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Perovskite-supported Pt single atom for methane activation

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Abstract: ABO₃ perovskites are increasingly being explored as catalysts, but it is unclear how they behave as supports for single atoms and how the subsequent single-atom catalysts can be employed for important reactions such as methane activation. Here we examine the stability of Pt single atom (Pt₁) on the commonly exposed (100) surfaces of SrBO₃ perovskites (B = 3d transition metals) and its methane-adsorption property by first principles density functional theory. We find that the stability and charge state of Pt₁ on the SrBO₃(100) surfaces are termination-sensitive. Due to polar compensation, Pt₁ is negatively charged on the A termination but positively charged on the B termination. This charge state greatly impacts methane adsorption: negatively charged Pt₁ on the A-termination chemisorbs methane (in some cases, dissociatively), but positively charged Pt₁ on the B-termination adsorbs methane physically. Analysis of density of states of the negatively charged Pt₁ reveals that its sp states are key to methane chemisorption and C-H activation. Our work shows that polar compensation on the perovskite surfaces can be used to tune the charge state of a single atom for methane chemisorption and C-H activation.

1. Introduction

Single-atom catalysts (SACs) are a prominent class of heterogeneous catalysts due to their unique activity and atomic efficiency.¹⁻³ In most cases, noble-metal atoms are atomically dispersed on an oxide support, such as Pt₁ on CeO₂.⁴⁻⁶ SACs also include surface-dispersed mononuclear organometallic catalysts,⁷ micropore-confined single atom catalyst,⁸ and atomically dispersed metal atoms on a metal surface⁹ or a nanoparticle.¹⁰ Moreover, SACs have also been increasingly used for electrocatalysis¹¹ and organic chemistry.¹²

The most studied oxide supports for SACS are binary oxides including FeO_x, Al₂O₃, TiO₂ and CeO₂.^{4, 13-15} A great deal of efforts have been devoted to understanding the interaction between the single atoms and the oxide supports, to avoid sintering of the single atoms into larger particles.¹⁶⁻¹⁹ On the other hand, more complex oxides have been explored as supports to tune the interactions.²⁰⁻²²

Perovskites (ABO₃) are the most common type of ternary oxides.^{23, 24} The great variability in choices of A and B serves as an ideal test ground for probing their interactions with a single atom.^{25, 26} Recently, there has been great interest in using perovskites for catalysis and understanding the structure-activity-selectivity relationships for various facets and terminations of perovskites.²⁷⁻²⁹

CH₄ activation and conversion on SACs have attracted interest lately.³⁰⁻³² For example, it was reported that Pt/Cu(111) single-atom alloys can activate C-H bond while efficiently preventing coke formation.³³ And density functional theory (DFT) predicted that single atoms such as Ir₁ and Pt₁ substitutionally doped on the (110) surface of rutile oxides can chemisorb methane, leading to a facile C-H activation.^{34, 35}

From the perspective of CH₄ adsorption and activation on SACs, we think that a great opportunity awaits in exploring how the single atoms interact with perovskites and how the resulting SACs adsorb and activate methane. Hence, herein we use Pt₁ as a prototypical single atom and Sr-based perovskite (SrBO₃) as the support, to examine from first principles the effect of varying B ions on the interaction between Pt₁ and SrBO₃ and the subsequent impact on CH₄ adsorption. Below we first describe the DFT method employed.

2. Computational method

The Vienna Ab Initio Simulation Package (VASP) was used to perform spin-polarized density functional theory calculations in the generalized-gradient approximation (GGA) with Perdew-

Burke-Ernzerhof (PBE) functional.³⁶⁻³⁸ (Here we did not employ any dispersion correction, so that we could clearly distinguish chemisorption and physisorption of methane, a strategy employed previously;³⁴ including the dispersion correction did not change our conclusions.) Electronic wave functions were expanded in plane waves with a cutoff energy of 450 eV and the core electrons with the nucleus were approximated by the projector augmented-wave (PAW) method.³⁹ The convergence criteria were 10^{-4} eV and 0.01 eV/Å for energy and force, respectively.

