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ABSTRACT

Supported single-atom catalysts (SACs) have gained increasing attention for improved catalytic activity and selectivity for industrially relevant reactions. In this study, we explore the hydrogenation of acetylene over single Pt, Ru, Rh, Pd, and Ir atoms supported on the $\text{Fe}_3\text{O}_4(001)$ surface using density functional theory calculations. The thermodynamic profile of H diffusion is significantly modified by the type of single metal atoms used, suggesting that H spillover from the single atom dopant to the $\text{Fe}_3\text{O}_4(001)$ surface is favored and will likely lead to high H coverages of the functioning catalyst. Correspondingly, as the surface H coverage increases, the important desorption step of ethylene becomes energetically competitive against the detrimental hydrogenation steps of ethylene to ethane. A kinetic model is employed to explore how the activity and selectivity of SACs toward ethylene production change as a function of mass of the catalyst loaded into a flow reactor. Overall, we show that the selectivity of SACs toward ethylene production can be tuned by considering the proper type of metal and controlling the redox state of the support.

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INTRODUCTION

Selective hydrogenation of acetylene to ethylene is an important class of chemical reactions in the large-scale production of polyethylene.^{1,2} A generally accepted reaction pathway for acetylene hydrogenation is the Horiuti–Polanyi mechanism, where adsorbed acetylene is sequentially hydrogenated with single hydrogen adatoms.³ In the Horiuti–Polanyi mechanism, complete acetylene hydrogenation to ethane competes with ethylene production.^{3,4} Extensive research efforts have been devoted to enhancing the reactivity and selectivity of metal catalysts responsible for acetylene conversion. Some of the most commonly used catalysts are Pd-based catalysts modified with the introduction of Ag.^{5,6} Pd can further be combined with other metals, including Au, Ga, and Zn, to create active and stable catalysts under different reaction conditions.^{7–12} Single Pd atoms have also been embedded with Cu and Ag to create single-atom alloys, which exhibit enhanced selectivity for hydrogenation reactions

relative to pure Pd catalysts.^{4,13–15} Non-precious alloys, such as Co–Ga and Ni–Zn, have been suggested as alternatives over expensive Pd-based catalysts for selective hydrogenation of acetylene.^{9,16} A wide variety of porous materials, including graphene or metal–organic frameworks (MOFs), have also been used to support these metal catalysts.^{17–21} Overall, it is clear that high ethylene selectivity and robust catalyst stability under reacting conditions have always been sought in developing these types of hydrogenation catalyst.

As a particularly promising catalytic system, single metal atoms are rapidly emerging as a new type of catalyst that demonstrate remarkable performance toward hydrogenation, water–gas shift, oxidation, and other types of industrially relevant reactions.^{22–24} It is well known that metals are extensively involved as heterogeneous catalysts in a broad range of industrial applications, including fuel cells, solar converters, pharmaceuticals, and automobile exhausts,^{25–29} and that the majority of catalytic reactions take place on the metal surface, with bulk metal atoms going to waste.

Creating smaller metal particles, finely dispersed on a suitable support, has accordingly been the go-to method of decreasing the consumption of precious metals.^{29,30} More interestingly, reducing the size of the metal particles often introduces improved reactivity and selectivity through metal–support interactions and quantum size effects.^{30–33} Much work has already reported that improved reactivity and selectivity are achieved over subnanometer-sized metal particles compared to nanometer-sized ones.³⁴

As mentioned, in the C_2H_2 hydrogenation applications, numerous single atom alloy catalysts have been investigated,^{4,14,35} but single metal atoms supported on metal oxides have not been extensively studied yet to the best of our knowledge. Previous work has shown that various single metal atoms can be stabilized on the $Fe_3O_4(001)$ surface.^{36–41} A hydrogen spillover onto $Fe_3O_4(001)$ with single Pd atom leads to the wide distribution of the resultant hydroxyl groups on the surface, lifting surface reconstruction and destabilizing the Pd atom as a consequence.^{40,42} The presence of single Pd atoms also lowers the barrier of methanol oxidation in comparison to Pd clusters supported on $Fe_3O_4(001)$, showing the unique nature of single atom catalysts.⁴³ Because of these numerous experimental and theoretical studies conducted on $Fe_3O_4(001)$, it is a suitable surface for a case study. In the present work, we explore selective hydrogenation of acetylene to ethane over single metal atoms (Pt, Ru, Rh, Pd, and Ir) supported on the $Fe_3O_4(001)$ surface using density functional theory (DFT) calculations. As expected, the energy profile of H diffusion on $Fe_3O_4(001)$ varies greatly with the type of single metal atom present on the surface. In all cases, the diffusion pathways suggest that H spillover is favored, which implies that H coverages should be quite high depending on H_2 exposure time. Accordingly, for acetylene hydrogenation, we find that the desorption of ethylene becomes energetically competitive against the hydrogenation of ethylene to ethane and the subsequent desorption of ethane as the surface H coverage increases. Furthermore, a kinetic model is developed to study the activity and selectivity of single metal atoms toward ethylene production as a function of mass of catalyst loaded into a model flow reactor. We show that the selectivity of single metal catalysts toward ethylene production can be tuned by a careful control over surface H coverage on the oxide support.

COMPUTATIONAL METHODOLOGY

We performed DFT calculations using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional,⁴⁴ including a Hubbard-like U_{eff} interaction,⁴⁵ as implemented in CP2K.⁴⁶ The effective Coulomb repulsion parameter of 4.0 eV was chosen for the Fe 3d states, similar to the values previously adopted for studying bulk Fe_3O_4 and the $Fe_3O_4(001)$ surfaces.^{40,42,43,47} Norm-conserving pseudo-potentials of the Goedecker–Teter–Hutter (GTH) type were applied to describe the nuclei and core electrons.⁴⁸ The Gaussian-plane wave hybrid basis set scheme was employed, where double- ζ Gaussian MOLOPT basis sets,⁴⁹ in conjunction with a plane wave cutoff of 450 Ry, were used. Only the Γ -point was used to sample the Brillouin zone as the computational unit cells are adequately large (see below). Geometry optimization was carried out based on the limited memory BFGS method.⁵⁰ A correction scheme to the asymmetric slab surface dipoles was adopted.⁵¹

