



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)

# Theoretical mechanistic insights into propylene epoxidation on Au-based catalysts: Surface O versus OOH as oxidizing agents

Lyudmila V. Moskaleva

Institute of Applied and Physical Chemistry and Center for Environmental Research and Sustainable Technology, Universität Bremen, 28359 Bremen, Germany

## ARTICLE INFO

### Article history:

Received 30 December 2015  
Received in revised form 25 April 2016  
Accepted 16 May 2016  
Available online xxx

### Keywords:

Density functional theory  
Au(321) surface  
Propylene epoxidation  
Propylene oxide  
Selectivity  
Hydroperoxyl

## ABSTRACT

Propylene oxide (PO) is an important bulk chemical used for synthesis of many value-added products. Much effort has been devoted to finding a simple and “green” process for PO production. Promising results in terms of activity and selectivity have been achieved for propylene oxidation on supported gold catalysts with a mixture of O<sub>2</sub> and H<sub>2</sub> or with O<sub>2</sub> and H<sub>2</sub>O. In this work a detailed transformation network of competitive reaction pathways following the initial steps of oxidation has been studied theoretically using density functional theory (DFT). The results of calculations question some of the earlier assumptions regarding the mechanism of PO formation. Surface hydroperoxo species (OOH) formed *in situ* are shown to be responsible for the high selectivity of propylene epoxidation with O<sub>2</sub> on gold-based catalysts using hydrogen or water as co-reactants.

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## 1. Introduction

Epoxidation of propylene is crucial in the manufacture of propylene oxide (PO), a valuable raw material for producing many value-added chemicals, such as polyether polyols, propylene glycol, and others [1]. At present, two major methods are used for the commercial PO production: the chlorohydrin process and the hydroperoxide processes. These processes proceed via multiple reaction steps and utilize hazardous chlorine and costly hydroperoxides as oxidants [1]. Therefore, efforts have been made to develop a “green” process that could directly and selectively epoxidize propylene to PO. Although silver supported on alumina is well known as a uniquely effective catalyst for ethylene epoxidation, Ag catalysts are far less effective for epoxidation of propylene (and other olefins with allylic C–H bonds) because of predominant total oxidation to CO<sub>2</sub> and H<sub>2</sub>O [2]. The low selectivity obtained for propylene epoxidation has been attributed to a weaker binding strength of allylic (–CH<sub>3</sub>) hydrogen in propylene than that of the vinyl hydrogen in ethylene [3].

Two other coinage metals, Au and Cu on appropriate supports, have also been tested as catalysts for propylene epoxidation [3]. As in the case of silver, the common challenge identified for all

of them is the need to suppress undesirable reaction pathways leading either to total oxidation or to the formation of other partial oxidation products, e.g., acrolein, acetone, propanal. Hayashi et al. [4], who first reported the selective epoxidation of propylene on supported 2–5 nm Au nanoparticles, proposed to use a sacrificial reductive agent (H<sub>2</sub>) to better control the reactivity of active oxygen species and suppress deep oxidation. This approach showed successful results in terms of the PO selectivity (~90%), although conversions were low (only 1–2%). Since then, several groups have been working on the optimization of propylene epoxidation over gold-based catalysts and significant progress has been achieved [5–11]. Recently, it was shown that, similarly to H<sub>2</sub>, water admixtures can also drastically increase the selectivity to PO [9]. It is therefore reasonable to expect that in both cases a surface hydroperoxide intermediate, OOH, formed *in situ* could play a role as a milder oxidant than atomic oxygen and could be responsible for the selective PO formation. Although a tentative mechanism of OOH formation and oxidation has been proposed by Haruta et al. [8,12], it has not yet been confirmed by unbiased computational models based on first principles calculations.

Herein, we present a comprehensive theoretical investigation of the reaction network involved in the oxidation of propylene on gold on the basis of DFT. We have chosen a stepped and kinked Au(321) surface as a convenient model to study the reactions taking place on the defect-rich surface of a nanoparticle gold catalyst.

E-mail address: [moskaleva@uni-bremen.de](mailto:moskaleva@uni-bremen.de)<http://dx.doi.org/10.1016/j.cattod.2016.05.034>

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This model has been previously successfully employed in a number of theoretical studies [13–19]. Although the oxide support is an indispensable component of a catalyst, in this work we focus on the metal component, assuming that the key reaction steps that determine the selectivity take place on the gold surface.

This study is the first to compare and contrast the chemisorbed O and OOH species as oxidizing agents for propylene oxidation on gold. We show why the oxidation with hydroperoxy species leads to a higher PO selectivity. An important aspect that has not received enough attention in earlier theoretical studies is the easy isomerization of the commonly considered PO precursor (a five-member ring oxametallacycle, OM<sup>2</sup>C) to propanal or acetone, which according to our calculations, always has a lower activation barrier than that required for epoxide formation. Thus, even if the H abstraction from the CH<sub>3</sub> group of propylene could be suppressed, that still would not solve the problem of low PO selectivity. Our study shows that, quite remarkably, the propylene oxidation with surface OOH allows for at least three low-energy reaction pathways not going through that five-member-ring OM<sup>2</sup>C intermediate, hence, suppressing the isomerization to carbonyl compounds. At the same time, the abstraction of the allylic H from propylene by adsorbed OOH has higher activation energy than in the case of H abstraction by surface O. That explains why high selectivities to PO can be achieved if chemisorbed atomic O as oxidant is replaced by a milder OOH counterpart. Furthermore, our study clearly shows that the key reaction pathways are structure sensitive. The reaction pathways taking place at low-coordinated edge Au atoms go through somewhat different intermediates than on flat terrace sites. In particular, four-member ring oxametallacycles bound on a single kink Au atom seem to be crucial precursors to epoxide formation.