As in previously pursued strategies,^{25,26,29} we focus on the two main terminations of the SrBO₃ (100) surface, one of the most stable and commonly exposed surfaces. The (100) facet of SrBO₃ in either A- or B-termination was modelled as a 2×2 supercell with a vacuum space of 15 Å along *z* direction. The surface slabs have six layers, with the bottom four layers fixed in their bulk positions, and were sampled by a 3×3×1 k-point mesh in the Monkhorst-Pack Scheme.⁴⁰ The interaction of Pt₁ with the surface was determined by the Pt₁ adsorption energy

$$E_{ads-Pt1} = E_{Pt1-ABO_3} - E_{Pt1} - E_{ABO_3},$$

where $E_{Pt1-ABO_3}$, E_{Pt1} and E_{ABO_3} represent energies of ABO₃-supported Pt₁ single-atom catalyst, a Pt atom in the gas phase, and the ABO₃ surface, respectively. The same approach was used to compute methane adsorption energy on ABO₃-supported Pt₁ single-atom catalysts. O vacancy formation energy (E_{O-VFE}) was calculated with the following equation:

$$E_{O-VFE} = E_{defect-ABO_3} - \frac{1}{2}E_{O_2} - E_{ABO_3},$$

where $E_{defect-ABO_3}$ and E_{O_2} represent the calculated energies of ABO₃ surface with an O vacancy and a gas phase O₂ molecule, respectively.

The charge-density difference was calculated with the following equation:

$$\Delta\rho = \rho_{Pt1-SrTiO_3} - \rho_{SrTiO_3} - \rho_{Pt1},$$

where $\rho_{Pt1-SrTiO_3}$, ρ_{SrTiO_3} and ρ_{Pt1} represent the calculated electron density of Pt₁-SrTiO₃, SrTiO₃, and Pt₁, respectively.

3. Results and discussion

Sr-based perovskites have been widely studied both from experiment and theory,²⁵ so we chose Sr²⁺ as the A cation in this work. We vary the B cation in SrBO₃ in 3d transition metals (B = Ti, V, Cr, Mn, Fe, Co, Ni, Cu). (100) facets are usually the most stable facets of perovskite (ABO₃).⁴¹

⁴² In this SrBO₃ (100) system, we first study the adsorption of Pt single atom on SrBO₃ (100) surface to evaluate the interaction between Pt₁ and perovskite oxide.

3.1. Adsorption of Pt single atom on SrBO₃ (100)

The SrBO₃ (100) facet can have either the A- or B-termination. The A-termination exposes the SrO layer (Fig. 1a) while the B-termination exposes the BO₂ layer (Fig. 1b). On A-termination, we found that Pt₁ prefers to locate at the top of a surface oxygen atom (Fig. 1c), while on B-termination, Pt₁ is most stable at the hollow site and coordinated by four O (Fig. 1d).

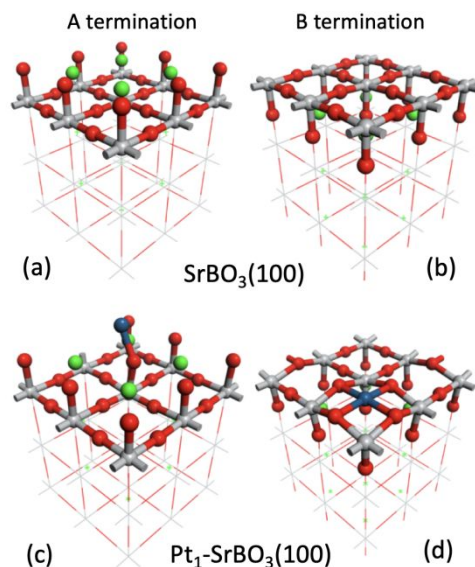


Fig. 1. Typical structures of SrBO₃(100) and Pt₁-SrBO₃(100): (a) SrBO₃(100) A-termination; (b) SrBO₃(100) B-termination; (c) Pt₁ on SrBO₃(100) A-termination; (d) Pt₁ on SrBO₃(100) B-termination. Color mode: O, red; Sr, green; B, gray; Pt, blue.

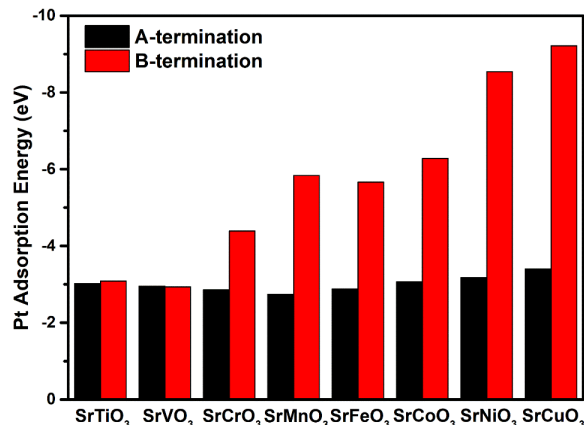


Fig. 2. Adsorption energies of Pt single atom on SrBO₃(100) surfaces, for B = Ti, V, Cr, Mn, Fe, Co, Ni, Cu.