We constructed a slab model of the $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ unit cell, consisting of seven layers of O and octahedral Fe and six layers of tetrahedral Fe, to simulate the reconstructed $Fe_3O_4(001)$ surface, based on the model proposed by Bliem *et al.*⁵² A vacuum region of at least 18 Å was placed above the Fe_3O_4 surface to remove any spurious interaction between periodic images, with the bottom three layers being fixed. In this study, the DFT adsorption energy (ΔE_{ads}) of reaction intermediates on single metal atoms over the $Fe_3O_4(001)$ surface was calculated as

$$\Delta E_{ads} = E_{surf-bound} - E_{surf} - E_{molecule}, \quad (1)$$

where $E_{surf-bound}$ represents the energy of surface-bound reaction intermediates on the single metal atom/ $Fe_3O_4(001)$, while E_{surf} and $E_{molecule}$ defines the energy of the single metal atom on $Fe_3O_4(001)$ and the molecule in the gas phase, respectively. Bader charges were also calculated to understand the charge state of single metal atoms and the $Fe_3O_4(001)$ surface.^{53,54}

To estimate Gibbs free energies within the harmonic approximation, vibrational analysis on the surface-bound intermediates and surface H atoms directly involved in acetylene hydrogenation is carried out using the finite difference method within the harmonic approximation, as implemented in CP2K. The presence of low-lying frequencies ($<50\text{ cm}^{-1}$) can introduce non-negligible errors into the calculations of entropy contribution. Accounting for anharmonicities and thereby enhancing the numerical accuracy of entropy estimation is possible,^{55–59} but such approaches require substantial computational effort when considering multiple configurations of large systems. Thus, the immobile adsorbate procedure was adopted where all the low-frequency vibrations were replaced by normal modes of 50 cm^{-1} for this study.^{60,61} Using the calculated frequencies, the adsorption entropies (ΔS_{ads}), enthalpies (ΔH_{ads}), and zero point energy corrections (ΔE_{ZPE}) were estimated,

$$\Delta H_{ads} = \Delta E_{ads} + \Delta E_{ZPE} + \Delta U_{trans} + \Delta U_{rot} + \Delta U_{vib} - RT, \quad (2a)$$

$$\Delta S_{ads} = \Delta S_{trans} + \Delta S_{rot} + \Delta S_{vib}, \quad (2b)$$

where the definition of translational, rotational, and vibrational enthalpies/entropies can be found in the previous literature.⁶² Finally, the Gibbs free energies of adsorption were computed at the operating temperature (T) as

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}. \quad (2c)$$

To also determine how the systems studied here affect activity and ethylene selectivity, we have developed a kinetic model to describe the rates of ethylene and ethane production. This model presupposes that the net forward elementary reaction steps are only rate limited by desorption steps. Thus, we expect facile acetylene hydrogenation relative to desorption such that the effective activation free energy barriers for ethylene and ethane production are simply the Gibbs free energy differences between ethylene and ethane desorbed states and the lowest free energy adsorbed state on the surface. The rates are then otherwise dependent on stoichiometric powers of the partial pressures of acetylene and hydrogen. Based on

these considerations, we have

$$r_{C_2H_4} = \frac{k_B T}{h} e^{-\beta \Delta G_{act, C_2H_4}} \left(\frac{P_{C_2H_2}}{P^0} \right) \left(\frac{P_{H_2}}{P^0} \right), \quad (3a)$$

$$r_{C_2H_6} = \frac{k_B T}{h} e^{-\beta \Delta G_{act, C_2H_6}} \left(\frac{P_{C_2H_2}}{P^0} \right) \left(\frac{P_{H_2}}{P^0} \right)^2, \quad (3b)$$

where $r_{C_2H_4}$ and $r_{C_2H_6}$ are the production rates of ethylene and ethane, respectively, k_B and h are Boltzmann's constant and Planck's constant, respectively, T and $\beta = \frac{1}{k_B T}$ are the absolute temperature and the thermodynamic beta, respectively, $P_{C_2H_2}$ and P_{H_2} are the partial pressures of acetylene and hydrogen, respectively, while P^0 is standard pressure (1 atm), and

$$\Delta G_{act, C_2H_4} = G_{C_2H_4}^\ddagger - G_{C_2H_2} - G_{min}, \quad (4a)$$

$$\Delta G_{act, C_2H_6} = G_{C_2H_6}^\ddagger - G_{C_2H_2} - G_{min} \quad (4b)$$

are the activation free energies of ethylene and ethane production, respectively. These activation free energies are defined by Eqs. (4a) and (4b), where $G_{C_2H_4}^\ddagger$ and $G_{C_2H_6}^\ddagger$ are free energies of the transition state of desorbing ethylene and ethane, respectively, taken to be that of an ideal gas minus one degree of translational freedom corresponding to the motion along the reaction path, G_{2H^*}/Fe_3O_4 and $G_{Fe_3O_4}$ are the Gibbs free energies of the $Fe_3O_4(001)$ surface subsequent ethylene and ethane desorption, respectively, and G_{min} is the lowest Gibbs free energy adsorbed state of hydrogenating acetylene. The turnover frequency (TOF) of each single-atom catalyst (SAC) is given by the sum of its ethylene and ethane production rates [Eqs. (3a) and (3b)].

To connect the rates shown in Eqs. (3a) and (3b) to activity, acetylene conversion, and ethylene selectivity, we devise a flow reactor model. We assume that some known mass of our SAC is monodispersed throughout this reactor, which then acts as an isothermal continuous stirred tank reactor (CSTR)⁶³ operating with negligible pressure drop. Reactants are fed in at a constant volumetric flow rate of $1.0 \text{ m}^3/\text{s}$ and a constant pressure of 1.0 atm (giving a total inlet molar flow rate of $\sim 1.6 \times 10^{25}$ molecules/s) but with a variable H_2/C_2H_2 ratio, which we treat as a model parameter. Finally, we assume that no product gases are present in the inlet stream. The resulting reactor model is shown in Fig. 1.

