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# Methane Chemisorption on Oxide-Supported Pt Single Atom

Victor Fung,<sup>[a]</sup> Guoxiang Hu,<sup>[b]</sup> Franklin (Feng) Tao,<sup>[c]</sup> and De-en Jiang<sup>\*[a]</sup>

Methane chemisorption has been recently demonstrated on the rutile IrO<sub>2</sub>(110) surface. However, it remains unclear how the general requirements are for methane chemisorption or complexation with a single atom on an oxide surface. By exploring methane adsorption on Pt<sub>1</sub> substitutionally doped on many rutile-type oxides using hybrid density functional theory, we show that the occupancy of the Pt d<sub>z<sup>2</sup></sub> orbital is the key to methane chemisorption. Pt single atom on the semiconducting or wide-gap oxides such as TiO<sub>2</sub> and GeO<sub>2</sub> strongly chemisorbs

methane, because the empty Pt d<sub>z<sup>2</sup></sub> orbital is located in the gap and can effectively accept  $\sigma$ -electron donation from the methane C–H bond. In contrast, Pt single atom on metallic oxides such as IrO<sub>2</sub> and RuO<sub>2</sub> does not chemisorb methane, because the Pt d<sub>z<sup>2</sup></sub> orbital strongly mixes with the support-oxide electronic states and become more occupied, losing its ability to chemisorb methane. This study sheds further light on the impact of the interaction between a Pt single atom and the oxide support on methane adsorption.

## 1. Introduction

Methane is an abundant and inexpensive resource for fuel and chemicals.<sup>[1–3]</sup> Understanding the interaction of methane with solids is a crucial first step towards designing materials with better performance for methane storage or catalysis. As a non-polar stable molecule with a strong C–H bond, the interaction of methane with surfaces can be best described as weakly physisorbing in the vast majority of cases.<sup>[4]</sup> Methane *chemisorption*, on the other hand, while possible for certain inorganic complexes,<sup>[5]</sup> is still an emerging topic for surfaces.<sup>[6–9]</sup> Starting with the joint computational and experimental discovery of methane  $\sigma$ -complex-like adsorption on PdO(101) in 2010,<sup>[7]</sup> Asthagiri, Weaver, and their coworkers subsequently demonstrated that methane can chemisorb on other oxides such as RuO<sub>2</sub><sup>[10,11]</sup> and IrO<sub>2</sub>.<sup>[12]</sup> They further found that the chemisorbed methane dissociates at cryogenic temperatures on the IrO<sub>2</sub>(110) surface.<sup>[13]</sup> These findings suggest that methane can chemisorb on late transition-metal oxides.<sup>[6,11]</sup>

Given the importance of methane chemisorption on oxide surfaces, it would be highly desirable to understand the physicochemical principles for methane chemisorption on IrO<sub>2</sub> and to expand to a wider range of possible oxide surfaces with this property. The Ir<sup>4+</sup> ion on the rutile IrO<sub>2</sub>(110) surface is at the square pyramidal site coordinated by five O atoms and has the d<sup>6</sup> configuration. Under the crystal field, the d-orbital

splitting would result in an empty d<sub>z<sup>2</sup></sub> orbital to accept the electron donation from the C–H  $\sigma$ -bond and a filled d<sub>xy</sub> orbital for the back-bonding to the C–H antibonding orbitals.<sup>[12,14,15]</sup> Using rutile TiO<sub>2</sub>(110) as a model substrate, we have previously demonstrated from an orbital picture that single atoms such as Pt substitutionally doped on the surface (by replacing a Ti atom) fulfill both geometry and electron occupancy requirements, thereby chemisorbing methane.<sup>[14]</sup> This prediction was corroborated by density functional theory (DFT) calculations, confirming that Pt<sub>1</sub>–TiO<sub>2</sub> has the strongest methane adsorption energy among the screened 3d, 4d, and 5d transition-metal single-atom dopants,<sup>[14]</sup> matching the similar interaction found between methane and inorganic complexes.<sup>[5]</sup>

On one hand, the predicted chemisorption of methane on M<sub>1</sub>-rutile-TiO<sub>2</sub>(110) such as Pt<sub>1</sub>–TiO<sub>2</sub> remains to be tested experimentally; on the other hand, one wonders if any other oxide beyond TiO<sub>2</sub> can also serve as a support for single atoms in chemisorbing methane. This question motivated us to examine other oxides, especially the rutile type, as a support for the Pt single atom. Below we first explain our computational method and then show that indeed there are other oxides on which Pt single atom can chemisorb methane. But surprisingly, Pt<sub>1</sub>–IrO<sub>2</sub> does not. We find that the interaction of the Pt d states and the support d states is the key factor.