The Pt₁ adsorption energies (relative to a gas-phase Pt atom) on the two SrBO₃(100) terminations with varying B are plotted in Fig. 2. Interestingly, one can see that on A-termination, Pt₁ adsorption energy is relatively constant, fluctuating slightly around -3.0 eV, with varying B cations. In contrast, the Pt₁ adsorption energy on the B-termination increases in magnitude from -3.09 eV on SrTiO₃(100) to -9.22 eV on SrCuO₃(100). Apparently, the changing B ion has a much greater impact for Pt₁ interaction on the B-termination than on the A-termination. This is consistent with the difference in the Pt₁ adsorption geometry on the two terminations (Fig. 1c, d): the formation of 4 Pt-O bonds in the B-termination suggests that the Pt adsorption on the B termination will be much more impacted by the B ion. Below we further examine this difference by correlating with descriptors that vary with the B ion.

3.2. Correlation with the vacancy formation energy

Commonly used descriptors for oxides and perovskites in terms of their surface reactivity include O-vacancy formation energy (O-VFE), H adsorption energy, and surface-oxygen Bader charges.^{19, 43, 44} To understand the trend of Pt adsorption on the B-termination (Fig. 2), we calculated surface O-VFE of the SrBO₃(100) B terminations. As one can see from Fig. 3, the O-VFE correlates well with Pt adsorption energy. In other words, as B changes from Ti to Cu, the surface becomes more reducible and the surface O becomes more reactive, leading to stronger interaction of Pt on the surface.

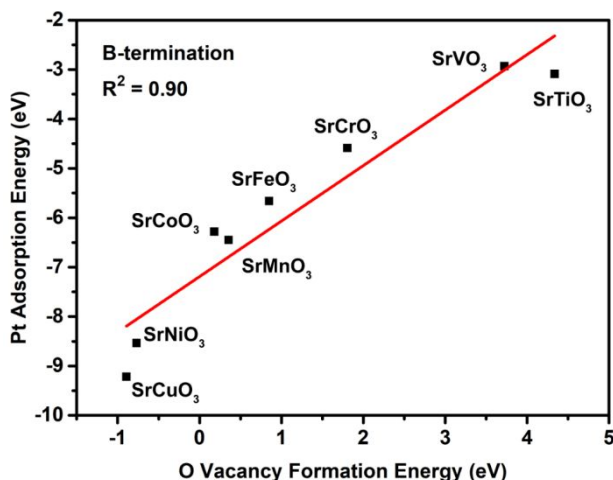


Fig. 3. Correlation between Pt single atom adsorption energy and surface O vacancy formation energy on SrBO₃(100) B termination. The red line represents the best linear fit.

3.3 Charge distribution on Pt₁ atom supported by SrBO₃ (100)

Since charge state is an important indicator of the reactivity of a single atom site, we have examined the Bader charge of the Pt single atom on SrBO₃ (100) in preparation for examining their methane-adsorbing ability.⁴⁵ Interestingly, Fig. 4 shows that Pt atoms are negatively charged on the A-termination but positively charged on the B-termination (Bader charges of other surface atoms are shown in Table 1 after/before Pt adsorption). When B cation changes from Ti to Cu, the Pt charge increases: becoming more positive on the B termination and less negative on the A termination.

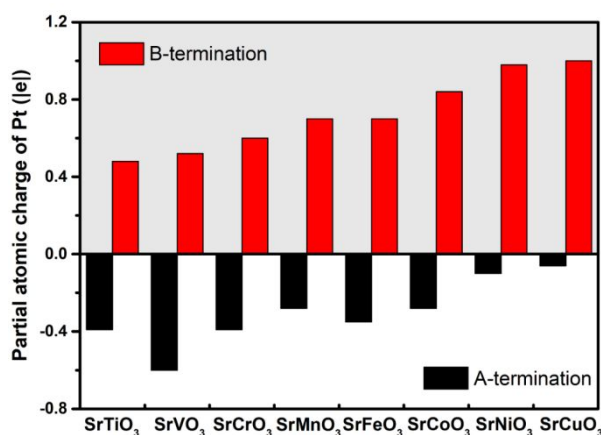


Fig. 4. Partial atomic charge of Pt single atom on SrBO₃(100).