Since our rates are on a basis of molecules turned over per second per single atom site, we arrive at the following design equations for the flow reactor:

$$\dot{N}_{C_2H_4} = r_{C_2H_4} M_S, \quad (5a)$$

$$\dot{N}_{C_2H_6} = r_{C_2H_6} M_S, \quad (5b)$$

$$\dot{N}_{C_2H_2} = \dot{n}_0 - (r_{C_2H_4} + r_{C_2H_6}) M_S, \quad (5c)$$

$$\dot{N}_{H_2} = \phi_{H_2} \dot{n}_0 - (r_{C_2H_4} + 2r_{C_2H_6}) M_S, \quad (5d)$$

where each $\dot{N}_i$ is the molar flow rate (in units of molecules per second) of species i within (and exiting) the reactor, $\dot{n}_0$ is the inlet molar flow rate (same units) of acetylene, ϕ_{H_2} is the H_2/C_2H_2 ratio, and M_S is the total number of active sites present within the reactor, related to mass of catalyst loaded via

$$M_S = m_c a_c \rho_s, \quad (5e)$$

where m_c is the mass of catalyst particles (in grams) loaded into the reactor, a_c is the BET surface area of the catalyst (taken to be

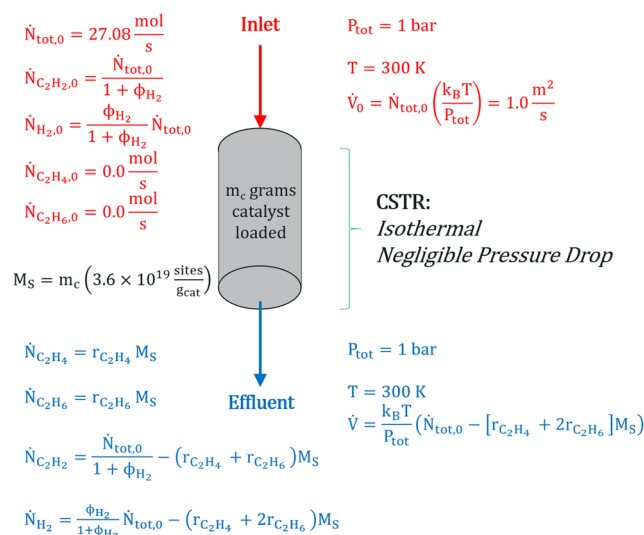


FIG. 1. Schematic and details of the flow reactor model used in this work. Mathematical quantities are defined within the main text.

$100 \text{ m}^2/\text{g}$ here), and ρ_s is the single atom site density at the surface of the catalyst particle (taken to be $\sim 0.36 \text{ sites}/\text{nm}^2$ based on the size of the supercell used in this study, which is 2.82 nm^2 and contains precisely one single atom site). We thus have $\sim 3.6 \times 10^{19} \text{ sites}/\text{g}_{cat}$ in our model. Assuming that the flowing reactant and product species behave as ideal gases, we determine that

$$P_{C_2H_4} = \frac{r_{C_2H_4} M_S}{(\phi_{H_2} + 1) \dot{n}_0 - (r_{C_2H_4} + 2r_{C_2H_6}) M_S} P_{tot}, \quad (6a)$$

$$P_{C_2H_6} = \frac{r_{C_2H_6} M_S}{(\phi_{H_2} + 1) \dot{n}_0 - (r_{C_2H_4} + 2r_{C_2H_6}) M_S} P_{tot}, \quad (6b)$$

$$P_{C_2H_2} = \frac{\dot{n}_0 - (r_{C_2H_4} + r_{C_2H_6}) M_S}{(\phi_{H_2} + 1) \dot{n}_0 - (r_{C_2H_4} + 2r_{C_2H_6}) M_S} P_{tot}, \quad (6c)$$

$$P_{H_2} = \frac{\phi_{H_2} \dot{n}_0 - (r_{C_2H_4} + 2r_{C_2H_6}) M_S}{(\phi_{H_2} + 1) \dot{n}_0 - (r_{C_2H_4} + 2r_{C_2H_6}) M_S} P_{tot}, \quad (6d)$$

where each P_i is the partial pressure of species i and P_{tot} is the total pressure of the gas stream. As designed, all partial pressure expressions shown in Eqs. (6a)–(6d) sum to P_{tot} .

To determine the ethylene and ethane production rates and thus the TOF, Eqs. (6a)–(6d) must be solved self consistently and then inserted into Eqs. (3a) and (3b). Additionally, acetylene conversion ($X_{C_2H_2}$) and ethylene selectivity ($s_{C_2H_4}$) are found from

$$X_{C_2H_2} = \frac{P_{C_2H_2,0} - P_{C_2H_2}}{P_{C_2H_2,0}}, \quad (7)$$

$$s_{C_2H_4} = \frac{P_{C_2H_4}}{P_{C_2H_4} + P_{C_2H_6}}, \quad (8)$$

where $P_{C_2H_2,0} = \frac{P_{tot}}{\phi_{H_2} + 1}$ is the inlet partial pressure of acetylene. It should be noted that the partial pressures in Eqs. (7) and (8) are simply surrogates for molar flow rates—equivalent due to the ideal gas assumption.

RESULTS AND DISCUSSIONS

To explore the hydrogenation process of acetylene over SACs, we considered the single metal atoms of Pt, Ru, Rh, Pd, and Ir supported on the $\text{Fe}_3\text{O}_4(001)$ surface. The bulk-like-open (BLO) site is chosen for the adsorption site of the single metal atoms, where the coordination of the metal adatom to two neighboring surface O atoms is possible due to the stabilization of SACs on such twofold sites over Fe_3O_4 surfaces.^{40,52,64} As already demonstrated in our previous study on $\text{Fe}_3\text{O}_4(001)$, the reaction pathways of H_2 dissociation over SACs can be significantly altered depending on the type of metal.⁴⁰ Thus, understanding the initial H spillover process on the $\text{Fe}_3\text{O}_4(001)$ surface is important since the subsequent hydrogenation of acetylene will be impacted by its proximity to nearby hydrogen on the surface. The initial H_2 dissociation process, reproduced from our previous study,⁴⁰ is shown in Fig. 2(a). It is a thermodynamically downhill process to initially dissociate the H_2 molecule onto the surface for all single metal atoms [steps 2 and 3, Fig. 2(a)]. Here, the formation of hydroxyl and hydride groups [step 3, Fig. 2(a)] is preferred on Ru, while the formation of a hydroxyl–hydroxyl pair [step 4, Fig. 2(a)] is favorable for Pt and Pd. There is an energetic competition between the formation of hydride–hydroxyl and hydroxyl–hydroxyl pairs for Rh and Ir.

