Dissociative Adsorption of Methane on Surface Oxide Structures of Pd–Pt Alloys

Arezoo Dianat, Nicola Seriani, Lucio Colombi Ciacchi, Wolfgang Pompe, Gianarelio Cuniberti, and Manfred Bobeth

Institute for Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, D-01062 Dresden, Germany, Fakultät Physik, Universität Wien, Sensengasse 8, 1090 Wien, Austria, Hybrid Materials Interfaces Group, Faculty of Production Engineering and Bremen Centre for Computational Materials Science, University of Bremen, D-28359 Bremen, Germany, and Fraunhofer Institute for Manufacturing Technology and Applied Material Research IFAM, D-28359 Bremen, Germany

Received: June 17, 2009; Revised Manuscript Received: September 17, 2009

The dissociative adsorption of methane on variously oxidized Pd, Pt, and Pd–Pt surfaces is investigated using density functional theory as a step toward understanding the combustion of methane on these materials. For Pd–Pt alloys, models of surface oxide structures are built on the basis of known oxides on Pd and Pt. The methane adsorption energy presents large variations depending on the oxide structure and composition. Adsorption is endothermic on the bare Pd(111) metal surface as well as on stable thin layer oxide structures such as the (√5 × √5) surface oxide on Pd(100) and the PtO2-like oxide on Pt(111). Instead, large adsorption energies are obtained for the (100) surface of bulk PdO, for metastable mixed Pd1−xPtO4/3 oxide layers on Pt(100), and for Pd–Pt(111) surfaces covered with one oxygen monolayer. In the latter case, we find a net thermodynamic preference for a direct conversion of methane to methanol, which remains adsorbed on the oxidized metal substrates via weak hydrogen-bond interactions.

1. Introduction

The catalytic oxidation of hydrocarbons in general, and of methane in particular, is considered as an effective method of power generation associated with low emissions of CO2 and NOx. Because of the high H/C ratio of methane, the heat of combustion per mole of generated CO2 is higher than for other fuels, for example, twice as much as for coal.¹ The interest toward the development and optimization of novel catalysts for the combustion of methane has thus considerably increased over the last years. Especially palladium-based catalysts have been extensively explored because of their high catalytic oxidation activity. Among those catalysts, the bimetallic system Pd–Pt has been the object of many investigations.²–¹¹ In several studies it was found that Pd–Pt catalysts exhibit higher methane conversion efficiency³–⁶,⁸–¹² and better long-term stability³,¹¹ than pure Pd.

The performance of Pd–Pt catalysts strongly depends on the chemical state of the metal surface at the conditions suitable for oxidation, which in many cases lead to the formation of superficial oxide phases. For pure Pd and Pt catalysts, there is agreement that oxide formation has a positive effect on their methane oxidation activity,¹³,¹⁴ although the active oxide phases have not been unequivocally determined yet. On the one hand, some authors have proposed that bulk PdO is less active than either a thin oxide layer¹⁵ or a layer of adsorbed oxygen on Pd.¹⁶,¹⁷ On the other hand, the formation of bulk oxide has been suggested to explain the observed increase in catalytic activity.¹⁸,¹⁹ Recently, Gabasch et al.²⁰ reported that bulk PdO seeds grown on a surface, otherwise covered by a Pd2O3 surface oxide, are the active phase for methane oxidation on a Pd(111) single crystal surface. The catalytic behavior of pure Pt metal is quite different. According to investigations in refs 18, 19, 21, and 22, its catalytic activity reaches a maximum at a submonolayer coverage of adsorbed oxygen, and further oxidation with formation of PtO2 leads to activity loss. Still, it is unclear whether a similar behavior can be expected also for other Pt oxide phases that could develop in an oxidizing atmosphere. Platinum bulk oxide phases comprise α-PtO2, β-PtO2, PtO, and PtO.²³–²⁵ Correspondingly, a large variety of surface oxides can be expected.²⁶,²⁷ Previous calculations have suggested that PtO2 might be an active phase for the catalytic oxidation of carbon compounds.²⁷ Similarly, in the case of palladium, besides PdO also other bulk oxide phases could form, as, for example, Pd2O3.²⁹ Different surface oxides have been observed on Pd(111),³⁰–³² Pd(100),³³ and on stepped surfaces.³⁴

Compared with the large amount of data available for pure Pd and Pt, little is known about the oxidation behavior of the bimetal Pd–Pt and its relation to the higher catalytic activity displayed by these alloys. Persson et al.¹⁰ suggested that Pd–Pt catalysts on alumina consist of a PdO-rich phase coexisting with a palladium-rich Pd–Pt alloy. Studying the composition dependence of the catalytic activity of Pd–Pt, Lapisardi et al.¹¹ found the highest activity for catalysts with very high Pd content Pd0.95Pt0.05O2. In a previous study,¹⁵ we have investigated by means of density functional theory (DFT) the thermodynamic stability of mixed bulk oxides Pd1−xPtO2 isomorphous to known bulk oxide phases of pure Pd and Pt. According to these calculations, the mixed oxide phase Pd1−xPtO2 with crystal structure analogous to α-PtO2 is stable only at rather low temperature (<500 K for atmospheric oxygen pressure). With increasing temperature, a phase mixture of PdO with first PtO2 and later PtO becomes stable. At higher temperature, the oxides

¹ To whom correspondence should be addressed. E-mail: arezoo.dianat@nano.tu-dresden.de.
² Dresden University of Technology.
³ Universität Wien.
⁴ University of Bremen.
⁵ Fraunhofer Institute for Manufacturing Technology and Applied Material Research IFAM.