Table 1. Bader charges (in |e|) of Pt₁, O atoms bound to Pt₁, and nearest A and B ions to Pt₁ on the surface after/before Pt adsorption on the A- and B-terminations of SrBO₃(100).

B in SrBO ₃	A-termination			B-termination		
	Pt ₁	O	Sr	Pt ₁	O	B
Ti	-0.39/0.00	-1.04/-1.27	1.57/1.58	0.48/0.00	-1.01/-1.11	1.85/1.91
V	-0.60/0.00	-1.02/-1.25	1.57/1.57	0.52/0.00	-1.00/-1.05	1.73/1.77
Cr	-0.39/0.00	-1.02/-1.21	1.56/1.57	0.60/0.00	-0.96/-0.99	1.66/1.71
Mn	-0.28/0.00	-0.95/-1.18	1.56/1.57	0.70/0.00	-0.91/-0.95	1.60/1.65
Fe	-0.35/0.00	-0.97/-1.30	1.57/1.62	0.70/0.00	-0.92/-0.94	1.50/1.53
Co	-0.28/0.00	-1.33/-1.16	1.37/1.56	0.84/0.00	-0.86/-0.83	1.32/1.37
Ni	-0.10/0.00	-0.81/-1.10	1.57/1.57	0.98/0.00	-0.79/-0.78	1.19/1.24
Cu	-0.06/0.00	-0.78/-1.10	1.57/1.57	1.00/0.00	-0.78/-0.77	1.15/1.17

To pinpoint how the electron transfer between Pt single atom and the surface, we use SrTiO₃ (100) as an example and analyzed the charge-density difference after supporting the Pt single atom.

As one can see from Fig. 5, Pt gains electron from the O atom underneath and becomes negatively charged on the A-termination (Fig. 5a), but on the B-termination, the charge transfer is more complex (Fig. 5b) and overall Pt₁ loses some electron density while Ti gains.

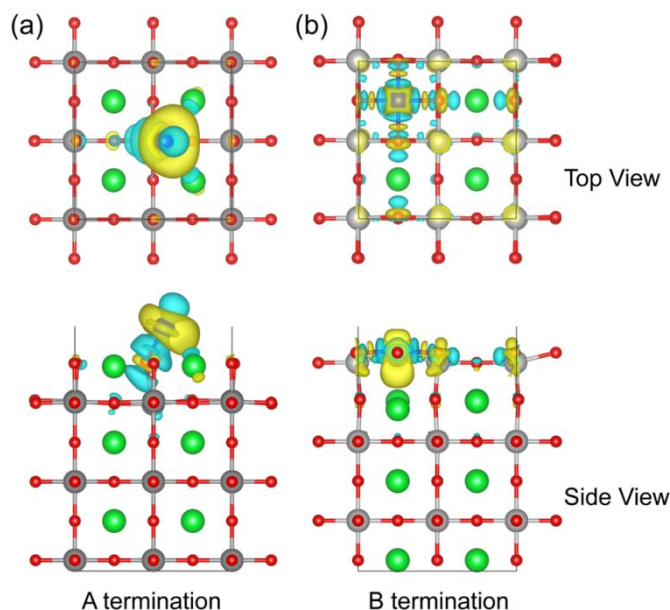


Fig. 5. Charge-density difference plots of Pt₁-SrTiO₃ (100): (a) A-termination; (b) B-termination. Blue denotes depletion of electron density while yellow represents accumulation. Color code: O, red; Sr, green; Ti, gray. Pt₁ is at the center of the charge transfer. Isosurface value equal to 0.0038 e/Å³.

The different charges of Pt₁ on A- and B-terminations of SrTiO₃(100) can be understood by polar compensation.⁴⁶⁻⁵¹ Using SrTiO₃(100) as an example, Fig. 6 shows that the A-termination is slightly positively charged, while the B-termination is negatively charged. This is in agreement with previous theoretical finding that the SrTiO₃(100) surfaces are slightly polar.⁵² To compensate the surface charges, Pt₁ should have negative charge on the A-termination and positive charge on the B-termination. That is exactly what we have found from Fig. 4.