The reaction pathway of subsequent H diffusion on $\text{Fe}_3\text{O}_4(001)$ in the presence of the selected single metal atoms is also shown in

Fig. 2(b). H atom diffusion is assumed to occur along the adjacent O row, as previously observed from experimental STM images.^{40,42} Energy changes due to diffusion away from the single metal atom are shown as reactions steps 5, 6, and 7, with reaction step 5 corresponding to the diffusion of H to the third nearest O atom and 7 corresponding to the diffusion to the O atom furthest from the single metal atom in our model. A slight preference for the third nearest O atom [step 5, Fig. 2(b)] is observed for Ir. However, all positions away from the single metal atom [from step 4–7, Fig. 2(b)] are roughly equivalent. Based on the diffusion profiles of H shown in Fig. 2, we conclude that H will likely spillover away from the single metal atom and fill the $\text{Fe}_3\text{O}_4(001)$ surface to near-saturation coverages depending on the level of H_2 exposure. The only potential exception is shown in the Rh system, but even at modest temperature, the energy differences between its H adsorption sites would also likely be surmountable (a maximum of ~ 0.55 eV/ H_2). Thus, higher coverages of H in the Rh system cannot be outright excluded from the realm of possibility. Due to this, we are obliged to consider the effect of surface H coverage for all single metal atoms in our subsequent DFT calculations on the selective hydrogenation of acetylene to ethylene.

With this in mind, we continue by determining the free energetics of the acetylene hydrogenation reaction pathway at two different H coverages, as shown in Fig. 3. As mentioned, the Horiuti–Polanyi mechanism is adopted to represent the hydrogenation process of acetylene (C_2H_2) in our study.³ Since the ultimate product

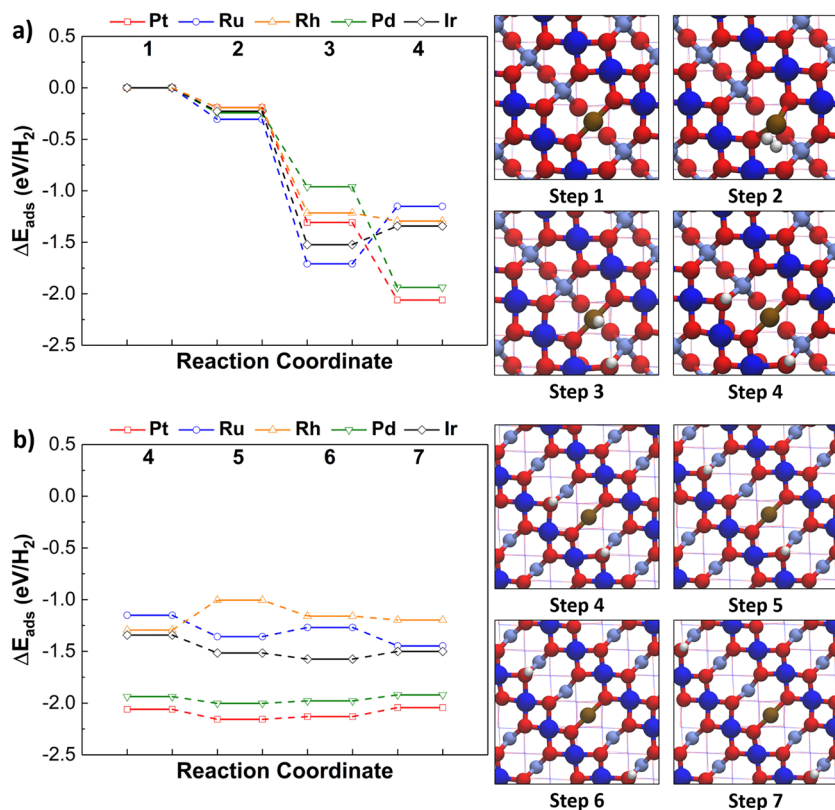


FIG. 2. DFT reaction pathways of (a) H_2 dissociation and (b) H diffusion over the single metal atom supported on $\text{Fe}_3\text{O}_4(001)$. In the surface model, the blue, light blue, brown, red, and white balls represent octahedral Fe, tetrahedral Fe, single metal (Pt, Ru, Rh, Pd, and Ir), O, and H atom, respectively. Note that the reference state is defined as the single metal atoms supported on $\text{Fe}_3\text{O}_4(001)$ with the H_2 molecule in the gas phase. For additional analysis on H_2 diffusion, see Sec. S1 of the supplementary material.

