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CO Oxidation at SnO$_2$/Pt$_3$Sn(111) Interfaces

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Abstract

Segregation induced formation of oxide/metal interfaces can significantly influence the catalytic activity of alloy nanoparticles. One example is Pt$_3$Sn nanoparticles, which are known to segregate into SnO$_x$ and an Sn deficient alloy phase during typical operating conditions for CO oxidation. Here, we use density functional theory calculations to investigate CO oxidation over Pt$_3$Sn(111) supported SnO$_2$ and (SnO$_2$)$_3$, representing the initial state of segregation. The results are compared to CO oxidation at an interface between bulk-like SnO$_2$ and Pt$_3$Sn(111). The barrier for CO oxidation via a Mars–van Krevelen mechanism is found to be lower on SnO$_2$ and (SnO$_2$)$_3$ as compared to the bulk-like model. However, the regeneration of the finite systems is associated with higher barriers for O$_2$ dissociation which may become the rate limiting step in the low temperature regime where the metal surface can be assumed to be CO covered.

Graphical Abstract

Keywords
Bimetallic catalysts · CO oxidation · Heterogeneous catalysis · Metal oxides

1 Introduction

Bimetallic alloys represent an important class of catalysts in heterogeneous catalysis where PtSn is one example that has been investigated for low-temperature CO oxidation [1–4]. The effects of alloying on catalytic properties are generally described in terms of ensemble, ligand and strain effects [5–8]. Ensemble effects refer to geometric adsorption constraints upon alloying, whereas ligand and strain effects denote changes in the electronic structure. The mixing pattern in metal nanoalloys is generally complex and depends both on the constituent metals and the synthesis method [9–11]. Nanoalloys have been investigated extensively...
computed [9], and recent efforts include examples where the chemical ordering of bimetallic nanoparticles is predicted on the basis of density functional theory (DFT) calculations [12]. Although this approach is suited to explore the homotop distribution for PtSn bimetallic nanoparticles of particular shape and composition [13], it does not describe adsorbate (or reaction) induced segregation phenomena. The dynamic response of metal nanoparticles to adsorbates makes it challenging to assess the origin of promoting effects upon alloying. Several studies have demonstrated that reactions may drive surface reconstruction and/or segregation [14–16]. Also in the case of PtSn nanoparticles, experimental evidence exists for adsorbate induced segregation during typical operating conditions for regular CO-oxidation and preferential CO-oxidation in the presence of H2 (PROX) [2–4]. In Ref. [3], ambient pressure X-ray photoelectron spectroscopy (XPS) showed the formation of an Sn-oxide phase during CO-oxidation over silica supported PtSn nanoparticles. Based on the experiments, [3] it was suggested that CO oxidation occurs with a low activation barrier at the interface between Pt and SnOx domains via a Mars–Van Krevelen mechanism [17]. Moreover, SnO2-phases in contact with a PtSn nanolloy have been observed during CO electro-oxidation over PtSn with transmission electron microscopy [18]. Furthermore, Pt-Sn segregation during CO exposure over alumina supported PtSn has been inferred from in situ diffuse reflectance IR Fourier transform spectroscopy following the CO stretch vibration [1, 2, 4]. In the case of Pt3Sn, adsorbate induced segregation is not limited to nanoparticles and it has been observed for Pt3Sn(111) during CO oxidation with X-ray photoemission spectroscopy (XPS) [19]. In particular, it was proposed that Pt3Sn(111) converts to an inverse catalyst with SnOx supported by metallic Pt5Sn [19]. Adsorbate induced segregation of bi-metallic nanoparticles leads to the creation of interfaces and during oxidation reactions, metaloxide/metal interfaces or metaloxide/metaloxide interfaces are formed. It is well known, that such interfaces can have superior catalytic performance in CO oxidation [20–26]. For example, low temperature activity has been observed for promoted Pt-group metals [23] and in the case of FeOx/Pt(111), the activity was rationalized by the possibility to have CO oxidation at the FeOx/Pt interface [20]. In case of Pt3Sn, segregation into an SnO2 phase supported by a Pt(111)/Pt3Sn (Pt-skin) was recently computationally predicted via ab initio thermodynamics [24]. Moreover, the importance of an oxide/metal interface for the reaction kinetics was explored using first principle micro-kinetic modeling for a periodic SnO2-rod supported by a Pt-skin [24]. The catalytic role of the SnOX-phase was manifested by a low temperature activity at the interface. The reaction path at the interface is of Mars–van Krevelen type which limits the effect of CO poisoning that controls the low temperature reaction rate on regular Pt, where the reaction proceeds via a Langmuir–Hinshelwood mechanism. Furthermore, the CO-oxidation barriers at the SnOx/Pt interface were found to be lower than the corresponding barrier on the metal-only system. As it is difficult to know the experimental degree of segregation, especially during the initial stages, it is unknown whether the results for the bulk-like SnO2 interface can be generalized to other SnOx-structures supported on Pt. Therefore, it is desirable to investigate how CO oxidation barriers and their regeneration with O2 depend on the size of the SnOx-phase. Herein, we use DFT calculations to investigate CO oxidation and O2 regeneration over finite size SnO2 and (SnO2)3 units supported on Pt3Sn(111). The results are compared to oxidation at a bulk-like metal supported SnO2-phase, represented by a SnO2-rod/Pt3Sn(111) model.