Fig. 6. Charge of surface layers on SrTiO₃ (100) for A-termination and B-termination. The surface-layer charge is determined by the sum of the Bader charges of all the atoms in the top layer of the surface before Pt₁ adsorption (Table 1).

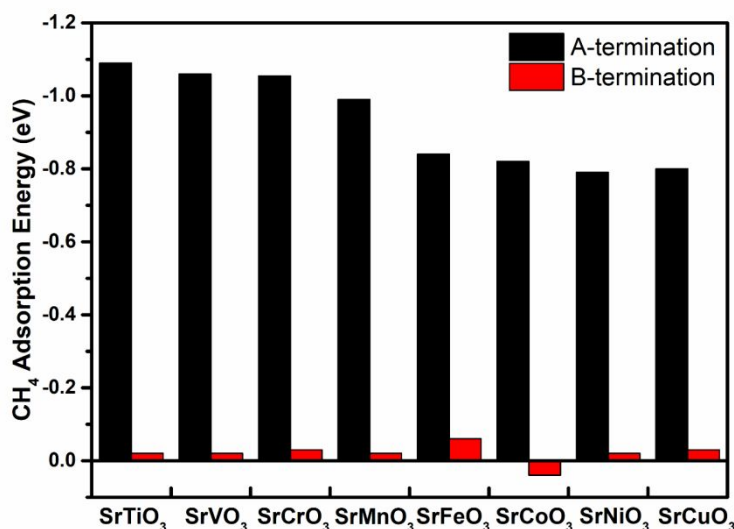


Fig. 7. CH₄ adsorption energy on Pt₁-SrBO₃(100).

3.4. CH₄ adsorption on Pt₁-SrBO₃(100)

We next examine CH₄ adsorption on Pt₁-SrBO₃(100). Fig. 7 shows that on the B-termination, adsorption of CH₄ on Pt₁-SrBO₃(100) is physical in nature and weak, but on the A-termination, CH₄ chemisorbs strongly with adsorption energies in the range of -0.8 to -1.1 eV. To understand this strong adsorption, we further inspected the optimized geometry of the adsorbed CH₄. As shown in Fig. 8, for B being the early transition metals, such as in SrTiO₃, SrVO₃ and SrCrO₃, dissociative adsorption happens, leading to co-adsorbed H and CH₃ on Pt₁. For B = Mn to Cu, one or two C-H bonds of CH₄ are significantly activated and elongated, though not broken, in the chemisorbed state (Fig. 8).

The spontaneous CH₄ dissociation that we found on systems such as Pt₁-SrTiO₃-(100)-A-termination is consistent with several recent studies of CH₄ activation by gas phase atom or clusters. For example, Perera *et al.*⁵³ found that the insertion of a gas-phase Pt atom into the C-H bond of CH₄ is barrierless to form CH₃-Pt-H, based on a joint vacuum ultraviolet photoionization and DFT investigation. More relevantly, Zhao *et al.* found from mass spectrometry and DFT calculations that small gas-phase anionic clusters such as PtAl₂O₄⁻ and AuTi₃O₇⁻ can activate CH₄.^{54, 55}