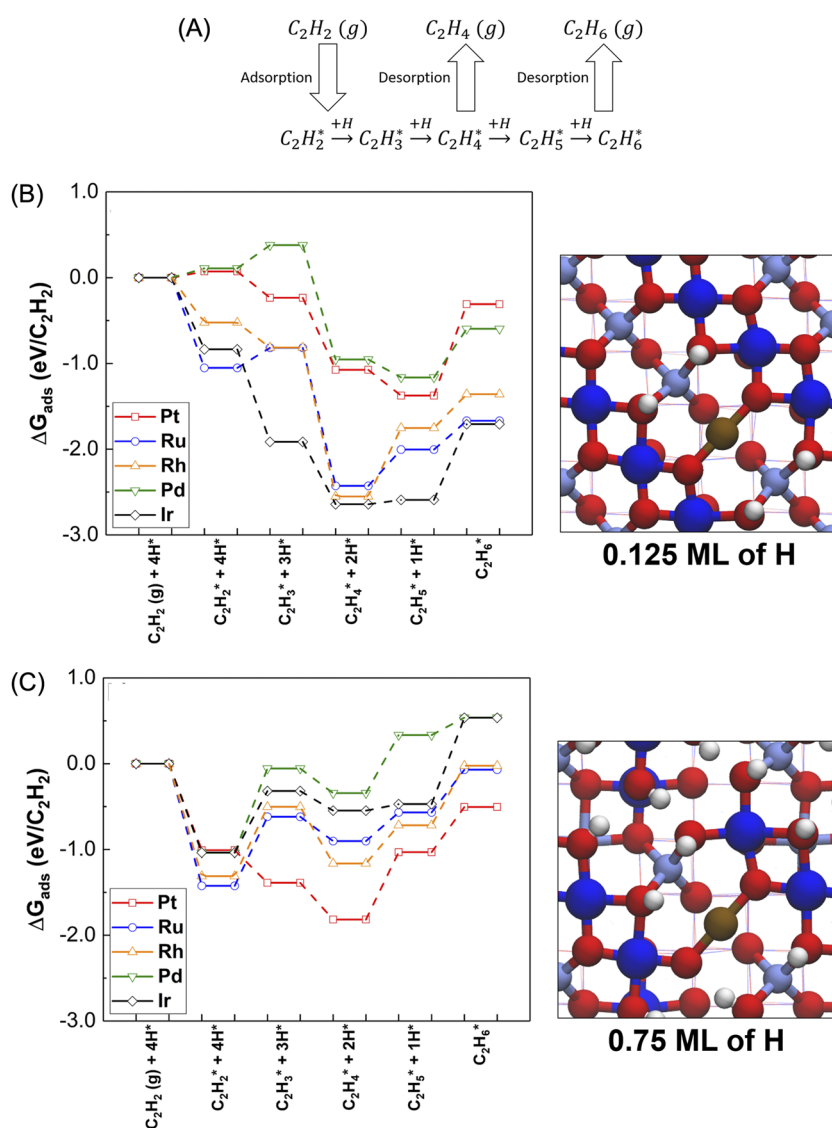


FIG. 3. Gibbs free energy pathways of (a) acetylene hydrogenation (at 300 K and 101.325 kPa) over single metal atom supported on $Fe_3O_4(001)$ with H coverage of (b) 0.125 ML and (c) 0.75 ML along with the corresponding surface $H/Fe_3O_4(001)$ model (see the caption of Fig. 2 for the schematic colors of the surface model). Note that the reference state is defined as the single metal atoms supported on $H/Fe_3O_4(001)$ with C_2H_2 molecule in the gas phase. For information regarding DFT-based reaction pathways of acetylene hydrogenation, see Sec. S3 of the [supplementary material](#).

of acetylene hydrogenation is ethane (C_2H_6), we consider the entire pathway to this product through the ethylene intermediate by following the procedure described in Sec. S2 of the [supplementary material](#). The reference point for the pathway at 0.125 ML of H coverage [Fig. 3(a)] is acetylene in the gas phase and four H atoms adsorbed at the O sites proximal to the single metal atom on the $Fe_3O_4(001)$ surface. While the lowest energy configuration of H on this surface would not be at the sites proximal to the single metal atom (as shown in Fig. 2), we wish to obviate the need for including diffusion steps from such a configuration to these sites here since it is the final reaction free energy where actual hydrogenation occurs that determines favorability. The second step in Fig. 3(a) shows the adsorption free energy of acetylene onto the single metal atoms with these four hydroxyl groups still present. All the remaining steps are hydrogenation steps that follow from this starting configuration (see

Sec. S2 of the [supplementary material](#) for additional details on the adsorption geometry of reaction intermediates).

From the pathways shown in Fig. 3(a), we see that a thermodynamic driving force toward adsorbed ethylene ($C_2H_4^*$) formation is present over Ru, Rh, and Ir, while the driving force is toward $C_2H_5^*$ over Pt and Pd. While ethane formation is energetically uphill from either of these starting points, we can expect that ethane formation and subsequent desorption will be most competitive with, specifically, ethylene desorption, which causes a loss in the desired selectivity toward ethylene. Furthermore, C_2H_3 is stable relative to acetylene for Pt, Rh, and Ir, meaning that so long as the reaction barriers connecting these states are not limiting, ethylene will be readily formed. In contrast, for the Ru and Pd systems, the formation of ethylene and subsequent C_2H_5 could be slowed by the necessity of forming a relatively unstable C_2H_3 . Combined with the analysis provided in

the previous paragraph, it can thus be expected that ethylene formation is most energetically promoted on Rh and Ir since it is preferred over further hydrogenation steps and is unhindered by the need to form an unstable intermediate C_2H_3 . However, we also observe that the production of desorbed ethylene is energetically unfavorable over hydrogenation of ethylene due to the relatively strong adsorption free energy of ethylene, especially for Ru, Rh, and Ir. Overall, at 0.125 ML of H, the production of ethylene is potentially energetically hindered for Pt and Pd due to their preference for further hydrogenation of C_2H_4 to C_2H_5 , while Ru, Rh, and Ir primarily suffer from the overstabilization of ethylene.

Figure 3(b) shows reaction energies with increased H coverage to 0.75 ML. Since a lifted surface reconstruction at the bare $Fe_3O_4(001)$ is seen at higher surface H coverages,⁴⁰ such a reconstruction-lifted surface is also adopted for representing 0.75 ML of H in this study. Complete hydrogenation to ethylene is energetically favored over its intermediate partial hydrogenation product, C_2H_3 , or its subsequent hydrogenation product, C_2H_5 , regardless of the metal used, which is in contrast to the energetics shown at 0.125 ML of H [Fig. 3(a)]. However, the relative stability of C_2H_3 compared to adsorbed acetylene (C_2H_2) is still metal dependent, albeit barely: there is an energetic barrier against hydrogenation to ethylene due to the relative instability of C_2H_3 for all metals other than Pt, despite an overall driving force toward ethylene in all cases. As a result, the performance of these metals will ultimately come down to the energetic competition between ethylene desorption and further ethylene hydrogenation to ethane plus subsequent desorption.

