



Nominate a Worthy Chemist Chemistry Europe Award

Subject:

chemistry for sustainability,
energy, materials,
environment

Consists of:

prize money amounting to
EUR 10,000, certificate

Deadline:

November 1, 2022

▶ [Click here for more
info & nomination](#)

Methane Chemisorption on Oxide-Supported Pt Single Atom

Victor Fung,^[a] Guoxiang Hu,^[b] Franklin (Feng) Tao,^[c] and De-en Jiang^{*[a]}

Methane chemisorption has been recently demonstrated on the rutile IrO₂(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 Pt₁ substitutionally doped on many rutile-type oxides using hybrid density functional theory, we show that the occupancy of the Pt d_{z²} orbital is the key to methane chemisorption. Pt single atom on the semiconducting or wide-gap oxides such as TiO₂ and GeO₂ strongly chemisorbs

methane, because the empty Pt d_{z²} orbital is located in the gap and can effectively accept σ -electron donation from the methane C–H bond. In contrast, Pt single atom on metallic oxides such as IrO₂ and RuO₂ does not chemisorb methane, because the Pt d_{z²} 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.^[1–3] 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.^[4] Methane *chemisorption*, on the other hand, while possible for certain inorganic complexes,^[5] is still an emerging topic for surfaces.^[6–9] Starting with the joint computational and experimental discovery of methane σ -complex-like adsorption on PdO(101) in 2010,^[7] Asthagiri, Weaver, and their coworkers subsequently demonstrated that methane can chemisorb on other oxides such as RuO₂^[10,11] and IrO₂.^[12] They further found that the chemisorbed methane dissociates at cryogenic temperatures on the IrO₂(110) surface.^[13] These findings suggest that methane can chemisorb on late transition-metal oxides.^[6,11]

Given the importance of methane chemisorption on oxide surfaces, it would be highly desirable to understand the physicochemical principles for methane chemisorption on IrO₂ and to expand to a wider range of possible oxide surfaces with this property. The Ir⁴⁺ ion on the rutile IrO₂(110) surface is at the square pyramidal site coordinated by five O atoms and has the d⁶ configuration. Under the crystal field, the d-orbital

splitting would result in an empty d_{z²} orbital to accept the electron donation from the C–H σ -bond and a filled d_{xy} orbital for the back-bonding to the C–H antibonding orbitals.^[12,14,15] Using rutile TiO₂(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.^[14] This prediction was corroborated by density functional theory (DFT) calculations, confirming that Pt₁–TiO₂ has the strongest methane adsorption energy among the screened 3d, 4d, and 5d transition-metal single-atom dopants,^[14] matching the similar interaction found between methane and inorganic complexes.^[5]

On one hand, the predicted chemisorption of methane on M₁-rutile-TiO₂(110) such as Pt₁–TiO₂ remains to be tested experimentally; on the other hand, one wonders if any other oxide beyond TiO₂ 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, Pt₁–IrO₂ 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).^[16,17] Unless otherwise noted, the calculations were performed with the Heyd-Scuseria-Ernzerhof screened hybrid functional (HSE06).^[18] The Perdew-Burke-Ernzerhof (PBE)^[19] functional was used for comparison. To focus on the chemical bonding contribution of the CH₄–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.^[14] 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.^[16,20] 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 3×2 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 \AA was added for the (110) surface slabs along the z-direction. The methane adsorption energy (E_{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_{surface} and E_{CH_4} are the energies of the surface slab with a methane, the surface itself, and an isolated CH_4 molecule, respectively. The energies of E_{CH_4} were computed by placing the adsorbate in a cubic cell with a 15 \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 Γ -point only for adsorption geometry and energy calculations. Comparison of adsorption energies using the Γ -only and the $3 \times 2 \times 1$ Monkhorst-Pack^[21] k-mesh showed close agreement. Charge densities and isosurfaces were visualized using the VESTA program.^[22]

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.^[23] 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 CH_4 -Pt adsorption energy. The clear correlation between the band gap of the rutile 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 computa-

Table 1. Methane adsorption energy on Pt single atom substitutionally doped on the (110) surface of a rutile oxide (Pt-MO_2), band gap of the bulk rutile MO_2 , and partial atomic charge of Pt on MO_2 .

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

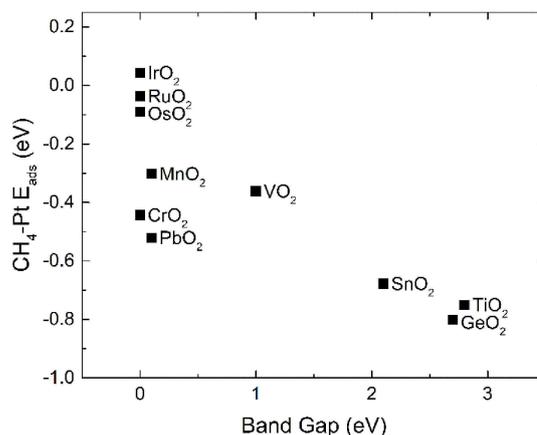


Figure 1. Methane adsorption energy on $\text{Pt}_1\text{-MO}_2(110)$ versus the band gap of the rutile MO_2 support.