10.1021/jp905689t © 2009 American Chemical Society
Published on Web 11/17/2009
TABLE 1: Calculated Average Oxygen Binding Energies (in eV) in the Case of Only On-Surface Adsorption (on) and for Simultaneous On-Surface and Subsurface Adsorption (on + sub) on Pd(111), Pt(111), and Pd/Pt/Pd(111) at Different O Coverages

<table>
<thead>
<tr>
<th>total O coverage in ML</th>
<th>Pd(111) on</th>
<th>Pd(111) on + sub</th>
<th>Pt(111) on</th>
<th>Pt(111) on + sub</th>
<th>Pd/Pt/Pd(111) on</th>
<th>Pd/Pt/Pd(111) on + sub</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>−1.34</td>
<td>0.36</td>
<td>−1.22</td>
<td>0.68</td>
<td>−1.39</td>
<td>0.64</td>
</tr>
<tr>
<td>0.50</td>
<td>−1.03</td>
<td>−0.93</td>
<td>−0.92</td>
<td>−0.52</td>
<td>−1.06</td>
<td>−0.85</td>
</tr>
<tr>
<td>0.75</td>
<td>−0.61</td>
<td>−0.72</td>
<td>−0.55</td>
<td>−0.47</td>
<td>−0.69</td>
<td>−0.68</td>
</tr>
<tr>
<td>1.00</td>
<td>−0.22</td>
<td>−0.42</td>
<td>−0.17</td>
<td>−0.27</td>
<td>−0.25</td>
<td>−0.41</td>
</tr>
</tbody>
</table>

*In the on + sub case, the amount of subsurface oxygen is always 0.25 ML and the remaining oxygen is on the surface, i.e., for 0.25 ML total coverage there is no oxygen on the surface in the on + sub case.

decompose directly to metallic Pd–Pt, except for Pd-rich systems, where PdO and metallic Pt coexist within a small temperature window.

In the present DFT study, in a first step we analyze the stability of oxidized Pd–Pt surfaces as a basis for investigating their interaction with methane. Because of the lack of relevant experimental information, known surface oxide structures of pure Pd and pure Pt are used as guidelines to construct Pd–Pt surface oxide models. In a second step, we compute the driving forces for the dissociative adsorption of CH4 on various oxidized Pd–Pt surfaces, which is commonly believed to be the rate-determining reaction in the catalytic combustion of methane.

The paper is outlined as follows. Computational details of the DFT analysis are briefly described in Section 2. In Section 3, we report on the calculated oxygen binding energies of various Pd–Pt oxide structures. The calculated methane adsorption energies on these oxide structures are then presented in Section 4. Finally, our results are discussed and interpreted in relation to experimental results in Section 5.

2. Computational Details

Our DFT calculations are performed by means of the Vienna ab initio simulation package (VASP),36–38 using the PBE generalized gradient approximation (GGA) for the exchange-correlation functional39 and the PAW method.40,41 The wave functions are expanded in plane waves up to a kinetic energy cutoff of 400 eV. The periodically repeated simulation cells include slabs of six substrate layers covered with either adsorbed oxygen or a thin oxide layer and with adsorbed CH4 and H. In all simulations, the vacuum gap between the slab surface models is larger than 15 Å. Unless stated otherwise, the size of the simulation cell corresponds to a (2 × 2) unit cell of the metal substrate. Integration in the first Brillouin zone is performed using Monkhorst-Pack grids42 including 25 k-points in the irreducible wedge. In all calculations, the positions of all atoms are optimized until all force components become less than 0.01 eV/Å. Convergence of energy differences with respect to the used cutoff energies and k-point grids is ensured within a tolerance of 10 meV/atom. Further computational details can be found in ref 43.

3. Surface Oxide Structures on Pd–Pt

The oxidation of Pd and Pt surfaces proceeds from the chemisorption of oxygen atoms through the formation of surface oxides to the development of bulk oxide. In the case of palladium, the structure of surface oxide phases has been the subject of many experimental44–47 as well as theoretical30,33,45,48–50 investigations. Phase diagrams of surface oxide structures in dependence on the chemical potential of oxygen have been thoroughly characterized for several surface orientations.30,33 On Pd(111), chemisorbed oxygen at low coverage is arranged with a p(2 × 2) periodicity. At higher coverage, several surface oxide phases form and coexist, as observed in STM investigations accompanied by theoretical modeling.30,44,48 On the contrary, on Pd(100) only one surface oxide has been found,33,45 consisting of two unit cells of PdO(101) over a (√3 × √3) Pd(100) cell. Investigations of oxide formation on platinum revealed the following. On Pt(111), the formation of a bulk-like, strongly distorted α-PtO2 surface oxide was observed at an oxygen partial pressure of 0.5 atm and temperatures from 520–910 K.51,52 α-PtO2 was predicted to be the stable low temperature phase also by DFT calculations.27,35 On Pt(100), DFT calculations suggest the formation of an α-PtO2-like surface oxide at low temperature27,28 and the existence of a stability region for a PtO2-like oxide layer at higher temperature.