## Computational Details

Density functional theory calculations were performed using the Vienna Ab Initio Simulation Package (VASP).<sup>[16,17]</sup> Unless otherwise noted, the calculations were performed with the Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE06).<sup>[18]</sup> The Perdew-Burke-Ernzerhof (PBE)<sup>[19]</sup> functional was used for comparison. To focus on the chemical bonding contribution of the CH<sub>4</sub>–Pt interaction, we opted out of using van der Waals corrections in this study, so close-to-zero adsorption energy means that there is no chemisorption. Our previous study found very similar energetic trends when van der Waals corrections were added.<sup>[14]</sup> All calculations were performed with spin polarization. The projector augmented wave

[a] Dr. V. Fung, Prof. Dr. D.-e. Jiang  
Department of Chemistry  
University of California  
Riverside, California 92521, United States  
E-mail: djiang@ucr.edu

[b] Dr. G. Hu  
Center for Nanophase Materials Sciences  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37831, United States

[c] Prof. Dr. F. Tao  
Department of Chemical and Petroleum Engineering  
University of Kansas, Lawrence, KS 66045

method was used to describe the electron-core interaction.<sup>[16,20]</sup> A kinetic energy cutoff of 450 eV was used for the plane waves.

The slab model for the (110) surface of the oxide support is a  $3 \times 2$  supercell and contains a total of four layers for a total of 108 atoms, with the bottom two layers fixed in their bulk positions. This yields a slab with dimensions of  $9 \text{ \AA} \times 13 \text{ \AA}$  on average. A vacuum layer of  $15 \text{ \AA}$  was added for the (110) surface slabs along the z-direction. The methane adsorption energy ( $E_{\text{ads}}$ ) was calculated with the equation  $E_{\text{ads}} = E_{\text{surface+CH}_4} - (E_{\text{surface}} + E_{\text{CH}_4})$  where  $E_{\text{surface+CH}_4}$ ,  $E_{\text{surface}}$  and  $E_{\text{CH}_4}$  are the energies of the surface slab with a methane, the surface itself, and an isolated  $\text{CH}_4$  molecule, respectively. The energies of  $E_{\text{CH}_4}$  were computed by placing the adsorbate in a cubic cell with a  $15 \text{ \AA}$  wide vacuum in each direction. Due to the computational cost of hybrid functional calculations for geometric relaxations for a relatively large system as ours (including over 100 atoms with the large vacuum space), the Brillouin zone was sampled at the  $\Gamma$ -point only for adsorption geometry and energy calculations. Comparison of adsorption energies using the  $\Gamma$ -only and the  $3 \times 2 \times 1$  Monkhorst-Pack<sup>[21]</sup> k-mesh showed close agreement. Charge densities and isosurfaces were visualized using the VESTA program.<sup>[22]</sup>

## 2. Results and Discussion

### 2.1. Adsorption on Different Rutile Substrates

Table 1 shows methane adsorption energies on the Pt single atom substitutionally doped on the (110) surfaces of different rutile substrates. These include Ti, V, Cr, Mn, Ru, Os, Ir, Ge, Sn, and Pb, which form stable rutile oxides.<sup>[23]</sup> Interestingly, metallic substrates (Ru, Os, Ir) have no chemical interaction with methane at all. Meanwhile, substrates with the largest band gaps have the strongest methane adsorption energies (Ge, Ti, Sn) and those with intermediate gaps fall somewhere in the middle (V, Mn, Pb). Cr, being a unique and well-known half-metal, allows for moderate  $\text{CH}_4$ -Pt adsorption energy. The clear correlation between the band gap of the rutile  $\text{MO}_2$  support and the methane adsorption energy on  $\text{Pt}_1\text{-MO}_2$  (Figure 1) strongly suggests that the interaction between the d states of the Pt single atom and the conduction band of the support is the key factor in dictating methane chemisorption. To reveal such interactions, below we compare in detail  $\text{IrO}_2(110)$ ,  $\text{Pt}_1\text{-IrO}_2(110)$ , and  $\text{Pt}_1\text{-TiO}_2(110)$  for methane adsorption, because the  $\text{IrO}_2(110)$  surface has already been both computationally