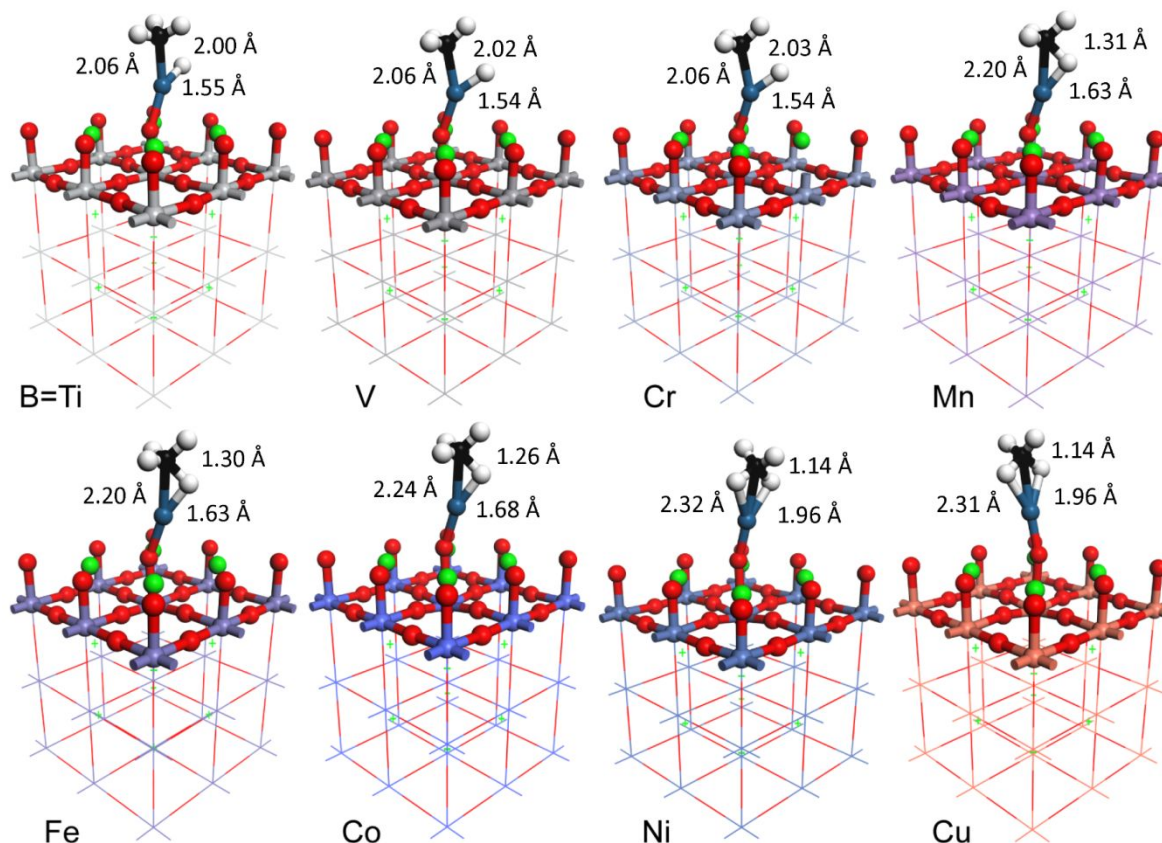


Fig. 8. Optimized configuration of CH₄ adsorption on Pt₁-SrBO₃ (100) A-termination. Color code: O, red; Sr atom, green; Pt atom, blue; C atom, black; H atom, white; B, varies. Key bond distances are also given for the C-H bond being activated: Pt-C (left), Pt-H (lower right), and C-H (upper right).

To understand why CH₄ adsorbs strongly on Pt₁-SrBO₃ (100) A-termination, we plotted the local density of states (DOS) of Pt₁ on SrTiO₃(100) (similar results have been found for other strong-interaction cases such as B = V and Cr). As one can see, there are empty 6s and 6p states (especially p_z) of Pt₁ right above the Fermi level (Fig. 9a). These states serve as acceptor for σ donation from the C-H bond of CH₄ and have much greater change after adsorption. As revealed previously,^{34, 35} the key to methane chemisorption from the d states is the empty d_{z²} orbital, but it is occupied in the case of Pt₁-SrTiO₃-(100)-A (Fig. 9b). Hence, the empty sp states on Pt₁-SrBO₃-(100)-A play the dominant role in methane chemisorption. In contrast, the weak methane chemisorption on Pt₁-SrTiO₃-(100)-B (Fig. 7) can be attributed to the lack of either empty sp states (Fig. 10a) or empty d_{z²} states near the Fermi level (Fig. 10b).