tionally and experimentally shown to chemisorb methane,^[12-15] 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^[12-14] that methane chemisorbs on $\text{IrO}_2(110)$ with an energy of -0.60 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 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 σ -bond (Figure 3). This orbital picture has

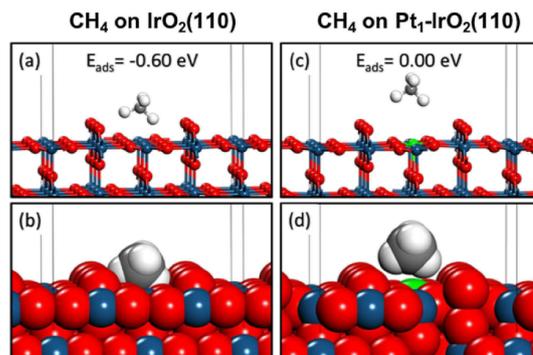


Figure 2. Adsorption energies and geometries of CH_4 on $\text{IrO}_2(110)$ (a, b) and on $\text{Pt}_1\text{-IrO}_2(110)$ (c, d). Color code: Pt, green; Ir, blue; O, red. On $\text{Pt}_1\text{-IrO}_2(110)$, Pt single atom replaces a surface Ir atom.

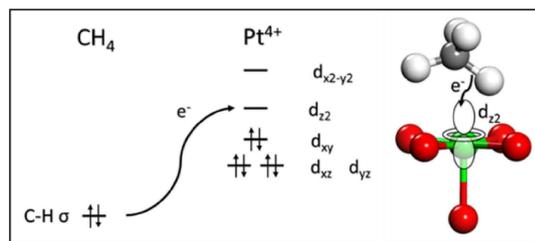


Figure 3. Schematic of methane complexation via C–H σ -bond donation into the d_{z^2} orbital on a Pt^{4+} (green) single atom in a square-pyramidal crystal field. Pt, green; O, red.

been confirmed to be the case for Pt₁ on rutile TiO₂(110),^[14] but might be perturbed by the interaction of Pt d states with those of the IrO₂ support. Table 1 already suggests that Pt₁–IrO₂(110) is metallic. To understand this deeper, we examined the changes to the d_{z^2} orbital in the electronic density of states for IrO₂(110), Pt₁–IrO₂(110), and Pt₁–TiO₂(110) (Figure 4). One can see that the empty Pt d_{z^2} states are located right in the gap of TiO₂ (Figure 4a), hence being ideal for chemisorbing methane via the complexation model in Figure 3. Although IrO₂(110) is also as metallic as is Pt₁–IrO₂(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 Pt₁–TiO₂(110). In contrast, the d_{z^2} states of Pt in Pt₁–IrO₂(110) hybridize more strongly with the states of IrO₂(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 IrO₂ prevents methane chemisorption.

In our earlier paper,¹⁴ the oxide substrate was fixed (rutile TiO₂) 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 σ^* . 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

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 Pt₁–TiO₂(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 MO₂ with close-to-zero band gaps can have very different methane adsorption energies on the Pt₁–MO₂(110). The MO₂ 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 MO₂ which overlap with the d_{z^2} states of the Pt single atom can still differ sizably for MO₂ of similar band gaps. For example, PbO₂, 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

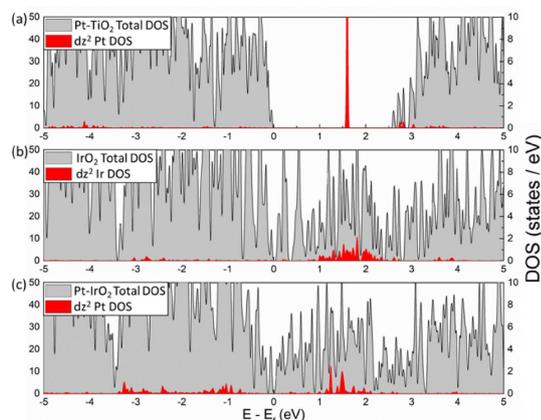


Figure 4. Total and local density of states (DOS): a) Pt₁–TiO₂(110); b) IrO₂(110); c) Pt₁–IrO₂(110). Total DOS (gray), left y-axis; projected d_{z^2} DOS (red), right y-axis. Fermi level is at energy zero.

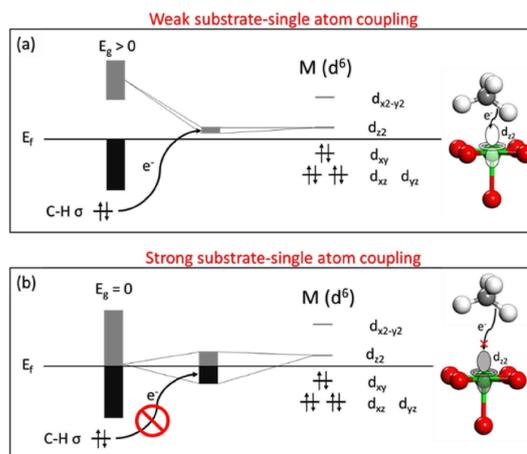


Figure 5. Two scenarios of methane adsorption on the Pt single atom on an oxide support as in Pt₁–MO₂: a) weak coupling of Pt d_{z^2} and MO₂ (gapped) states, leading to methane chemisorption; b) strong coupling of Pt d_{z^2} and MO₂ (metallic) states, leading to weak interaction with methane.