In order to determine which single metal atom provides the greatest driving force toward ethylene desorption (thus decreases selectivity toward ethane), we consider the free energy difference between the desorption states of ethylene and ethane. In principle, it is required to compare the desorption energy of ethylene against the desorption energy of ethylene. However, since these two processes have the same branching point [adsorbed ethylene ($C_2H_4^* + 2H^*$)], comparing the energy difference between the two final states accomplishes the same thing. We perform these calculations for both 0.125 ML and 0.75 ML of H and summarize them in Fig. 4, where a negative value indicates a preference toward desorption of ethylene over ethane. At low H coverage, the desorption of ethylene over the desorption of ethane is favored for only Pt and Pd; the C_2H_x

ad-species are simply too strongly adsorbed for the other metal systems, putting the energy state of gaseous ethylene far above the energy state of C_2H_5 for Ru, Rh, and Ir. However, increasing the H coverage destabilizes the C_2H_x ad-species, decreasing the energy difference to gaseous ethylene and thus enhancing selectivity toward this desired product. This destabilization occurs for all systems except Pt and Pd, but the energy differences shown in Fig. 4 all become negative, favoring desorption of ethylene over ethane.

We then investigate how this analysis plays out in our reactor model, which was shown in Fig. 1, using the kinetic model represented by Equations (3)–(8). To approximate conditions that likely lead to low H coverages ($\theta_{H_2} = 0.125$ ML), we use a H_2/C_2H_2 ratio (ϕ_{H_2}) of 0.5 so that acetylene is in twofold excess compared to hydrogen. We hold the total pressure constant at 1 atm and the temperature at 300 K. Using these parameters, we compute the SAC activity and acetylene conversion as a function of catalyst loading (in grams) and present the result in Fig. 5. As can be seen in Figs. 5(a) and 5(b), the only systems that are active for acetylene hydrogenation are Pt and Pd, which have initial TOFs of $\sim 10^3$ and $\sim 10^8$ molecules/site/s compared to initial TOFs of Ir, Rh, and Ru, which are all at or below 10^{-10} molecules/site/s. As the amount of catalyst in the reactor is increased, acetylene conversion increases monotonically, with the Pt SAC achieving $\sim 15\%$ conversion with 1 kg of catalyst loading [Fig. 5(c)] and the Pd SAC achieving $\sim 25\%$ conversion with only 0.2 g catalyst [Fig. 5(d)]. Conversely, Ir, Rh, and Ru are so inactive that acetylene conversion is essentially zero even up to 1 kg catalyst loading. Regardless of catalyst loading, Pt and Pd show nearly unity selectivity toward ethylene, while what little product is formed using Ir, Rh, and Ru is essentially always 100% ethane. Interestingly, TOFs also decrease as conversion increases with catalyst loading, while TOFs stay constant if conversion stays constant at $\sim 0\%$. It is important to note that this is not due to the intrinsic kinetics of the SACs changing but is a direct result of decreasing the partial pressures of hydrogen and acetylene as they are consumed during reaction—having the effect of lowering reaction rates according to Eqs. (3a) and (3b).

The overall low conversions seen in Fig. 5, even for the very active Pt and Pd, are at least, in part, a result of the excess acetylene used (needed to maintain congruence with a low H coverage): there is simply insufficient hydrogen to convert all of the acetylene, the

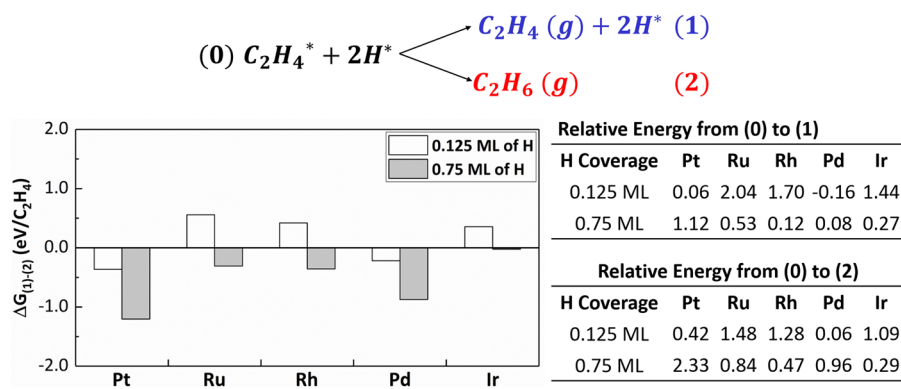


FIG. 4. Gibbs free energy difference (at 300 K and 101.325 kPa) between desorbed ethylene [$C_2H_4(g) + 2H^*$] and desorbed ethane [$C_2H_6(g)$] over single metal atom supported on $Fe_3O_4(001)$ at 0.125 ML and 0.75 ML of H. More negative values of $\Delta G_{(1)-(2)}$ indicate energetically more favorable drive toward ethylene desorption. The associated tables also indicate the relative energy difference from step 0 to 1 and from step 0 to 2.