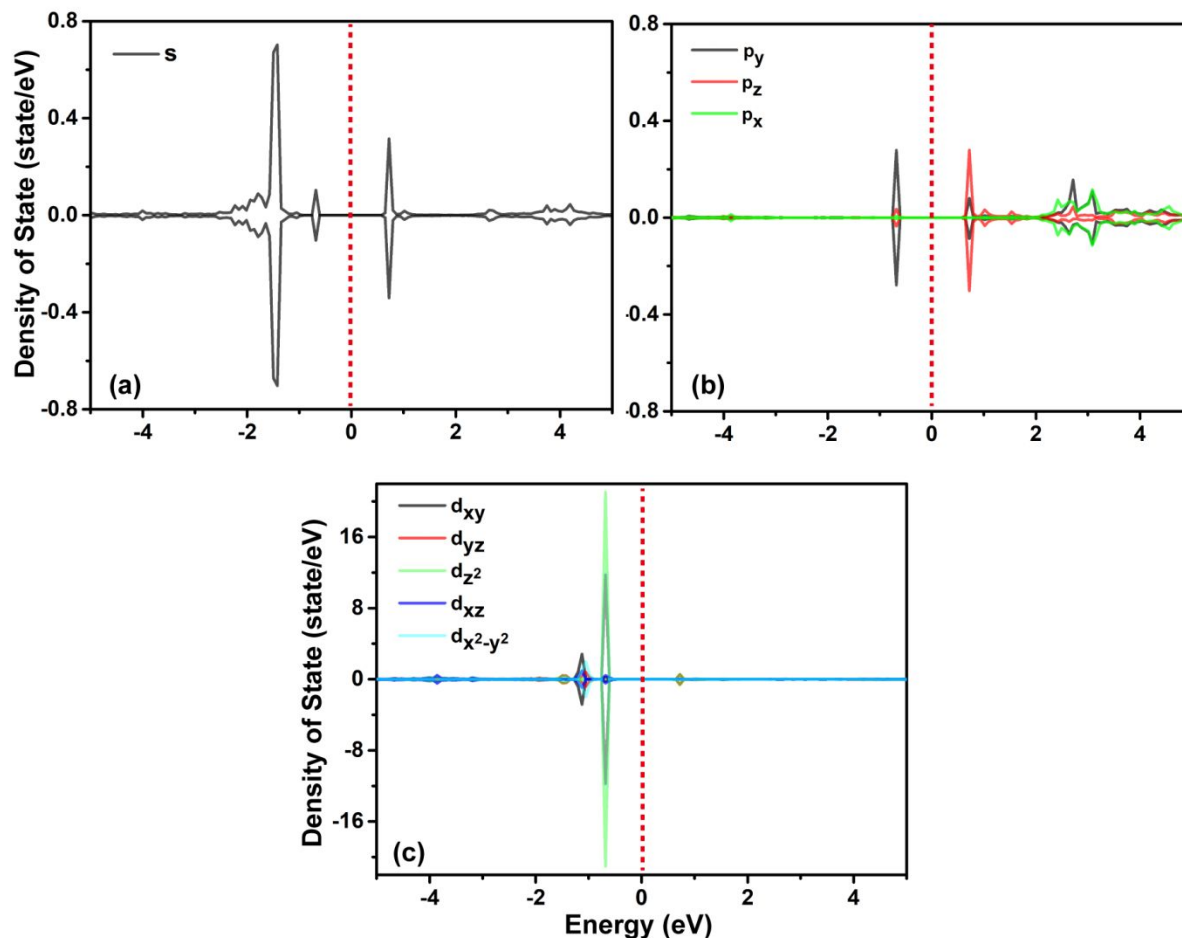


Fig. 9. Projected density of state plots of Pt single atom supported on SrTiO₃ (100) A-termination before CH₄ adsorption: (a) 6s states; (b) 6p states; (b) 5d states. The Fermi level is set to 0 eV.