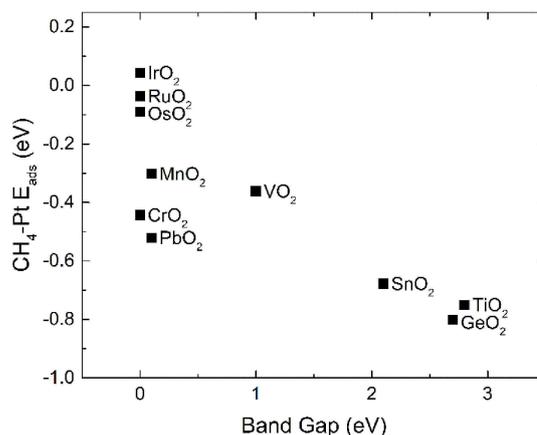


Figure 1. Methane adsorption energy on  $\text{Pt}_1\text{-MO}_2(110)$  versus the band gap of the rutile  $\text{MO}_2$  support.

and experimentally shown to chemisorb methane,<sup>[12–15]</sup> but Table 1 surprisingly shows that the Pt single atom on  $\text{IrO}_2(110)$  does not chemisorb methane while the Pt single atom on  $\text{TiO}_2(110)$  does chemisorb methane.

### 2.2. Comparison of $\text{IrO}_2(110)$ , $\text{Pt}_1\text{-IrO}_2(110)$ , and $\text{Pt}_1\text{-TiO}_2(110)$ for Methane Adsorption

To understand why methane does not chemisorb on  $\text{Pt}_1\text{-IrO}_2(110)$ , here we first compare  $\text{IrO}_2(110)$  and  $\text{Pt}_1\text{-IrO}_2(110)$  for methane adsorption (Figure 2). Indeed, we confirmed the previous studies<sup>[12–14]</sup> that methane chemisorbs on  $\text{IrO}_2(110)$  with an energy of  $-0.60 \text{ eV}$  (Figure 2a,b). One would expect that by replacing a surface Ir atom with Pt would result in similar if not stronger adsorption energy, but methane was found to be non-interacting with the Pt atom and sits high above the surface on  $\text{Pt}_1\text{-IrO}_2(110)$  (Figure 2c, d).

For a  $\text{Pt}^{4+}$  ion under the square-pyramidal crystal field, the empty  $d_z^2$  orbital is key to methane complexation by accepting electrons from C–H  $\sigma$ -bond (Figure 3). This orbital picture has

**Table 1.** Methane adsorption energy on Pt single atom substitutionally doped on the (110) surface of a rutile oxide ( $\text{Pt-MO}_2$ ), band gap of the bulk rutile  $\text{MO}_2$ , and partial atomic charge of Pt on  $\text{MO}_2$ .

Substrate	$E_{\text{ads}}$ [eV]	Band gap [eV]	Pt partial charge [ $ e $ ]
Pt–GeO <sub>2</sub>	–0.80	2.7	1.61
Pt–TiO <sub>2</sub>	–0.75	2.8	1.59
Pt–SnO <sub>2</sub>	–0.68	2.1	1.59
Pt–PbO <sub>2</sub>	–0.52	0.1	1.63
Pt–CrO <sub>2</sub>	–0.44	half-metal	1.63
Pt–VO <sub>2</sub>	–0.36	1	1.55
Pt–MnO <sub>2</sub>	–0.30	0.1	1.63
Pt–OsO <sub>2</sub>	–0.09	metallic	1.36
Pt–RuO <sub>2</sub>	–0.04	metallic	1.42
Pt–IrO <sub>2</sub>	0.00	metallic	1.36

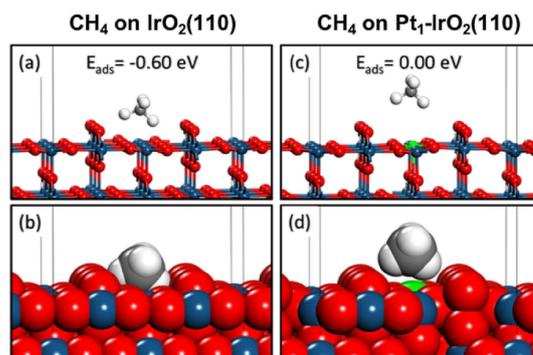
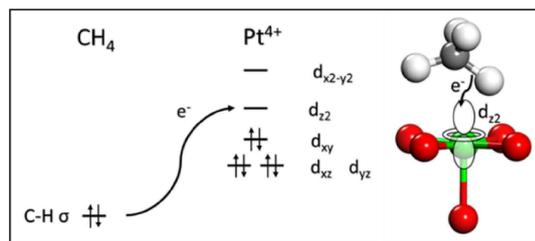