3.1. On-Surface and Subsurface Adsorbed Oxygen. To characterize the binding strength of oxygen atoms adsorbed at metal surfaces, we calculate an average oxygen binding energy $E_b$ per O atom according to the formula

$$E_b = \frac{1}{N_O} \left[ E_{O\@S} - E_s - \frac{N_O}{2} E_{O_2} \right]$$

where $E_{O\@S}$ is the total energy of the oxygen–metal system, $E_s$ the energy of the bare metal substrate, $E_{O_2}$ the energy of a free oxygen molecule, and $N_O$ the number of O atoms. The oxygen atoms in formula 1 include oxygen located on the surface as well as in subsurface positions. The calculated oxygen binding energies on (111) surfaces are listed in Table 1 for different oxygen coverages up to 1 monolayer (ML). The values in the last column are obtained for a stack of atomic layers with Pd in the surface layer, Pt in the subsurface layer, and Pd in the remaining layers. In a previous DFT study,35 we have calculated oxygen adsorption energies on mixed Pd–Pt surface and subsurface layers. For the considered Pd–Pt compositions and configurations, the oxygen adsorption energies have been found to vary between −1.26 and −0.94 eV. In the case of stacks of pure Pd and Pt layers, we have obtained an adsorption energy of −0.99 eV on Pd/Pt/Pd/Pd(111) and −1.26 eV on Pd/Pt/Pd(111). The latter values present the strongest oxygen binding that we have found on all considered stacks of mixed metal layers. This strong binding has been attributed to charge transfer from Pd to Pt which causes a strong binding between the more electropositive Pd atoms and electonegative O atoms.

The most stable oxygen adsorption sites on the (111) surface of Pd and Pt are the fcc hollow sites.53,54 According to the energy values in Table 1, the oxygen binding energies on pure Pt(111) are significantly smaller than on pure Pd(111) for all considered coverages. The strongest oxygen binding is found for the Pd/Pt/Pd(111) layer stack.

Further calculations are performed for the case of fixed subsurface oxygen coverage of 0.25 ML and increasing on-surface coverage up to 0.75 ML, thus giving a maximum total...
coverage of 1 ML. Between the first and second metal layer there are three high-symmetry positions, an octahedral site underneath the fcc on-surface hollow site, a tetrahedral site (tetra I) below the fcc on-surface hollow site, and a second tetrahedral site (tetra II) directly below a surface metal atom.\(^5\) For simultaneous on-surface and subsurface adsorption, the fcc hollow site on the surface and the tetra I subsurface position are found to be the most stable oxygen positions for all considered oxygen coverages. The corresponding average oxygen binding energies are given in Table 1 (referred to as on + sub). They reveal that in addition to on-surface adsorption oxygen incorporation underneath the surface layer becomes favorable for a total oxygen coverage \(\theta_{\text{tot}} \geq 0.75\) ML on Pt(111) and for \(\theta_{\text{tot}} = 1\) ML on Pt(111). This result is in agreement with other DFT calculations for Pd(111).\(^5\) For solely on-surface adsorption, the binding of oxygen is slightly stronger on Pt/ Pt/Pt(111) than on Pt(111), whereas with subsurface oxygen the average binding energy is larger for pure Pt(111) due to the unfavorable binding of oxygen to the Pt subsurface layer in the case of Pt/Pt/Pt(111).

### 3.2. Thin Oxide Layers

With increasing oxygen coverage, surface oxide phases start forming on Pd and Pt surfaces. To our knowledge, there is no experimental information concerning the structure of such phases on the Pd–Pt bimetal. For this reason, model structures of possible Pd–Pt surface oxides are constructed here on the basis of the known oxide structures of pure Pd and Pt. In particular, we consider the experimentally observed PdO(101)-like\(^3\),\(^4\) and the theoretically predicted Pt\(_2\)O\(_4\)-like\(^7\) oxide layers on the (100) surface, as well as the \(\alpha\)-PtO\(_2\)-like\(^27\) layer on the (111) surface. According to our previous calculations,\(^5\) these layers are characterized by small lattice misfits between oxide and metallic substrate, namely 2\% for PdO(101)/Pd(100), 3.5\% for \(\alpha\)-PtO\(_2\)(0001)/Pt(111), and less than 1\% for Pt\(_2\)O\(_4\)(100)/Pt(100). The corresponding oxide structures obtained after DFT geometry optimization are shown in Figure 1.

In the case of PdO(101)/Pd(100), the Pd atoms of the oxide are located above the surface hollow sites of the substrate. The oxygen amount in the oxide layer corresponds to a coverage of 0.8 ML, referred to the surface metal atoms. In the case of \(\alpha\)-PtO\(_2\)(0001)/Pt(111), the Pt atoms of the oxide are located above top sites, fcc hollow sites, as well as hcp hollow sites of the substrate, and the oxygen coverage is 1.5 ML. The epitaxial Pt\(_2\)O\(_4\)(100)/Pt(100) oxide layer corresponds to an oxygen coverage of 1 ML. In this case, the oxide layer includes two metal layers (cf. Figures 1e,f).

In the case of mixed Pd–Pt systems, we consider special Pd–Pt configurations in the oxide layers and in the metal surface layers which are generated by the following replacements. For example, starting from a pure Pd system in the case of Figure 1a, we first replace Pd atom 1 in the oxide layer by Pt. With increasing Pt concentration in this layer Pd atoms 2, 3, and 4 are replaced by Pt. The Pt concentration in the metal surface layer is increased in the same manner starting with Pd atom 5. For the other two layer systems (Figures 1c,e), the Pt atoms are replaced by Pd in analogous manner.