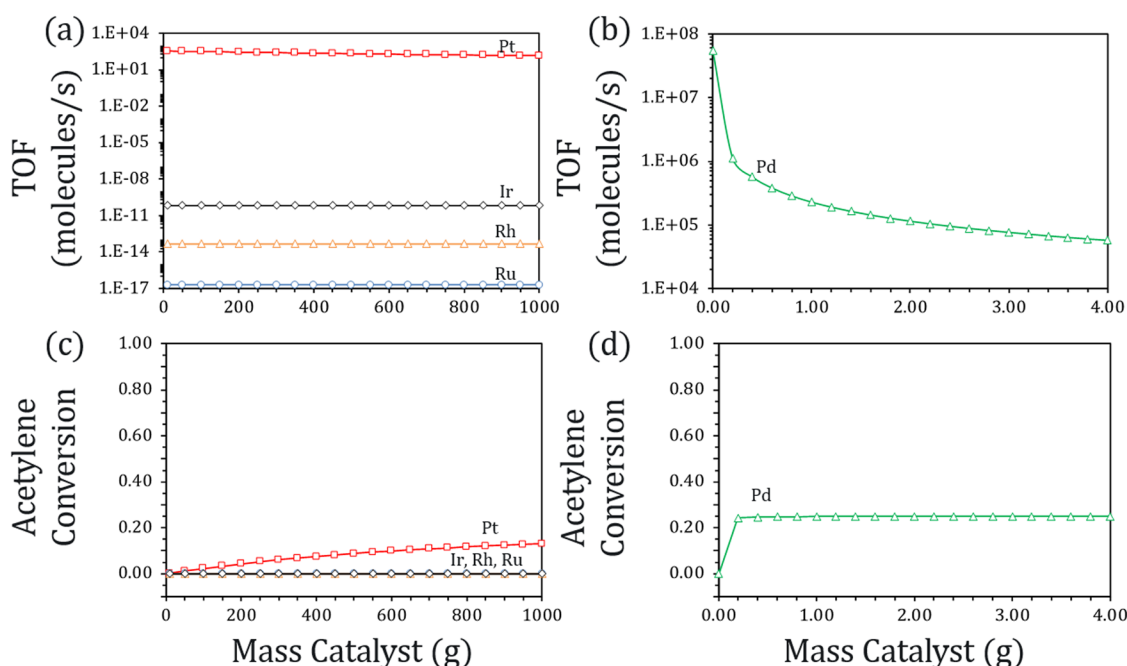


FIG. 5. [(a)–(b)] Activity (measured as TOF) and [(c)–(d)] acetylene conversion of each SAC studied here as a function of the mass of catalyst particles loaded into our model flow reactor. Due to the high activity of the Pd SAC, a much smaller amount of catalyst is required to reach 100% conversion, necessitating that its values be plotted on a different x-axis [panels (b) and (d)]. Selectivities are essentially unity for Pt and Pd and zero for Ir, Rh, and Ru. $P_{\text{tot}} = 1 \text{ atm}$, $T = 300 \text{ K}$, $\phi_{\text{H}_2} = 0.5$, and $\theta_{\text{H}_2} = 0.125 \text{ ML}$. Colors used are the same as those used in Figs. 2 and 3.

theoretical maximum being 50% conversion based on stoichiometry. Calculated results for a value of ϕ_{H_2} of 1 and 10 are shown in the Figs. S4 and S5 of the [supplementary material](#), where the theoretical maximum acetylene conversion is 100% based on stoichiometry. For both $\phi_{\text{H}_2} = 1$ and 10, the Pd SAC achieves nearly 100% conversion at a catalyst loading of only 4 g and 0.2 g, respectively, while the Pt SAC achieves ~35% and 67% acetylene conversion with 1 kg catalyst loading for $\phi_{\text{H}_2} = 1$ and 10, respectively. However, these high $\text{H}_2/\text{C}_2\text{H}_2$ ratios would likely lead to higher H coverages than what our low H coverage model [Fig. 3(a)] reflects, making the values used for the Gibbs free activation barriers [i.e., $\Delta G_{\text{act}, \text{C}_2\text{H}_4}$ and $\Delta G_{\text{act}, \text{C}_2\text{H}_6}$ in Eqs. (3a) and (3b)] incongruent with such ratios. Thus, we set ϕ_{H_2} to 10 and switch to the Gibbs free activation barriers extracted from the 0.75 ML H coverage model [Fig. 3(b)] to maximize congruence. The newly computed TOFs and acetylene conversions based on these values are shown in Fig. 6.

While the ratio of ethylene to ethane desorption free energies is largely skewed toward ethylene production as shown in Fig. 4, the absolute values themselves result in still quite low TOFs for all SACs (except for Rh), despite the TOFs increasing by numerous magnitudes for Ru (~7 magnitude increase) and Ir (~6 magnitude increase) due to the destabilization of adsorbed C_2H_x^* species seen in Fig. 3(b). Conversely, Pt and Pd both decrease their TOFs by ~12 magnitudes and ~8 magnitudes, respectively. On the other hand, the TOF for the Rh SAC increases by a remarkable magnitude of 17, resulting in essentially 100% acetylene conversion with 1 kg catalyst loading and 100% ethylene selectivity regardless of catalyst loading.

Commensurate with the analysis shown in Fig. 4, the primary product formed by all SACs is indeed ethylene (selectivities are unity for Pt, Pd, Rh, and Ru and ~0.74 for Ir), although only with the Rh SAC is the yield appreciable. Calculated results for $\phi_{\text{H}_2} = 1$ and 2 for this high H coverage model are shown in Figs. S6 and S7 of the [supplementary material](#). For $\phi_{\text{H}_2} = 1$ and 2, the Rh SAC exhibits a small decrease in acetylene conversion for the Rh SAC to ~0.8 and ~0.95, respectively, while the other metals unsurprisingly remain conversionless.

To determine the source of the aforementioned destabilization of adsorbed ethylene, we explore how the redox state of single metal atoms is affected by the change in surface H coverages, and Bader charges of single Pt, Ru, Rh, Ir, and Pd are obtained for each reaction intermediate of acetylene hydrogenation as a function of surface H coverage. This is summarized in Fig. S8 of the [supplementary material](#). The decrease in the positive charge on the single metal atoms (without adsorbate) is seen with the increase in surface H coverages except Pt, as already reported in our previous study on single Pd SAC/ $\text{Fe}_3\text{O}_4(001)$.⁴⁰ Such variation in the charge state of single metal atoms is also reflected in the d states of the metal, where the change of d band, as well as the number of d electrons, can clearly be seen especially for Rh and Pd as a function of surface H coverage (see Table S1 and Fig. S9 of the [supplementary material](#)), mirroring the large changes in activities of these SAC metal atoms seen in Figs. 5 and 6. The single metal atom more positively charged upon the adsorption of acetylene. This tendency is sustained as the hydrogenation reaction proceeds toward the formation of ethane.

