

# Metal–support frontier orbital interactions in single-atom catalysis

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Single-atom catalysts (SACs) with maximized metal use and discrete energy levels hold promise for broad applications in heterogeneous catalysis, energy conversion, environmental science and biomedicine<sup>1–7</sup>. The activity and stability of SACs are governed by the pair of metal–adsorbate and metal–support interactions<sup>8–10</sup>. However, the understanding of these interactions with their catalytic performance in nature is challenging. Correlations of activity with the charge state of metal atoms have frequently reached controversial conclusions<sup>11–15</sup>. Here we report that the activity of palladium ( $Pd_1$ ) SACs exhibits a linear scaling relationship with the positions of the lowest unoccupied molecular orbital (LUMO) of oxide supports across 14 types of semiconductor. Elevation of the LUMO position by reducing the support particle size to a few nanometres boosts a record high activity along with excellent stability in the semi-hydrogenation of acetylene. We show that the elevated LUMO of support reduces its energy gap with the highest occupied molecular orbital (HOMO) of  $Pd_1$  atoms, which promotes  $Pd_1$ –support orbital hybridizations for high stability and further amends the LUMO of anchored  $Pd_1$  atoms to enhance  $Pd_1$ –adsorbate interactions for high activity. These findings are consistent with the frontier molecular orbital theory and provide a general descriptor for the rational selection of metal–support pairs with predictable activity.

Metal–support interactions (MSIs) in single-atom catalysts (SACs) often induce substantial electronic perturbations to the metal<sup>16,17</sup>, the so-called electronic MSI (EMSI)<sup>18,19</sup>. The charge state of metal atoms inferred from X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure and infrared vibrational spectroscopy has often been used to depict the strength of EMSI and to explain the catalytic activity<sup>11,12,20–22</sup>. However, it leads to intensive debates on which charge state of metal atoms is catalytically more active<sup>11–15</sup>. Meanwhile, the character of discrete energy structures of SACs also raises questions about the *d*-band theory, which is widely adopted for metal nanoparticle catalysts with continuous energy band structures<sup>23</sup>. Alternatively, frontier molecular orbital (FMO) theory, frequently applied to homogeneous molecular catalysts<sup>24,25</sup>, has also been advocated to depict  $M_1$ –adsorbate orbital interactions in SACs<sup>8–10,26</sup>. However, the panoramic illustration of  $M_1$ –support and  $M_1$ –adsorbate orbital interactions in SACs has not yet been demonstrated either theoretically or experimentally to the best of our knowledge. Fundamental questions about the nature of these interactions in single-atom catalysis remain unanswered.