To characterize the stability of oxide structures with different Pd–Pt configurations and variable oxygen coverage, an average oxygen binding energy can be defined as

\[
E_b = \frac{1}{N_O} \left[ E_{\text{Layer@S}} - E_S \right] - N_{\text{Pd}}^\text{Layer} E_{\text{Pd}}^{\text{bulk}} - N_{\text{Pt}}^\text{Layer} E_{\text{Pt}}^{\text{bulk}} - \frac{N_O}{2} E_{\text{O}_2} \tag{2}
\]

where \(E_{\text{Layer@S}}\) is the total energy of the substrate together with the oxide layer, \(E_S\) is the energy of the substrate alone, \(E_{\text{Pd}}^{\text{bulk}}\) and \(E_{\text{Pt}}^{\text{bulk}}\) are the energies of Pd and Pt atoms in their bulk phases, and \(N_O, N_{\text{Pd}}^\text{Layer}\) and \(N_{\text{Pt}}^\text{Layer}\) are the numbers of oxygen, Pd, and Pt atoms in the oxide layer. The binding energy (2) corresponds to the energy gained by deposition of molecular oxygen and formation of an oxide with metal atoms from ideal bulk metal reservoirs. With this definition, we neglect the difference of chemical potentials of the metal atoms in the pure metal bulk and in a Pd–Pt alloy. Since the free energy of mixing of Pd–Pt is of the order of few tens of millielectronvolts per metal atom, while the oxygen binding energies are of the order of one electronvolt, this approximation will not significantly influence our conclusions.

To study the effect of the Pd–Pt composition on the oxygen binding energy, we vary the Pd/Pt ratio both in the oxide layer and in the outermost substrate-layer. All other substrate layers are composed of Pd in the case of the PdO(101) layer on Pt(100), and of Pt for the other two cases. The calculated oxygen binding energies for the three oxide layers are shown in Figure 2 as a function of the Pt concentration of the outermost substrate layer. The different curves presented correspond to different compositions of the oxide layer. Every curve point represents one special Pd–Pt configuration as noted above. Test calculations for another configuration at fixed composition for Pd\(_{0.75}\)Pt\(_{0.25}\)/Pt(111) and for \(\alpha\)-Pd\(_{0.33}\)Pt\(_{0.67}\)/Pt(111) yield only small differences in the average oxygen binding energy of 0.012 and 0.006 eV, respectively.

For the PdO(101) layer structure (Figure 2a), the maximum variation of the oxygen binding energy with the substrate-layer composition is less than 0.05 eV. Similarly, the binding energy varies less than 0.1 eV for the \(\alpha\)-PtO\(_2\) structure (Figure 2b, note the different energy scale). Replacement of Pd atoms of the PdO-like layer with Pt is energetically unfavorable. Namely, the O binding energy changes from −1.15 to −0.90 eV passing from a pure PdO to a pure PtO layer. The same holds for replacing Pt atoms of the \(\alpha\)-PtO\(_2\) layer with Pd. An analogous result has previously been found for mixed bulk oxides of Pd–Pt.\(^5\) For the case of the PtO\(_2\)-like oxide layer (Figure 2c), the changes in the binding energy with the substrate-layer composition are also small (less than 0.12 eV). For this oxide layer, it is very unfavorable to replace Pt atoms with Pd. Indeed, a Bader analysis\(^55\) reveals that the oxygen atoms in Pd\(_{0.33}\)Pt\(_{0.67}\)/Pt(100) gain 0.67 e from metal atoms, while the corresponding value for Pt\(_{0.33}\)O\(_{0.67}\)/Pt(100) is 0.73 e, reflecting the stronger oxygen binding in the latter case. For the other two oxide structures considered, the charge transfer from metal atoms to oxygen does not change.

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**Figure 1.** Top- and side-views of optimized atomic structures of different oxide layers. (a,b) PdO(101) on Pd(100), (c,d) \(\alpha\)-PtO\(_2\)(0001) on Pt(111), and (e,f) Pt\(_2\)O\(_4\)(100) on Pt(100) (O, red small spheres; metal, large spheres). In the case of mixed oxide and surface metal layers, Pt atoms are replaced by Pt (and vice versa) as described in the text.
perform zero-point energy corrections of the calculated adsorption energies since we think that these corrections lead to comparatively small shifts of energy values (see, e.g., ref 57), which is of minor importance for comparing adsorption energies on different systems as main goal of this study.

### 4.1. CH₄ Adsorption on Clean Metal Surfaces

We first report on our calculations concerning methane adsorption on pure metallic (111) and (100) surfaces. In agreement with other DFT calculations,⁵⁸,⁵⁹ we find that on the (111) surface the most stable adsorption site for CH₄ is on top of metal atoms and for H on fcc hollow sites. This applies to pure Pd(111) and Pt(111) as well as to the Pd/Pt/Pd(111) layer stack with Pd in the surface and Pt in the subsurface atomic layer. The calculated adsorption energies, shown in Table 2, are −0.08 eV for the Pt(111) surface and 0.19 eV for the Pd(111) surface. The positive value for Pd(111) corresponds to an endothermic reaction. This is in agreement with previous DFT calculations for methane adsorption on Pd(111) within the generalized gradient approximation (GGA) \( E_a = 0.27 \) eV), whereas an exothermic reaction was found by using the local density approximation (LDA) \( E_a = 0.62 \) eV).⁵⁹ For comparison, at the LDA level we obtain adsorption energies of −0.43, −0.66, and −0.45 eV on Pd(111), Pt(111), and Pd/Pt/Pd(111), respectively. Thus, for all considered systems, the LDA values are shifted roughly by −0.6 eV with respect to the GGA values.

In the case of all (100) surfaces, CH₃ on top of metal atoms and H on bridge sites are the most stable adsorption configurations. On Pd(100) and Pd/Pt/Pd(100), dissociative adsorption of methane is found to be endothermic, in agreement with DFT calculations in ref 60. Only on Pt(100), methane adsorption is exothermic with an adsorption energy of −0.31 eV.