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.^[24] 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^[24–26] or via more complex machine-learned regression models.^[27–29] 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.^[30] 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.^[31] 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 σ -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.

Acknowledgements

This research is sponsored by Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of

Science, U.S. Department of Energy, under Grant No. DE-SC0014561. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: density functional theory · electronic structure · metal oxides · methane adsorption · single atom

- [1] R. Horn, R. Schlögl, *Catal. Lett.* **2015**, *145*, 23–39.
- [2] M. Ravi, M. Ranocchiari, J. A. van Bokhoven, *Angew. Chem. Int. Ed.* **2017**, *56*, 16464–16483; *Angew. Chem.* **2017**, *129*, 16684–16704.
- [3] P. Schwach, X. Pan, X. Bao, *Chem. Rev.* **2017**, *117*, 8497–8520.
- [4] A. A. Latimer, A. R. Kulkarni, H. Aljama, J. H. Montoya, J. S. Yoo, C. Tsai, F. Abild-Pedersen, F. Studt, J. K. Nørskov, *Nat. Mater.* **2017**, *16*, 225–229.
- [5] J. Y. Saillard, R. Hoffmann, *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.
- [6] J. F. Weaver, *Chem. Rev.* **2013**, *113*, 4164–4215.
- [7] J. F. Weaver, C. Hakanoglu, J. M. Hawkins, A. Asthagiri, *J. Chem. Phys.* **2010**, *132*, 024709.
- [8] P. G. Lustemberg, P. J. Ramirez, Z. Liu, R. A. Gutierrez, D. G. Grinter, J. Carrasco, S. D. Senanayake, J. A. Rodriguez, M. V. Ganduglia-Pirovano, *ACS Catal.* **2016**, *6*, 8184–8191.
- [9] A. Antony, A. Asthagiri, J. F. Weaver, *J. Chem. Phys.* **2013**, *139*, 104702.
- [10] T. Li, M. Kim, R. Rai, Z. Liang, A. Asthagiri, J. F. Weaver, *Phys. Chem. Chem. Phys.* **2016**, *18*, 22647–22660.
- [11] J. F. Weaver, C. Hakanoglu, A. Antony, A. Asthagiri, *Chem. Soc. Rev.* **2014**, *43*, 7536–7547.
- [12] C.-C. Wang, S. S. Siao, J.-C. Jiang, *J. Phys. Chem. C* **2012**, *116*, 6367–6370.
- [13] Z. Liang, T. Li, M. Kim, A. Asthagiri, J. F. Weaver, *Science* **2017**, *356*, 299–303.
- [14] V. Fung, F. Tao, D.-e. Jiang, *Phys. Chem. Chem. Phys.* **2018**, *20*, 22909–22914.
- [15] Y. Tsuji, K. Yoshizawa, *J. Phys. Chem. C* **2018**, *122*, 15359–15381.
- [16] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- [17] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186.
- [18] A. V. Krutau, O. A. Vydrov, A. F. Izmaylov, G. E. Scuseria, *J. Chem. Phys.* **2006**, *125*, 224106.
- [19] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [20] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953–17979.
- [21] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188–5192.
- [22] K. Momma, F. Izumi, *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276.
- [23] Z. Hiroi, *Prog. Solid State Chem.* **2015**, *43*, 47–69.
- [24] H. Xu, D. Cheng, D. Cao, X. C. Zeng, *Nat. Catal.* **2018**, *1*, 339–348.
- [25] V. Fung, F. F. Tao, D. E. Jiang, *J. Phys. Chem. Lett.* **2017**, *8*, 2206–2211.
- [26] F. Calle-Vallejo, D. Loffreda, M. T. Koper, P. Sautet, *Nat. Chem.* **2015**, *7*, 403–410.
- [27] Z. Li, X. Ma, H. Xin, *Catal. Today* **2017**, *280*, 232–238.
- [28] A. Nandy, C. Duan, J. P. Janet, S. Gugler, H. J. Kulik, *Ind. Eng. Chem. Res.* **2018**, *57*, 13973–13986.
- [29] J. P. Janet, L. Chan, H. J. Kulik, *J. Phys. Chem. Lett.* **2018**, *9*, 1064–1071.
- [30] Y.-Q. Su, J.-X. Liu, I. A. W. Filot, L. Zhang, E. J. M. Hensen, *ACS Catal.* **2018**, *8*, 6552–6559.
- [31] H. Prats, R. A. Gutiérrez, J. J. Piñero, F. Viñes, S. T. Bromley, P. J. Ramirez, J. A. Rodriguez, F. Illas, *J. Am. Chem. Soc.* **2019**, *141*, 5303–5313.

Manuscript received: May 16, 2019

Revised manuscript received: July 1, 2019

Accepted manuscript online: July 16, 2019

Version of record online: July 29, 2019