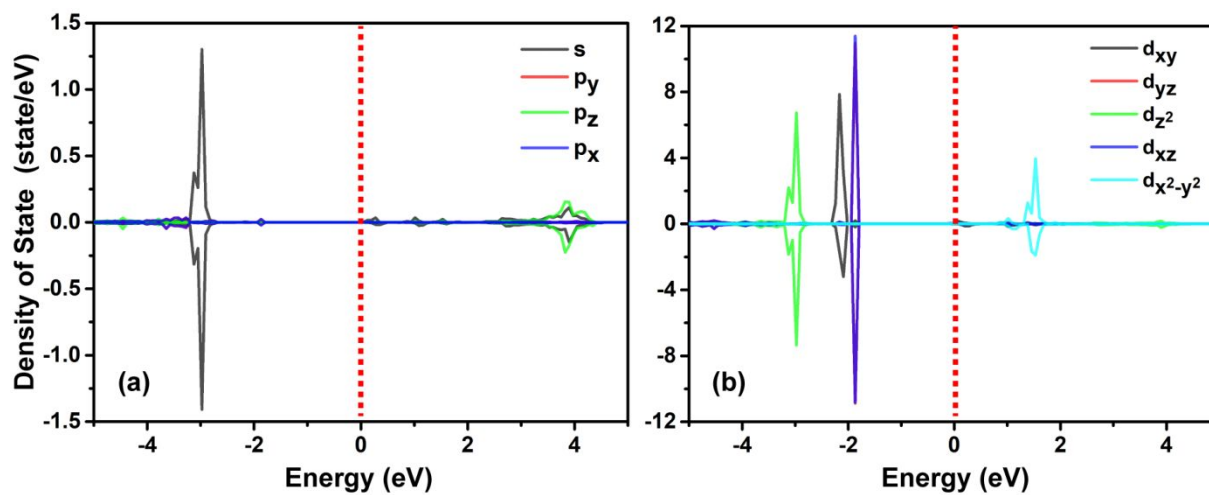


Fig. 10. Projected density of state plots of Pt single atom supported on SrTiO₃ (100) B-termination before CH₄ adsorption. (a) s, p states; (b) d states. The Fermi level is set to 0 eV.

3.5. Implications for methane activation

Considering both the stability (Figure 2) and methane adsorption (Figure 7), one can see that the A terminations of SrTiO₃(100) and SrVO₃(100) are the most promising to realize methane chemisorption and facile activation at the Pt₁ site, because Pt₁ has about equal stability on the A and B terminations of those two surfaces. For the (100) surfaces of the other perovskites explored, Pt₁ strongly prefers the B termination where methane only physisorbs at the Pt₁ site; but as shown previously,²⁴ the perovskite surfaces can reconstruct at various pretreatment methods and at certain conditions the A termination can be exposed. In this case, Pt₁ can be anchored on the A termination to test methane activation. Fig. 2 shows that the adsorption energy of Pt₁ on the A terminations is about -3.0 eV relative to a gas-phase Pt atom, while bulk Pt has a cohesive energy of 5.5 eV/atom from our DFT calculation. This means that Pt₁ on the A terminations is much less stable than bulk Pt and may sinter at high temperatures, which brings challenges in synthesis. On the other hand, Pt₁ may be kinetically stabilized on the A termination. We have investigated minimum-energy diffusion pathways of Pt₁ on the A- and B-terminations of SrTiO₃(100), as an example. We found that the diffusion barrier is actually higher on the A-termination ($E_a = 1.37$ eV) than on the B-termination ($E_a = 1.18$ eV).

4. Conclusions

In summary, we have studied methane adsorption on the Pt single atom stabilized on the (100) surfaces of SrBO₃ perovskites (B = 3d transition metals) by first principles density functional theory. We found that as B varies from Ti to Cu, the binding energy of Pt₁ with the A (or SrO) termination is about the same, but the binding of Pt₁ with the B (or BO₂) termination becomes stronger which correlates with the increasing reducibility as measured by the oxygen-vacancy formation energy. More interestingly, Pt₁ is negatively charged on the A termination but positively charged on the B termination, due to polar compensation. This charge state has a profound impact on methane adsorption: methane adsorbs strongly, chemically, and, in some cases, dissociatively on Pt₁-SrBO₃(100)-A-termination, but weakly and physically on Pt₁-SrBO₃(100)-B-termination. Analysis of local density of states revealed that the sp states of the negatively charged Pt₁ is key to methane chemisorption and C-H activation. Our work shows that negatively charged Pt₁ single

atom on the A termination of the SrBO₃(100) has the potential to achieve facile C-H activation of methane.

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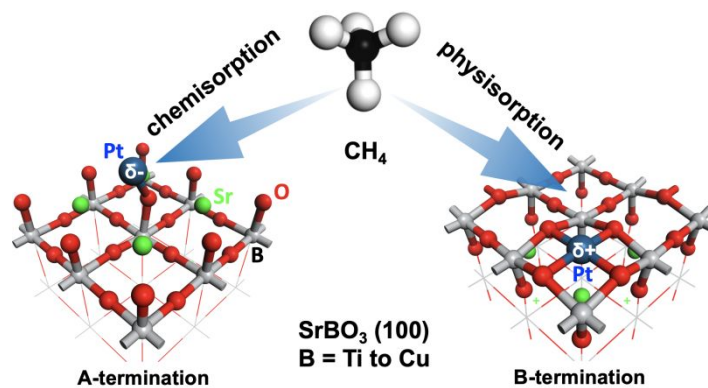
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TOC graphic



Due to polar compensation, Pt₁ is negatively charged on the A termination of SrBO₃(100) surfaces but positively charged on the B termination, which greatly impacts methane adsorption