### 4.2. CH₄ Adsorption on Surfaces with Adsorbed Oxygen

After analyzing methane adsorption on clean metal surfaces, we investigate here the adsorption on metal surfaces covered with 1 ML oxygen. A first set of calculations is performed starting with 1 ML of oxygen adsorbed solely on the (111) surface. As initial condition for the DFT calculations, the following positions of adsorbed CH₃ and H are chosen: H always on top of oxygen atom, and (i) CH₃ on top of metal atom, (ii) CH₃ on top of oxygen atom, and (iii) CH₃ on hcp hollow site. For these three cases, the calculated adsorption energies after structural relaxation are listed in Table 2. The corresponding optimized atomic structures are shown in Figures 3 and 4 for the Pd(111) and Pt(111) surfaces. The structures obtained for the Pd/Pt/Pd(111) layer stack are qualitatively the same as for Pd(111). The largest adsorption energies are obtained starting with CH₃ on top of a metal atom and H on top of an oxygen atom. In particular, the adsorption energy on Pd/Pt/Pd(111) is slightly higher than on Pd(111). In the latter two cases, structural optimization leads to a remarkable reconstruction of the adsorbate layer (Figure 3a). Both the CH₃ group and the H atom move away from their initial adsorption sites and bind to the same O atom, thus forming an adsorbed methanol molecule. Notably, if CH₃ and H are initially placed over other adsorption sites on Pd(111), CH₃ and H also detach from the metal atoms but bind separately to different O atoms of the surface, resulting in adsorbed OH and CH₃O groups and no methanol formation. The same is found in the case of the Pt(111) surface where CH₃ and H remain bound to separate sites. In this case, the Pt atoms to which CH₃ is bound are lifted off the surface layer by 2.2 to 2.5 Å, depending on the initial configuration (cf. Figure 4).

Analogous calculations of methane adsorption energies have been performed for surfaces covered with 0.75 ML oxygen on the surface and 0.25 ML in subsurface positions. Again, three
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**TABLE 2: Calculated Adsorption Energies (in eV) for the Dissociative Adsorption of Methane on Clean (111) and (100) Surfaces of Pd, Pt, and Pd/Pt/Pd, and on Surfaces Covered with 1 ML Oxygen on the Surface, As Well As with 0.75 ML on the Surface and 0.25 ML in Sub-Surface Positions**

<table>
<thead>
<tr>
<th>Clean Surfaces</th>
<th>1 ML Oxygen on (111) Surfaces</th>
<th>0.75 ML Oxygen on-Surface/0.25 ML Oxygen Subsurface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(111)</td>
<td>CH₃-top and H-fcc</td>
<td>CH₃-fcc and H-fcc</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>−2.42</td>
<td>−1.65</td>
</tr>
<tr>
<td>Pd/Pt/Pd(111)</td>
<td>−2.13 (−2.27)</td>
<td>−1.62</td>
</tr>
<tr>
<td></td>
<td>−2.47</td>
<td>−1.74</td>
</tr>
</tbody>
</table>

*a For clean surfaces, the values in squared brackets (in italics) correspond to adsorption energies within LDA. In the calculations, the initial positions of CH₃ and H have been chosen on high-symmetry sites of the (111) metal surface; CH₃ on top of metal atom (-top) and H on fcc hollow site on top of oxygen (-fcc) in case of the clean surfaces. For the systems with sub-surface oxygen, two fcc sites have been considered, CH₃ on fcc hollow site on oxygen atom (-fcc) and CH₃ on oxygen vacancy (-fcc*). The values in parentheses are the adsorption energies of methanol formation on the surfaces, irrespective of the reaction path. (These value are not related to the initial CH₃ and H positions in the table and are arbitrarily reported besides the corresponding highest energy values obtained for the other initial configurations).*

**Figure 3.** Optimized atomic structures of adsorbed CH₃ and H on a Pd(111) metal surface covered with 1 ML oxygen. In the calculations, the initial lateral positions of CH₃ and H have been chosen as follows: (a) CH₃ on top of a metal atom and H on top of oxygen, (b) CH₃ and H on top of oxygen atoms, and (c) CH₃ on hcp hollow site and H on top of oxygen. The largest adsorption energy is obtained for (a). Distances between adsorbed atoms and nearest neighbor substrate atoms in Å are the following: (a) d_C-Pd = 4.00, d_C-O = 1.43, d_H-O = 0.98; (b) d_C-Pd = 3.04, d_C-O = 1.41, d_H-O = 1.00; (c) d_C-Pd = 3.05, d_C-O = 1.40, d_H-O = 0.98.

**Figure 4.** Optimized atomic structures of adsorbed CH₃ and H on a Pt(111) metal surface covered with 1 ML oxygen. In the calculations, the initial lateral positions of CH₃ and H have been chosen as follows: (a) CH₃ on top of a metal atom and H on top of oxygen, (b) CH₃ and H on top of oxygen atoms, and (c) CH₃ on hcp hollow site and H on top of oxygen. The largest adsorption energy is obtained for (a). Distances between adsorbed atoms and nearest neighbor substrate atoms in Å are the following: (a) d_C-Pt = 2.97, d_C-O = 1.42, d_H-O = 0.99; (b) d_C-Pt = 3.03, d_C-O = 1.41, d_H-O = 1.00; (c) d_C-Pt = 2.92, d_C-O = 1.41, d_H-O = 1.00.

different initial positions of adsorbed CH₃ and H have been chosen: H always on top of oxygen, and (i) CH₃ on top of metal atom, (ii) CH₃ on top of oxygen atom, and (iii) CH₃ on fcc hollow site (oxygen vacancy). The largest adsorption energy results for CH₃ and H initially on top of oxygen for all considered surfaces (denoted by CH₃ -fcc and H-fcc in Table 2). The energy values in Table 2 indicate that methane adsorption on surfaces with subsurface oxygen is about 1 eV weaker than for the case of oxygen adsorbed solely on the surface. In the presence of subsurface oxygen, methanol does not form spontaneously starting from the initial geometries above, H and CH₃ remaining separately bound to different oxygen atoms.