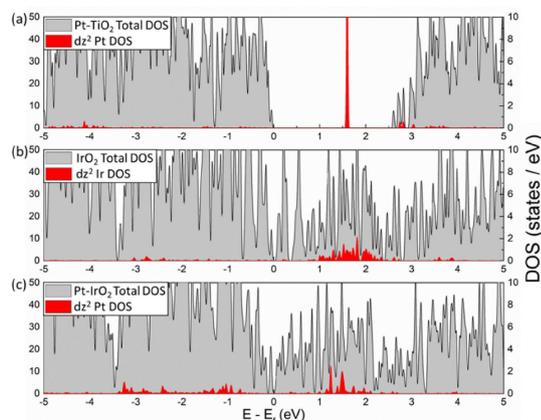
Figure 2. Adsorption energies and geometries of  $\text{CH}_4$  on  $\text{IrO}_2(110)$  (a, b) and on  $\text{Pt}_1\text{-IrO}_2(110)$  (c, d). Color code: Pt, green; Ir, blue; O, red. On  $\text{Pt}_1\text{-IrO}_2(110)$ , Pt single atom replaces a surface Ir atom.



**Figure 3.** Schematic of methane complexation via C–H  $\sigma$ -bond donation into the  $d_{z^2}$  orbital on a  $Pt^{4+}$  (green) single atom in a square-pyramidal crystal field. Pt, green; O, red.

been confirmed to be the case for Pt<sub>1</sub> on rutile TiO<sub>2</sub>(110),<sup>[14]</sup> but might be perturbed by the interaction of Pt d states with those of the IrO<sub>2</sub> support. Table 1 already suggests that Pt<sub>1</sub>–IrO<sub>2</sub>(110) is metallic. To understand this deeper, we examined the changes to the  $d_{z^2}$  orbital in the electronic density of states for IrO<sub>2</sub>(110), Pt<sub>1</sub>–IrO<sub>2</sub>(110), and Pt<sub>1</sub>–TiO<sub>2</sub>(110) (Figure 4). One can see that the empty Pt  $d_{z^2}$  states are located right in the gap of TiO<sub>2</sub> (Figure 4a), hence being ideal for chemisorbing methane via the complexation model in Figure 3. Although IrO<sub>2</sub>(110) is also as metallic as is Pt<sub>1</sub>–IrO<sub>2</sub>(110), its  $d_{z^2}$  states are mainly above the Fermi level (that is, empty), albeit in a less localized fashion (Figure 4b); this may explain why it still chemisorbs methane, though not as strong as does Pt<sub>1</sub>–TiO<sub>2</sub>(110). In contrast, the  $d_{z^2}$  states of Pt in Pt<sub>1</sub>–IrO<sub>2</sub>(110) hybridize more strongly with the states of IrO<sub>2</sub>(110) (Figure 4c), leading to a large portion of Pt  $d_{z^2}$  states being occupied and pushed below the Fermi level. The disrupted  $d_{z^2}$  states of Pt by IrO<sub>2</sub> prevents methane chemisorption.

In our earlier paper,<sup>14</sup> the oxide substrate was fixed (rutile TiO<sub>2</sub>) and the single atom varied, so the filling of the single-atom  $d_{xy}$  states varied and also played a role in methane adsorption via back donation to methane  $\sigma^*$ . In the present work, we fixed the single atom (Pt) and varied the oxide support. In this case, the single-atom  $d_{xy}$  states are fully



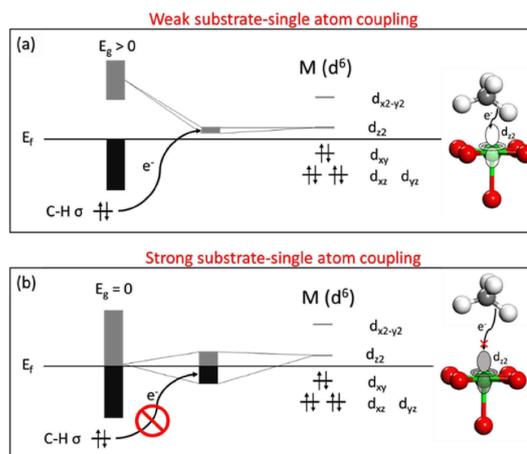
**Figure 4.** Total and local density of states (DOS): a) Pt<sub>1</sub>–TiO<sub>2</sub>(110); b) IrO<sub>2</sub>(110); c) Pt<sub>1</sub>–IrO<sub>2</sub>(110). Total DOS (gray), left y-axis; projected  $d_{z^2}$  DOS (red), right y-axis. Fermi level is at energy zero.

occupied and their contribution to methane chemisorption remains approximately constant in all cases.