The paper is structured as follows. Section 2 describes the models and computational approach. Section 3.1 discusses the reaction pathways of propylene with chemisorbed O. Section 3.2 considers the oxidation with chemisorbed hydroperoxy radical and highlights an important difference to the atomic-oxygen induced pathways. Section 4 summarizes the most important findings.

## 2. Models and computational details

In this study we use the Au(321) surface, as in Fig. 1(a,b), as a model to represent the defect-rich surface of gold nanoparticles, with the typical structural features expected for these particles, such as small terraces of (111) type, steps and kinks. Of course, the real catalyst has a more complex structure, where the particle size, shape, and the perimeter interface of metal particles and the oxide support definitely play a role in the activity. However, we concentrate on the reaction steps that determine the selectivity and which are expected to take place on the gold surface. Hence, the choice of this relatively simple but computationally affordable model is justified. A comparison with the work of Chang et al. [20], who calculated some of the reactions discussed below using a Au<sub>38</sub> nanocluster model, shows that we predict the same chemistry and our results agree qualitatively, only the adsorption energies are much stronger on a nanoparticle surface, which is expected because of a small particle size.

The slab model has been constructed using the bulk lattice parameter of Au 4.173 Å obtained from a calculation with the PBE form of the generalized-gradient approximation (GGA) for the exchange-correlation functional [21,22]. The slab model contains 14 atomic layers corresponding to the thickness of the resulting slab of ~7.2 Å and the vacuum spacing between periodically repeated slabs of ~8.5 Å. We use a (2 × 1) surface unit cell containing 28 metal atoms. The uppermost 14 metal atoms were allowed to fully relax, whereas the lower 14 atoms were kept fixed at their optimized bulk positions.

The calculations have been carried out with the VASP code [23,24] using PBE functional and projector augmented wave (PAW) method [25,26] with an energy cutoff of 415 eV. The choice of the PBE functional is justified by its very good performance in describing bulk properties of transition metals [27,28]. The *k* point sampling was generated by the Monkhorst-Pack procedure [29]; a 5 × 5 × 1 *k* point mesh was used for geometry optimizations. The structures were relaxed until the force acting on each atom was ≤ 2 × 10<sup>-2</sup> eV Å<sup>-1</sup>. The spin polarization has been taken into account for all reactions involving paramagnetic O<sub>2</sub> molecule. For the remaining reactions the spin-restricted formalism was used, as justified by test studies for adsorption systems on non-magnetic metallic surfaces [30].

Transition states (TSs) of the reactions were determined by applying the dimer method [31]. To verify the nature of a TS, the minima connected through the TS were identified by following the steepest descent reaction pathway downhill from the TS to the reactant and product valleys.

The adsorption energy of a stable molecule  $E_{\text{ads}}(X)$  was calculated as follows:

$$E_{\text{ads}}(X) = (E_{X^*} - E_{\text{substrate}} - E_X) \quad (1)$$

where  $E_{X^*}$  denotes the total energy of the adsorbed  $X^*$  on the surface in the optimized geometry;  $E_{\text{substrate}}$  and  $E_X$  are the total energies of the clean surface (or a surface with pre-adsorbed co-adsorbate in the case of co-adsorption) and of the  $X$  molecule in the gas phase, respectively. With this definition, negative values of adsorption energy indicate exothermic adsorption. For a chemisorbed O atom, the adsorption energy is calculated by taking one-half the energy of a gas-phase O<sub>2</sub> molecule plus the energy of clean Au(321) as reference.

Importantly, the relative energies of various species and transition states shown in the calculated energy profiles are computed using the clean Au(321), gas-phase propylene, gas-phase O<sub>2</sub>, and, where relevant, gas-phase H<sub>2</sub> as reference. For example,

$$E_{\text{rel}}(\text{C}_3\text{H}_6^* + \text{OOH}^*) = E_{\text{C}_3\text{H}_6^* + \text{OOH}^*} - E_{\text{Au}(321)} - E_{\text{C}_3\text{H}_6} - E_{\text{O}_2} - \frac{1}{2}E_{\text{H}_2} \quad (2)$$

where  $E_{\text{C}_3\text{H}_6^* + \text{OOH}^*}$  is the total energy of co-adsorbed propylene and hydroperoxyl,  $E_{\text{Au}(321)}$  is the total energy of the clean Au(321) slab  $E_{\text{C}_3\text{H}_6}$ ,  $E_{\text{O}_2}$  and  $E_{\text{H}_2}$  are the total energies of gas-phase propylene, O<sub>2</sub> and H<sub>2</sub>, respectively, and here and further on a \* symbol denotes an adsorbed species. A single exception is Fig. 9(b), where gas-phase O<sub>2</sub> and H<sub>2</sub>O are used as reference species. Relative energies do not include zero-point energy corrections.

## 3. Results and discussion

### 3.1. Reaction of propylene with chemisorbed O atoms

The epoxidation of propylene on gold and other coinage metals is believed to proceed by analogy to the accepted mechanism of ethylene epoxidation, via an oxametallacycle intermediate formed from addition of surface O to the C=C bond of propylene [32]. A competing H abstraction from the CH<sub>3</sub> group of propylene forming surface allyl species is thought to be leading to total combustion [3,33]. Studies of propylene oxidation on oxygen covered Au(111) and Au(100) single-crystal surfaces in ultrahigh vacuum reported either CO<sub>2</sub> and H<sub>2</sub>O [34] or acrolein [35] as main products but no propylene oxide was detected. The differences in observed main products in Refs. [34] and [35] were attributed to the different methods used for O deposition. Earlier theoretical studies of propylene oxidation by surface O on gold [36,37] focused on the primary reaction steps leading either to metallacycles or allyl but refrained

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