2 Theoretical Methodology

DFT is applied with the gradient corrected exchange-correlation functional according to Perdew, Burke and Ernzerhof [27]. In particular, the Vienna Ab Initio Simulation Package [28, 29] is used. The one-electron Kohn–Sham orbitals are expanded in a plane-wave basis-set with a kinetic energy cutoff of 450 eV. PAW potentials are employed to describe the interaction between the valence electrons and the core [30]. Reciprocal space integration over the Brillouin zone is approximated with finite sampling using Monkhorst–Pack grids [31, 32]. Bulk calculations of Pt, PtSn, SnO2 are performed with a k-point grid of at least 12 × 12 × 12. Surface calculations are performed using 5 layered orthorhombic (SnO2)3 units. A (6 × 2√3)rect surface cell is used to model a metal-supported periodic (SnO2)12-rod. k-point grids are employed depending on the size of the surface cell being either 3 × 3 × 1 or 2 × 3 × 1. A vacuum layer of at least 20 Å is used in the calculations.

The systems are structurally optimized until the largest force is smaller than 0.03 eV/Å. Transition states are obtained initially with the climbing image nudged elastic band method [33, 34] and further refined with the dimer method [35]. The convergence criteria for the transition state searches are set to at least 0.03 eV/Å. For the O2 dissociation reactions, spin polarized calculations are employed for both reactants and transition states. To verify transition states and local minima, a partial Hessian vibrational analysis (PHVA) is employed. The PHVA is performed only for the surface species while keeping the rest of the system fixed. The numerical partial Hessian is calculated by displacements in x, y and z-directions of ±0.02 Å.
The stability of the segregated systems of the form (SnO$_2$)$_X$ is assessed by referencing to SnO$_2$-bulk. The stability ($\Delta E$) is calculated according to:

$$\Delta E = E_{(\text{SnO}_2)_x/\text{Pt}(111)/\text{Pt}_3\text{Sn}} - xE_{\text{SnO}_2, \text{bulk}} - E_{\text{Pt}(111)/\text{Pt}_3\text{Sn}}$$

Here, $E_{(\text{SnO}_2)_x/\text{Pt}(111)/\text{Pt}_3\text{Sn}}$ is the energy of the system under consideration, $E_{\text{SnO}_2, \text{bulk}}$ is the energy of the SnO$_2$-bulk and $E_{\text{Pt}(111)/\text{Pt}_3\text{Sn}}$ is the energy of a Pt$_3$Sn slab with the top layer being only Pt (a Pt-skin).

### 3 Results and Discussion

The reaction induced segregation process is complex on Pt$_3$Sn–nanoparticles. From experiments, it is clear that SnO$_X$ is formed during CO oxidation, [3, 19] however, the morphology is unknown. Here, we present first different SnO$_2$/Pt interface models and their relative stability with respect to bulk SnO$_2$ (Sect. 3.1). Thereafter, CO adsorption, the stability of the interface O atoms and CO oxidation are investigated (Sect. 3.2). The closing of the catalytic cycle by regeneration of SnO$_X$ via O$_2$ dissociation is investigated in Sect. 3.3.

#### 3.1 Interface Models and Their Relative Stability

Different SnO$_X$ model structures are constructed on a Pt-skin model, thus a Pt$_3$Sn(111) slab with the top-most metal layer being Pt-only. A Pt-skin is used instead of regular Pt$_3$Sn(111) to model the Sn-deficiency in the alloy. This model system was previously used to explore CO oxidation routes on PtSn nanoparticles [24]. The studied interface models studied herein are displayed in Fig. 1. ROD represents a (SnO$_2$)$_{12}$-rod, with exposed SnO$_2$(110)-surfaces as the (110) facet is known to be the stable SnO$_2$ surface [36, 37]. The TRIMER system is a trimeric (Sn$_3$O$_3$)$_3$O$_3$ structure and the MONOMER unit is a single Sn ad-atom with two oxygen atoms. For each of the models, a favorable orientation was obtained by optimizing a set of different generated structures. Here, only the lowest energy orientation is considered for further studies.

