxidation, the effect of surface and sub-surface oxygen coverage on EO selectivity has been subject to extended debate [13,23–26].

Besides the detailed O-Ag interaction itself, the use of promoters is another key step to improve the EO selectivity [27–30]. Monometallic Ag catalysts supported on α-Al_2O_3, achieve selectivities to EO of ~45% for an average diameter of 1 μm [31]. In contrast, an 80–85% selectivity is industrially reached for optimized alkali- and chlorine-promoted catalysts [32]. The actual role of the promoters that have to be added to the Ag catalysts in order to obtain such high selectivity is hereby not yet well understood. A more uniform oxygen distribution or an enhancement of the thermodynamic stability of sub-surface oxygen compared to unpromoted catalysts is among the reasons that have been suggested [29]. Recently, Christopher and Linic have explored a new

---

* Corresponding author.
E-mail address: monica.garcia-mota@basf.com (M. García-Mota).

http://dx.doi.org/10.1016/j.jcat.2014.10.009
0021-9517/

strategy to enhance the EO selectivity without the addition of promoters [33,34]. This strategy relies on the manipulation of the selectivity of Ag catalysts by controlling the shape and size of the Ag catalytic particles [33–35]. The selectivity measured for the obtained large Ag cubes, predominantly exposing Ag(100) facets and only promoted with Cl, was found to approach that achieved by commercial catalysts [34]. This result is consistent with density-functional theory (DFT) calculations suggesting the Ag(100) surface facet to be inherently more selective toward EO than Ag(111) [33].

In the present work, we continue along this route and use first-principles atomistic thermodynamic calculations to predict the equilibrium shape of unpromoted Ag-supported particles on α-Al_2O_3(0001). Specifically, we aim to know if supported Ag cube particles with exposed Ag(100) facets, and therewith arguably highly selective toward EO, correspond to the equilibrium geometry under gas-phase conditions representative of EO; i.e., $T = 500$ K and 1 atm oxygen partial pressure. For this, we first establish the thermodynamically favorable surface terminations of the α-Al_2O_3(0001) support, and then, the equilibrium structures and surface free energies (γ) of the low-index surfaces of Ag. Combining these results by means of a Wulff–Kaichew construction, we obtain the equilibrium shape and surface composition of the Ag nanoparticles under the conditions applied for the EO production. In agreement with previous experimental reports [16], this shape is rather hemispherical with prominent presence of (111) facets. We observe that to fulfill the condition for cubic growth, predicted for $\gamma_{100}/\gamma_{111} < 1/\sqrt{3}$ in the Wulff–Kaichew model (*vide infra*), the surface energy of Ag(100) have to be lowered by about 40% of its current value. This suggests that the cubic shape obtained by Christopher and Linic is stabilized kinetically. The synthesis of only kinetically stabilized new catalyst shapes at the operation temperature of EO is not feasible [34]. The ultimate aim of our work was thus to setup a solid framework from which novel strategies to thermodynamically stabilize particles exposing (100) facets can be explored. We identify the stable Ag surface oxide terminations under the EO conditions, and propose the fraction $\gamma_{100}/\gamma_{111}$ as a suitable descriptor in the computational screening of surface additives promoting the stabilization of particles exhibiting highly selective Ag(100) facets.

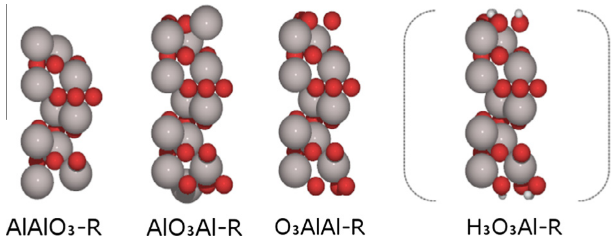

Fig. 1. Side view of one surface unit cell of the three different terminations obtained by cleaving the Al_2O_3 unit cell at unique positions along the [0001] direction; namely $AlAlO_3$-R (double Al-terminated); AlO_3Al-R (single Al-terminated); and O_3AlAl-R (single O-terminated). A totally hydroxylated O-terminated surface is also shown in the rightmost panel; namely H_3O_3Al-R. Red, gray, and white spheres represent oxygen, aluminum, and hydrogen atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Computational approach