While in the simulations so far the formation of methanol takes place only on Pd(111) and Pd/Pt/Pd(111) with oxygen on-surface coverage, we now calculate the adsorption energy after methanol formation on all other surfaces, irrespective of the initial geometry chosen. To this end, a novel set of DFT structural relaxations is performed starting with methanol adsorbed on all surfaces, including those with subsurface oxygen, using the atomic configuration obtained for Pd(111). In all cases, the adsorption energies are higher than for separately adsorbed CH₃ and H, as reported in Table 2. As visible in Figure 3a, the methanol molecule remains loosely adsorbed to the surface, mainly via a hydrogen-bond between the OH group of methanol and a surface O atom. The methanol adsorption energies amount to −0.11 eV on Pd(111) and Pd/Pt/Pd(111) and −0.08 eV on Pt(111) for 1 ML on-surface oxygen coverage, reflecting weak molecule-surface interactions.

4.3. CH₄ Adsorption on Superficial Oxide Layers. With increasing oxygen supply, the oxidation of the metallic catalyst is expected to proceed with formation of thin oxide layers. Correspondingly, we further investigate methane adsorption on the thin oxide layer structures described in Section 3.2. The most favorable adsorption sites of methyl and hydrogen are determined via relaxation of different structures with the following initial positions of the adsorbates: both CH₃ and H on top of oxygen or metal atoms, CH₃ on top of oxygen and H...
on top of metal atom, and vice versa. The optimized atomic structures on the PdO(101)/Pd(100), R\text{-PtO}_2(0001)/Pt(111), and Pt_3O_4(100)/Pt(100) layers are shown in Figure 5. The Pd–Pt composition is varied both in the oxide layer and the outermost layer of the metal substrate (cf. Figure 6). For all compositions, the stable atomic configurations of adsorbed CH_3 and H have been found to be qualitatively equal. However, the values of the adsorption energy, presented in Figure 6, show comparatively large variations. Every curve point in Figure 6 represents a special Pd–Pt configuration in the oxide and metal surface layer as described above. Test calculations of another Pd–Pt configuration for a PdO(101)- and PtO_2-like oxide layer at fixed composition (see Section 3.2) yield only small differences in the methane adsorption energy of less than 0.05 eV.

For the PdO(101)-like oxide layers, the most stable adsorption sites for CH_3 are either on Pd, if only Pd atoms are present, or on Pt, if Pt replaces Pd atoms in the oxide (Figure 5a). The corresponding adsorption energy values (Figure 6a) indicate that the methane decomposition reaction on this oxide structure is endothermic for all Pd–Pt compositions considered. As a general trend, for a given composition of the oxide layer, the reaction is the more endothermic the more Pd atoms are present in the outermost layer of the metal substrate, except for pure PdO(101) where the adsorption energy is independent of the substrate composition. For a given substrate composition, increasing the Pd/Pt ratio in the oxide from 0 to 1 results in a rather complex behavior of the adsorption energy values, whereby pure PdO(101) layer is the least reactive structure in all cases.

In the case of the \textalpha-PtO_2-like layer, where all metal atoms are fully coordinated by oxygen, adsorption of both CH_3 and H occurs necessarily on the O atoms (Figure 5b). The adsorption energy depends only weakly on the Pt concentration in the outermost substrate-layer, whereas a strong dependence on the oxide layer composition is observed (Figure 6b). While the reaction is clearly endothermic for the pure PtO_2 oxide layer, it becomes exothermic for a Pd/Pt ratio in the oxide larger than about 0.5. Thus, the driving force for methane dissociation increases monotonously with the Pd content in the oxide.

In the case of the Pt_3O_4-like oxide layers, both CH_3 and H adsorb strongly on the undercoordinated exposed oxygen atoms (Figure 5c), as found also previously for a pure Pt_3O_4 layer. The adsorption energy of −1.74 eV obtained here is comparable to the value of −1.47 eV computed in ref 27 using norm-conserving pseudopotentials. Increasing the Pd concentration in the oxide layer leads to stronger and stronger adsorption with little dependence on the composition of the outermost substrate-layer (Figure 6c). In particular, the large adsorption energy of −2.5 eV, computed for the Pd_3O_4/Pt(100) oxide, is comparable to the driving force for methane dissociation and methanol formation computed for the case of an oxygen ML adsorbed on the Pd/Pt/Pd(111) surface (see Table 2).
adsorption is endothermic, for the PdO bulk phase the adsorption reaction is exothermic. Regarding the dependence of the adsorption energy on the oxide composition, the largest value of $-1.0 \text{ eV}$ is obtained for the (100) surface of pure PdO (cf. Figure 5a). This value is however considerably lower than the energy values calculated for the Pt$_2$O$_3$-like oxide layers on Pt(100) and for the oxygen adlayers on Pd(111) (cf. Figure 6c and Table 2).