In earlier work, the exothermicity of segregation was validated for the formation of the rod model onto a five layer Pt$_3$Sn slab in absence of CO [24]. It was found that the required oxygen chemical potential for segregation of this slab into an Sn-deficient Pt-skin system and bulk SnO$_2$ is $-1.53$ eV. If instead of bulk SnO$_2$ a rod-model is formed (Fig. 1a), an oxygen chemical potential of $-1.17$ eV is required. With respect to bulk SnO$_2$, the stabilities ($\Delta E$) are 0.72 eV (rod), 1.24 eV (trimer) and 1.44 eV (monomer) (see Fig. 1). From the stability difference, the minimum oxygen chemical potential to form the (SnO$_2$)$_3$ and (SnO$_2$)$_2$ is calculated to be $-0.91$ eV and $-0.81$ eV, respectively. In the presence of CO and O$_2$, the formation of monomeric and trimeric SnO$_2$ units should precede the formation of more bulk like SnO$_2$-phases, such as the rod model. However, due to the lower stability of the monomer and the trimer, their formation requires higher oxygen chemical potentials and, thus, higher oxygen pressures than the formation of the rod. The minimal oxygen pressure needed to form monomers at a temperature of 400 K is still very low, being $\sim 10^{-11}$ bar [24]. The corresponding pressures for the trimer and the rod are about $10^{-13}$ and $10^{-19}$ bar, respectively.

#### 3.2 Relative Stability of Interface Oxygens, CO Adsorption and CO Oxidation at SnO$_X$ Interfaces

The model systems have, completely oxygen saturated, three or two oxygen atoms available for reaction, see Fig. 1. A measure of their reactivity is given by the stability which could be assessed by calculating the energy required to form oxygen vacancies. The vacancy formation energies, defined as the energy needed to form 1/2 O$_2$ in the gas phase, are given in Table 1. For rod and trimer models, the oxygen with the lowest vacancy formation energy is denoted position in B. Owing to symmetry, the two atoms (A and C) are
equivalent for the monomer. The vacancy formation energies to go from state ABC to A*C are 1.24 and 0.61 eV, for the rod and the trimer, respectively. For the monomer, the vacancy formation energy going from A*C to C is 0.59 eV. The vacancy formation energies on the trimer and monomer models are, thus, considerably lower than on the rod model. In case of the trimer, vacancy formation from A or C atoms requires more energy than from B, whereas the differences are moderate for the rod.

CO oxidation is one possibility to deplete oxygen atoms by reactions from the SnOX systems. Here, we assume the consumption of the oxygen atom in position B via CO oxidation forming A*C for rod and trimer models and consumption of position A for the monomer model forming **C. CO can adsorb on a multitude of positions on the Pt-skin. In particular, there are different types of sites with respect to the underlying Pt3Sn lattice. The different types of hollow sites (fcc-Pt, fcc-Sn, hcp-Pt and hcp-Sn) are visualized in Fig. S1 of the Electronic Supplementary Material (ESM). For example, fcc-Pt refers to a site where a Pt atom is situated in the third layer below the site, for fcc-Sn an Sn atom appears in the third layer. The CO adsorption energies are −1.99 eV (fcc-Pt, rod), −1.70 eV (bridge, trimer) and −1.88 eV (bridge, monomer). The CO adsorption energies near the trimer and the monomer deviate markedly from the adsorption energy of CO on a (4 × 2√3)rec Pt-skin system, being −2.09 eV in the fcc-Pt position which is related to repulsive CO–SnOx interactions.

Barriers for all model systems are evaluated with respect to CO adsorbed in an fcc-Pt or bridge position near the consumed oxygen (see * in Fig. 1). The CO oxidation barriers from the (SnO2)X-state [ABC → A*C for rod and trimer, and A*C → **C for monomer] are 0.91 eV, 0.29 eV and 0.63 eV for the rod, trimer and monomer, respectively. If instead the same reference state for CO is used, being CO on the Pt-skin far from the metal oxide phase in an fcc-Pt position, the barriers are 1.01 eV (rod), 0.67 eV (trimer) and 0.83 eV (monomer), see Table 1. The CO oxidation barriers on the smaller SnOX models are, thus, considerably lower than for the rod-model. This is evident also in the large variation of the O–CO transition state structures, see Fig. 2. From the A*C configuration, the subsequently consumed oxygen is chosen to be A for the rod and trimer models. While the barrier for (A*C → **C), is about 0.20 eV higher than ABC → B*C, for the rod, the increase is within 0.10 eV for the trimer (see Fig. 4 and Table S1). We conclude that the barrier for CO oxidation is considerably lower on the finite systems than on the rod-model.