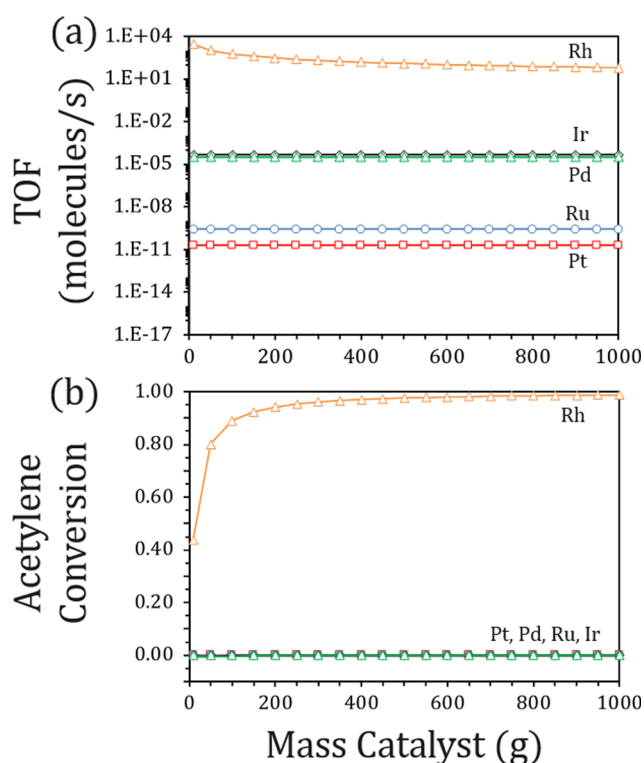


FIG. 6. (a) Activity (measured as TOF) and (b) acetylene conversion of each SAC studied here as a function of the mass of catalyst particles loaded into our model flow reactor. While conversion is only appreciable for the Rh SAC, selectivities for all SACs are essentially unity except for Ir, which maintains ~74% selectivity at all catalyst loadings. $P_{\text{tot}} = 1 \text{ atm}$, $T = 300 \text{ K}$, $\phi_{\text{H}_2} = 10$, and $\theta_{\text{H}_2} = 0.125 \text{ ML}$. Colors used are the same as those used in Figs. 2, 3, and 5.

Compared to the single metal atom, the averaged change in charges of first nearest O atoms is relatively small throughout the process of hydrogenation reaction (see Figs. S10 of the [supplementary material](#)).

We can analyze these results and develop a physical/chemical picture of the acetylene hydrogenation process. Acetylene can be reasonably expected to abstract the H adatoms from their respective hydroxyls as protons. However, the acetylene is clearly reduced, meaning that coupled electron transfer must still occur. Combined with our Bader charge analysis, this suggests that the electron previously attached to the H adatom must spill into the $\text{Fe}_3\text{O}_4(001)$ surface via the deprotonated O atom (a reasonable assertion based on both O electronegativity and simple proximity). This electron must then be passed through the O atom completely since its Bader charge is shown to be essentially unchanged before and after hydrogenation. The electron must then be passed through the metal adatom completely as well to ultimately reduce the acetylene. Since the metal adatoms are, in fact, shown to be partially oxidized, more charge must then be pushed into the hydrogenated acetylene to explain the destabilization seen with the increase in oxidation. At low H coverages, non-hydroxylated O atoms can be expected to partially scavenge the charge from the abstracted H adatom since under-coordinated O atoms easily take up excess charge. However, at

high H coverages, the electron cannot be so easily scavenged and should thus remain largely localized. Based on our Bader charge analysis, this clearly forces more charge into the newly hydrogenated acetylene (see Table S2 of the [supplementary material](#) for details), ultimately destabilizing it and promoting the desorption of the first gas-phase-stable intermediate: ethylene. Such trends in Bader charges indicate that the single metal atoms supported on $\text{Fe}_3\text{O}_4(001)$ mainly act as a conduit for transferring electrons to the adsorbate.

CONCLUSIONS

In summary, we have investigated the hydrogenation of acetylene over $\text{Fe}_3\text{O}_4(001)$ in the presence of single Pt, Ru, Rh, Pd, and Ir atoms as a function of surface H coverage, using DFT and thermal Gibbs free energy corrections. The initial diffusion profile of H indicates that the adsorbed H will diffuse away from each of the single metal atoms, apart possibly from Rh, depending on the temperature used. Furthermore, at low H coverage, adsorbed ethylene is over-stabilized on the single metal atoms, which promotes the hydrogenation of adsorbed ethylene toward ethane over the desorption of adsorbed ethylene to gas phase ethylene. In contrast, at high H coverage, adsorbed ethylene is destabilized, which makes the desorption of adsorbed ethylene energetically favorable over its hydrogenation for all metals. We then inserted Gibbs free energetics into a flow reactor model to examine how these results affect the potential kinetics of these single atom catalysts. This analysis shows that Pt and Pd are the only active metals at low H coverage. While all metals destabilize adsorbed ethylene (except Pt) and all metals promote selectivity to ethylene as H coverage is increased, only Rh shows high enough activity to achieve reasonable acetylene conversions at high H coverage. Pt and Pd become less active with the increase in H coverage, while both Ru and Ir experience a substantial increase in calculated TOF by many magnitudes, just not enough to become truly active given our reactor parameters. However, based on these trends, Pt and Pd can be made more active by decreasing the H coverage or otherwise oxidizing the magnetite surface while Ru, Rh, and Ir may be tuned toward higher activity by increasing the H coverage or otherwise reducing the magnetite surface. Bader charge analysis indicates that the single metal atoms mainly act as a conduit for transferring electrons to the adsorbate during the hydrogenation process; more of the electron charge is forced into the hydrogenated species at higher H coverages, thereby destabilizing them and promoting subsequent ethylene desorption over further hydrogenation and desorption of ethane. Overall, the selectivity toward the production of ethylene can be tuned by the choice of metal catalysts and the redox state of the oxide support, which can be controlled via the surface H coverage.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for (S1) convergence of H_2 adsorption energy over single metal atoms supported on $\text{Fe}_3\text{O}_4(001)$, (S2) adsorption procedure of reaction intermediates over single metal atoms supported on $\text{Fe}_3\text{O}_4(001)$, (S3) DFT-based reaction pathways of C_2H_2 hydrogenation over single metal atoms supported on $\text{Fe}_3\text{O}_4(001)$, (S4) activities and acetylene conversion of single metal atoms supported on $\text{Fe}_3\text{O}_4(001)$ in a model CSTR, (S5)

electronic structures of single metal atoms supported on $\text{Fe}_3\text{O}_4(001)$, and (S6) Cartesian coordinates (in Å) of key structures for single metal atoms/ $\text{Fe}_3\text{O}_4(001)$ system.

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