### 2.3. Revised Model for Methane Chemisorption

Table 1 and Figure 4 shed new light to methane chemisorption beyond the simple picture in Figure 3 based on a Pt single atom with its first coordination shell. One also has to include the strength of coupling between the single-atom d states and those of the support beyond the first coordination shell. In the situation where the support band gap is sufficiently large (Figure 5a), the  $d_{z^2}$  orbitals of the single atom lie between the valence and conduction bands, and the coupling between the support states in the conduction band with the single atom d orbitals is weak. Consequently, the  $d_{z^2}$  orbital remains localized above the Fermi level, allowing it to accept electrons from the C–H bond (as seen in Pt<sub>1</sub>–TiO<sub>2</sub>(110) in Figure 4a) and leading to methane chemisorption. In the situation of strong coupling or hybridization and a delocalization of the  $d_{z^2}$  orbital of the Pt single atom with the metallic substrate (Figure 5b), many of the  $d_{z^2}$  states are occupied by the support electrons, leading to no methane chemisorption.

Figure 1 also shows that MO<sub>2</sub> with close-to-zero band gaps can have very different methane adsorption energies on the Pt<sub>1</sub>–MO<sub>2</sub>(110). The MO<sub>2</sub> band gap serves as an approximate descriptor of the oxide-support/single-atom electronic coupling. However, the population of d states near the Fermi level of MO<sub>2</sub> which overlap with the  $d_{z^2}$  states of the Pt single atom can still differ sizably for MO<sub>2</sub> of similar band gaps. For example, PbO<sub>2</sub>, despite its close-to-zero band gap, has only a few states in the energy region of Pt  $d_{z^2}$ , and so the coupling is weak and methane adsorption remains strong. Factors such as the strength of the M–O bond, the spin states on the M centers, and the ionicity vs covalency of the M–O bond can all contribute to the variation of the mixing. Further analysis of



**Figure 5.** Two scenarios of methane adsorption on the Pt single atom on an oxide support as in Pt<sub>1</sub>–MO<sub>2</sub>: a) weak coupling of Pt  $d_{z^2}$  and MO<sub>2</sub> (gapped) states, leading to methane chemisorption; b) strong coupling of Pt  $d_{z^2}$  and MO<sub>2</sub> (metallic) states, leading to weak interaction with methane.

such involved and subtle interaction in greater detail is warranted.

Recent theoretical studies have speculated the chemical properties of a single atom on a substrate can be determined primarily by the local properties of the single atom and the neighboring coordinating atoms.<sup>[24]</sup> By using these local properties such as the atom electronegativity, coordination number, and other parameters, predictions can be made on the basis of linear relationships<sup>[24–26]</sup> or via more complex machine-learned regression models.<sup>[27–29]</sup> Here we reveal that non-local factors such as the interaction between empty single-atom d states and the conduction band of the support can also impact the single-atom's ability to adsorb molecules and hence its catalytic property. Our work shows that the electronic or chemical properties of the single atom may also arise from the tuning of the support band gap.

The surface-doped systems can be further extended beyond a single atom to two or three ions on an oxide support. For example, Hensen and coworkers have predicted from DFT that substitution of  $Ce^{4+}$  on  $CeO_2(111)$  by two  $Pd^{2+}$  ions also leads to methane chemisorption on one of the two Pd ions.<sup>[30]</sup> Rodriguez, Illas, and their coworkers found from a joint computational and experimental study found that small Ni Clusters (4 to 10 atoms) supported on  $TiC(001)$  can chemisorb methane which is subsequently activated at room temperature.<sup>[31]</sup> These recent advances indicate that methane chemisorption could be a new area of exploration for surface chemistry and catalysis in low-temperature activation of methane.

### 3. Conclusions

Using hybrid density functional theory, we have explored methane adsorption on Pt single atom substitutionally doped on many different oxides of the rutile type to understand how the general requirements are for methane chemisorption. We found that Pt single atom on the gapped oxides strongly chemisorbs methane, while Pt single atom on metallic oxides does not chemisorb methane. Comparison of methane adsorption on  $Pt_1-TiO_2(110)$ ,  $Pt_1-IrO_2(110)$ , and  $IrO_2(110)$  as well as analysis of the local density of states showed that the key is the occupancy of the Pt  $d_z^2$  orbital. The empty and isolated Pt  $d_z^2$  orbital located in the band gap of a semiconducting or insulating oxide support can effectively accept  $\sigma$ -electron donation from the methane C–H bond, while the Pt  $d_z^2$  orbital strongly couples with the metallic oxide support's electronic states and become more dispersed and occupied, losing ability to complex methane. Our work may be helpful in designing single-atom catalysts for methane activation.

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### Conflict of Interest

The authors declare no conflict of interest.

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