### 3.3 SnOx Regeneration via Molecular O2 Dissociation

To maintain a catalytic cycle, the SnOx phases should be regenerated by O2 adsorption and dissociation. O2 adsors on Pt(111)/Pt3Sn with an adsorption energy of −0.90 eV in a fcc-Pt position (Fig. 3a). The O–O distance is in this state elongated from 1.23 Å in gas phase to 1.41 Å. The transition state for dissociation occurs with an O–O distance of 1.83 Å and a barrier of 0.27 eV (Fig. 3a). The O2 dissociation is, thus, only weakly activated on the Pt-skin which is in agreement with previous reports for Pt(111) [38]. The barrier calculated with respect to O2 in the gas phase is −0.64 eV.

At low temperature, the catalyst is expected to be CO poisoned, with only a limited number of empty sites available for O2 dissociation on the metal phase. Therefore, O2 dissociation is here investigated at the (SnO2)/Pt interface of the different SnOX models in their **C state requiring only one empty metal site, rather than two metal sites.

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**Table 1** Oxygen vacancy formation energies and reaction barriers for the considered systems

<table>
<thead>
<tr>
<th></th>
<th>Rod (SnO2)3/Pt-skin</th>
<th>Trimer (SnO2)3/Pt-skin</th>
<th>Monomer (SnO2)/Pt-skin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eads,O–A</td>
<td>−1.30‡</td>
<td>−1.11</td>
<td>−0.59a</td>
</tr>
<tr>
<td>Eads,O–B</td>
<td>−1.24‡</td>
<td>−0.61</td>
<td>−</td>
</tr>
<tr>
<td>Eads,O–C</td>
<td>−1.30‡</td>
<td>−0.92</td>
<td>−0.59a</td>
</tr>
<tr>
<td>Eads,CO near O–B</td>
<td>−1.99‡ (fcc-Pt)</td>
<td>−1.70 (bridge)</td>
<td>−1.88 (bridge)</td>
</tr>
<tr>
<td>ΔE‡,int</td>
<td>0.91‡</td>
<td>0.29</td>
<td>0.63</td>
</tr>
<tr>
<td>ΔE‡,CO/Pt-skin</td>
<td>1.01‡</td>
<td>0.67</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The reaction barrier ΔE‡ is calculated with respect to CO adsorbed in an fcc-Pt position in a (4 × 2√3)rec unit cell, thus in the absence of repulsive interactions with the SnOx-phase. The positions for the oxygen atoms in the rod are labeled according to Fig. 1. The energies are reported in eV without zero-point corrections

‡From Ref. [24]

aFor monomer, the A and C positions are equivalent
In this section, we will discuss the dissociation of $O_2$ on Pt-alloys nanoparticles taking place at the SnO$_2$/Pt$_3$Sn interface. When the Pt phase is CO poisoned, the SnO$_2$/Pt$_3$Sn interface enables a pathway for low temperature CO oxidation. Dependent on the degree of segregation, different interface effects can be anticipated and here we have investigated monomeric, trimeric and periodic (SnO$_2$)$_X$-rod models. Regardless of the size of the studied (SnO$_2$)$_X$-phase, CO oxidation can proceed with low barriers, which explain the experimentally observed low temperature activity. The reoxidation with $O_2$ is, however, more activated for the monomer and the trimer than on the rod-model, potentially forming a bottleneck for low temperature CO oxidation on the finite SnOX-units. Summarizing, the co-catalytic role of an SnO$_X$/Pt$_3$Sn interface will manifest itself in a low temperature activity provided that the SnO$_X$-phase can be regenerated with oxygen.

**4 Conclusions**

This work emphasizes interface effects during CO oxidation on Pt-alloys nanoparticles taking place at the SnO$_2$/Pt$_3$Sn interface. When the Pt phase is CO poisoned, the SnO$_2$/Pt$_3$Sn interface enables a pathway for low temperature CO oxidation. Dependent on the degree of segregation, different interface effects can be anticipated and here we have investigated monomeric, trimeric and periodic (SnO$_2$)$_X$-rod models. Regardless of the size of the studied (SnO$_2$)$_X$-phase, CO oxidation can proceed with low barriers, which explain the experimentally observed low temperature activity. The reoxidation with $O_2$ is, however, more activated for the monomer and the trimer than on the rod-model, potentially forming a bottleneck for low temperature CO oxidation on the finite SnOX-units. Summarizing, the co-catalytic role of an SnO$_X$/Pt$_3$Sn interface will manifest itself in a low temperature activity provided that the SnO$_X$-phase can be regenerated with oxygen.
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References


Fig. 4 Schematic representation of putative catalytic cycles of CO oxidation for the considered systems. The O₂ dissociation barriers are here given with respect to adsorbed O₂.