We present a DFT-based Wulff–Kaichew construction [36,37] of the equilibrium shape of supported Ag nanoparticles on α-Al_2O_3(0001) in an oxygen and water containing environment. All calculations are performed using the GPAW code [38], the PBE exchange–correlation functional [39], PAW pseudopotentials [40], and a uniform real-space grid with a spacing of 0.14 Å for the representation of the electronic wavefunctions. Bulk α-Al_2O_3 is described in a conventional hexagonal unit cell with six Al_2O_3 formula units. The optimized cell parameters, calculated with a (6 × 6 × 6) Monkhorst–Pack *k*-point sampling [41], are (4.828 Å × 4.828 Å × 13.170 Å), which is in reasonable agreement with previous studies [11]. Cleaving the crystal along the (0001) basal plane yields three possible types of unreconstructed (1 × 1) terminations, namely the AlO_3Al-R (single Al-terminated), O_3AlAl-R (single O-terminated), and $AlAlO_3$-R (double Al-terminated) terminations, see Fig. 1. We also consider partially and totally hydroxylated surfaces (H_iO_3Al-R, with $i = 1$, 2, and 3) to simulate a nonzero coverage of hydroxyl groups under gas-phase conditions representative of EO [6–9]. All surfaces are modeled in supercell geometries with (1 × 1) surface unit cells and symmetric Al_2O_3(0001) slabs that are separated by more than 16 Å of vacuum. The slabs are composed of six stoichiometric vertically repeating units of Al–3O–Al, and (5 × 5 × 1) Monkhorst–Pack *k*-point sampling is used. Keeping only the middle repeating unit fixed, all surfaces are fully relaxed until residual forces fall below 0.05 eV/Å.

We expect extended Ag films to be a good approximation to represent the interaction of large Ag nanoparticles with alumina. It has been shown that the optimization of one Ag monolayer on α-Al_2O_3(0001) leads to a buckled Ag(111) monolayer [15]. Space and symmetry compatibility arguments additionally motivate to model the Ag nanoparticle/corundum interface as composed of α-Al_2O_3(0001) and Ag(111) planes. We correspondingly compute extended and optimized Ag(111) films positioned atop-Al sites on the different alumina terminations to obtain the adhesion energies E_{adh} needed for the Wulff–Kaichew construction, as further specified below. E_{adh} is defined as the energy needed to pull the interfacial system apart in its two constituents, assuming no plastic or diffusional modifications. It is calculated as the difference between the total energies for the Ag–Al_2O_3 slab system ($E_{\text{Ag/Al}_2\text{O}_3\text{slab}}$) and the ones of the corresponding isolated subsystems with the same geometry as the optimized interface system ($E_{\text{Ag slab}} + E_{\text{Al}_2\text{O}_3\text{ slab}}$) [15]:

$$E_{\text{adh}} = E_{\text{Ag/Al}_2\text{O}_3\text{slab}} - (E_{\text{Ag slab}} + E_{\text{Al}_2\text{O}_3\text{slab}}). \tag{1}$$

In these calculations, the Ag films are positioned on one side of the (1 × 1) α-Al_2O_3(0001) slabs, and the Ag layers as well as the two top alumina-layers are allowed to relax while the lowest layers are kept frozen at their bulk positions. As summarized in Table 1, we obtain for all alumina terminations no further significant changes within 0.1 eV in E_{adh} calculated with two and three layer Ag(111) films, and correspondingly take the three Ag layer values to model the interfacial interaction with a larger Ag nanoparticle.

The Wulff–Kaichew construction additionally requires the calculation of surface free energies of different Ag facets. Specifically, we analyze the stability of various oxygen adatom structures on the low-index surfaces, Ag(100), Ag(111), and Ag(110). The oxygen species investigated include on-surface sites for a wide range of coverages, sub-surface sites, and oxide-like structures, see Fig. S2 of the Supplementary material. The surface oxygen coverage (Θ_{O}) on Ag(111) ranges from 1/16 to 1/2 monolayer (ML). We simulate such coverages in $p(4 \times 4)$ and $p(3 \times 3)$ supercells, using compatible (3 × 3 × 1) and (4 × 4 × 1) Monkhorst–Pack *k*-point sampling, respectively. For the more reactive Ag(100) and Ag(110) surfaces, the considered coverage range is ¼ ML $\leqslant \Theta_{\text{O}} \leqslant$ ½ ML, modeled in a $p(2 \times 2)$ surface unit cell and with a (5 × 5 × 1) *k*-point sampling. As oxide-like structures, we consider (with a (3 × 3 × 1) *k*-point sampling) the silver oxide model proposed by Schnadt et al. on Ag(111) [20]. On Ag(100), we include (with a (5 × 7 × 1) *k*-point sampling) the missing-row