5. Discussion

The dissociative adsorption of methane on noble metal surfaces represents an essential reaction step of the catalytic combustion of methane and is thought to limit the reaction kinetics. As a first effort toward a deeper understanding of this catalytic reaction, we have studied methane adsorption on various oxide structures of Pd, Pt, and Pd−Pt alloy surfaces. The choice of the investigated systems is motivated by the facts that palladium oxide phases, in particular PdO, have been suggested to be catalytically more active than pure Pd,\textsuperscript{18,19} and that mixed Pd−Pt catalysts have been found to possess higher conversion efficiency for methane combustion, especially on the long-term. Our investigation includes chemisorbed O atoms, thin oxide layers, and bulk PdO-like oxide surfaces, addressing both their thermodynamic stability and their reactivity toward methane dissociation.

5.1. Formation of Oxide Layers on Pd−Pt Surfaces.

The thermodynamic stability of different oxidized Pd−Pt structures has been addressed by calculating average oxygen binding energies at 0 K. In general, superficial oxide layers are found to be more stable than oxygen adlayers (including subsurface O atoms) at the corresponding oxygen coverages, as displayed in Table 2 and Figure 2. The larger stability of oxygen adlayers on Pd compared to those on Pt can be understood simply from the lower electronegativity of palladium. Consistently with previous findings,\textsuperscript{43} the largest binding energy is found for a Pd/Pt/Pd(111) layer stack, due to the partial donation of electrons from the Pd surface layer to the Pt subsurface layer, which increases the surface reactivity.

In the case of surface oxide layers, the Pd−Pt composition of the outermost layer of the metal substrate has only a minor influence on the oxygen binding strength. Changes of the binding strength due to varying the Pd/Pt ratio in the oxide can be explained on the basis of the stability of the corresponding bulk oxide phases, as thoroughly addressed in refs 27 and 35. Namely, mixed oxides with PdO structure are destabilized by replacing Pd atoms with Pt, while mixed oxides with α-PtO$_2$ or PtO$_2$ structure are destabilized by replacing Pt atoms with Pd.

5.2. Dissociative Adsorption of CH$_4$ on Oxidized Pd−Pt Surfaces.

Concerning the dissociative adsorption of methane, our DFT calculations at the GGA level suggest, in agreement with existing literature,\textsuperscript{55} that Pd metal surfaces are not reactive, and Pt surfaces are only little reactive. Since CH$_4$ and H possess an electron-donor character, they are expected to bind better to electronegative elements. Indeed, binding to pure Pt (electronegativity 2.3 on the Pauling scale) is stronger than to pure Pd (electronegativity 2.2). However, if adsorbed oxygen (electronegativity 3.4) is present on the surface, either in the form of an oxygen adlayer or as surface oxide, then binding to oxygen provides a strong driving force for methane dissociation.

Correspondingly, we have obtained the largest adsorption energies for 1 ML of oxygen adsorbed on the (111) metal surfaces, in particular on Pd(111) and on the Pd/Pt/Pd(111) layer stack, with an energy gain of about $-2.4 \text{ eV}$ (cf. Table 2). A

TABLE 3: Calculated Methane Adsorption Energies (in eV) on the (101) and (100) Surfaces of the PdO Bulk Oxide Phase with One Mixed Oxide Surface Layer Pd$_{x}$-Pt$_{1-x}$O

<table>
<thead>
<tr>
<th>structure</th>
<th>$x = 0$</th>
<th>$x = 0.25$</th>
<th>$x = 0.5$</th>
<th>$x = 0.75$</th>
<th>$x = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdO(101)</td>
<td>-0.37</td>
<td>-0.63</td>
<td>-0.82</td>
<td>-0.61</td>
<td>-0.45</td>
</tr>
<tr>
<td>PdO(100)</td>
<td>-1.00</td>
<td>-0.94</td>
<td>-0.57</td>
<td>-0.51</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

4.4. CH$_4$ Adsorption on Bulk PdO-like Oxides.

After considering methane adsorption on thin oxide layers on Pd−Pt metal substrates, it is interesting to compute, for comparison, the methane adsorption energies on the corresponding bulk oxide surfaces. We note that for α-PtO$_2$ the adsorption on a single layer is already representative of the behavior of the bulk oxide, which consists of stacked PtO$_2$ layers weakly bound by van der Waals forces.\textsuperscript{27} Furthermore, the surface of bulk PtO$_2$ with lowest surface energy is nearly identical to the surface of the thin oxide layer considered above. In the following, we thus consider only surfaces of mixed Pd−Pt oxides with the structure of the well-known PdO bulk oxide phase. In particular, methane adsorption energies are calculated on the (100) and (101) surfaces, which present low surface energies.\textsuperscript{30}

As a model of a mixed oxide Pd$_{x}$-Pt$_{1-x}$O, we analyze a slab of five PdO layers covered with a mixed Pd$_{x}$-Pt$_{1-x}$O layer, in which Pd and Pt are arranged in a chess-like pattern for $x = 0.5$ (adsorption energies for the row-like Pd−Pt pattern differ less than 0.025 eV from the chess-like one). Our analysis shows that on the (100) surface CH$_4$ and H adsorb preferentially on top of oxygen atoms, in agreement with previous calculations.\textsuperscript{45} (Figure 7a). On the (101) surface, H adsorbs on top of oxygen and CH$_4$ on top of metal atoms, preferentially on Pt in the case of a mixed Pd$_{x}$-Pt$_{1-x}$O bulk oxide, as also found for the thin oxide layer in the previous section (Figure 7b). The calculated adsorption energies on the different surfaces are listed in Table 3. With increasing Pt content in the oxide, a nontrivial dependence on the Pt content, similarly as in the case of the thin Pd(101)-like oxide layer considered above. Unlike the case of thin PdO-like oxide layers, where methane...
peculiar effect observed on the latter two surfaces is the spontaneous formation of a methanol molecule which remains only loosely bound to the surface via hydrogen bonds and weak metal–oxygen interactions (Figure 3a). We observe a net thermodynamic preference for methanol formation on all three surfaces considered with the largest values being obtained on Pd(111). An analysis of the energy barriers associated with the CH₃ → CH₃OH conversion reaction exceeds the scope of the present investigation. However, the possibility of a direct methane to methanol conversion on the (111) surface of transition metals has been recently put forward in a theoretical DFT study. It has to be noted, however, that the further combustion of methanol on Pd–Pt surfaces is expected to take place at the temperatures required to dissociate the C–H bonds of methane. Therefore, in general the selectivity toward methanol formation is found to decrease by increasing the overall conversion efficiency.

In the case of superficial oxide layers formed on Pd–Pt, we have found that methane adsorption is clearly endothermic both on the thin PdO(101)-like layer on (100) surfaces and on the thin α-PtO₂-like layer on (111) surfaces. Since the same was noted for oxidation of carbon monoxide, these phases may be considered as a kind of passivation layer on the metal substrate, whose formation may suddenly reduce the oxidation activity of the catalysts. This property, however, is not shared by the surfaces of bulk oxides, where both the (101) and the (100) surfaces are reactive toward methane dissociation (Table 3). This behavior can be understood by considering the charge transfer between the CH₃ molecule and the surface atoms. According to a Bader analysis, in the case of bulk PdO the CH₃ molecule donates electrons to the surface and becomes positively charged (+0.44e), while in the case of the PdO-like oxide layer CH₃ gains electrons (−0.13e). This indicates a strongly reduced electronegativity of the metal atoms of the thin oxide layer due to the presence of the underlying metal substrate, compared with the surfaces of bulk oxides. As a consequence, binding of CH₃ to the surface of the bulk oxide is favorable, in contrast to the oxide monolayer over the metal substrate. This finding is consistent with experimental observations that oxidation of Pd with formation of PdO is beneficial for methane oxidation. In comparison, bulk α-PtO₂ is inert with respect to methane dissociation in the absence of defects (see also ref 27). This again is consistent with observations that formation of bulk oxide phases is beneficial for methane oxidation on Pd, but not on Pt. Oxidation of Pt might be beneficial if the reaction conditions allow the formation of PtO-like phases (see also the discussion in 24, 27, and 28). Namely, our DFT calculations predict adsorption energies of CH₃ and H on PtO and Pt₂O₃ that are higher than those on PdO surfaces and comparable with that on oxygen adlayers covering Pd(111). This is due to the availability of undercoordinated oxygen sites on the exposed PtOₓ(100) surface to which electron acceptance from CH₃ and H is very favorable.

Concerning effects on methane adsorption resulting from Pd–Pt alloying, we note that in most of our calculations the composition of the metal substrate underneath the thin oxide layer does not show a pronounced effect on the methane adsorption energy. However, the effect of the composition of the oxide layer is evident and the reactivity decreases with increasing Pt content. An exception is the thin PdO(101)-like oxide layer on (100) surfaces, where the CH₃ group binds preferentially to the metal atom rather than to oxygen. In this case, the presence of Pt atoms does increase the reactivity since they are stronger electron acceptors, as mentioned above. However, at the same time the presence of Pt results in a decrease of the reactivity of the O atoms toward the adsorption of H. These two counteracting effects result in a nontrivial trend of the computed adsorption energies with increasing Pt content, both in the case of the thin layers (Figure 6) and of bulk PdO(101) (Table 3). The actual adsorption energies in this case depend on the specific arrangements of Pt, Pd, and O atoms close to the adsorption sites of CH₃ and H, both in the oxide layer and in the metal substrate. However, in none of the cases considered is the adsorption reaction exothermic, as discussed previously.

6. Conclusions

In conclusion, we have performed extensive calculations of the driving force for methane dissociation on clean and oxidized Pd–Pt surfaces. Both in the case of Pd and Pt, formation of stable thin layer oxide structures such as the PdO(101)-like layer on the (100) surface and the α-PtO₂-like layer on the (111) surface, leads to a reactivity loss toward the dissociative adsorption of methane. Methane adsorption is instead favored on metastable surface oxide structures such as a Pt₂O₅-like layer, whose reactivity increases with increasing Pd content. Furthermore, reactivity is recovered for exposed surfaces of bulk PdO, consistently with existing experimental results.

In the case of oxygen adlayers, we have found that the formation of a methanol molecule after methane dissociation is thermodynamically favored. This may suggest that selective conversion of methane to methanol rather than total oxidation can be achieved under pressure and temperature conditions that prevent the formation of surface oxides. However, the further combustion of the produced methanol over other sites of the Pd–Pt surface cannot be excluded, reducing the selectivity of the conversion reaction.

As a final remark, we would like to note that our investigation, being concerned with the thermodynamic driving force for the methane dissociation reaction, should be considered only as a preliminary indication about the reactivity of different surface structures. On the basis of the results presented here, more thorough calculations of the corresponding activation barriers, which can be directly related to the kinetic constants for adsorption, shall be the subject of forthcoming works.

Acknowledgment. Computational resources were provided by the Center for Information Services and High Performance Computing (ZIH) of the Technische Universität Dresden. This work was partially supported by the Deutsche Forschungsgemeinschaft under contract CI 144/1-2 and CU 44/9-2. L.C.C. acknowledges support by the Deutsche Forschungsgemeinschaft within the Emmy Noether Programme. N.S. acknowledges support by the FWF.