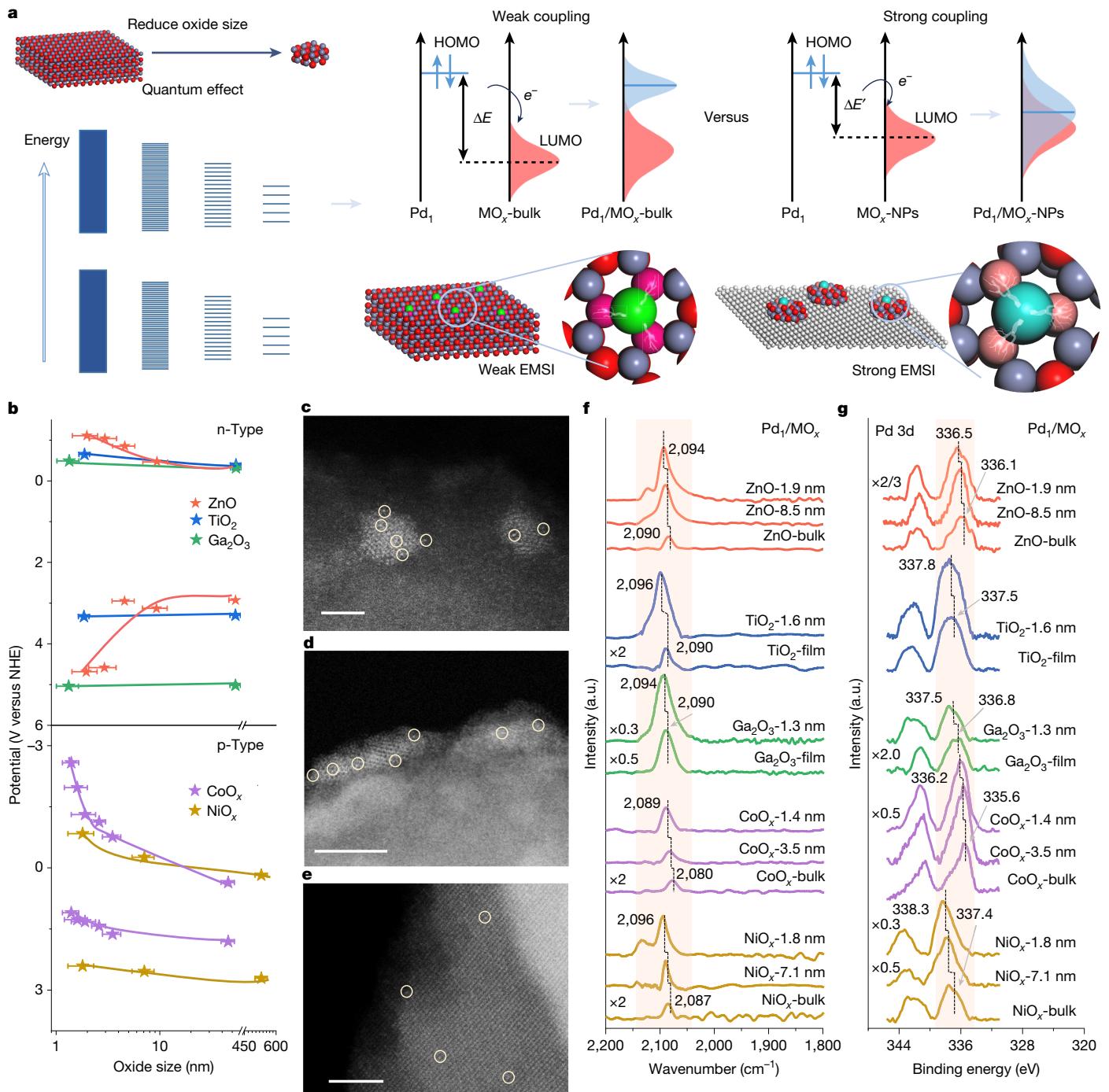
To obtain a deep insight of these interactions, we synthesized 34  $Pd_1$  SACs across 14 types of semiconducting support, in which the size

of supports was also tuned to further modulate their electronic band structures (Fig. 1a). First, a series of semiconducting oxide particles ( $MO_x = ZnO, CoO_x, NiO_x, TiO_2$  and  $Ga_2O_3$  with varied sizes) were grown on a spherical  $SiO_2$  substrate using atomic layer deposition (ALD) by varying the number of ALD cycles<sup>27</sup> (Supplementary Figs. 1–6). These supports are denoted as  $MO_x$ –y nm, where  $y$  is the average size of oxide particles. Ultraviolet–visible (UV–Vis) spectroscopy and Mott–Schottky plots measurements<sup>28,29</sup> showed that the n-type bulk  $ZnO$  has the lowest unoccupied molecular orbital (LUMO) position of  $-0.35$  V (versus normal hydrogen electrode (NHE)), and a band gap ( $E_g$ ) of  $3.29$  eV (Fig. 1b and Supplementary Figs. 7 and 8). As the size of  $ZnO$  decreased from bulk (about  $46$  nm) to about  $1.9$  nm, the LUMO position upshifted gradually to  $-1.12$  V (versus NHE), and the band gap became considerably broader to  $5.82$  eV (Supplementary Figs. 9 and 10), in good agreement with the literature<sup>28</sup>. Similar phenomena were also observed for other  $MO_x$  particles, regardless of whether they were n- or p-type semiconductors<sup>30</sup> (Fig. 1b, Supplementary Figs. 11–20 and Supplementary Table 1). Therein, the upshift of LUMO positions is big for p-type  $CoO_x$  samples, but small for  $NiO_x, TiO_2$  and  $Ga_2O_3$  with the change of particle size.

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# Article



**Fig. 1 | Variation of EMSIs in  $\text{Pd}_1/\text{MO}_x$  SACs on support particle size.**

**a**, Schematic of tailoring EMSIs in  $\text{Pd}_1/\text{MO}_x$  SACs by changing the energy band structures of oxide supports by size variation. **b**, Energy-level diagrams of n- and p-type metal oxides with different particle sizes as determined by TEM, UV-Vis and Mott-Schottky plots. Here the size of the spherical  $\text{SiO}_2$  substrate was used to represent the size of the  $\text{TiO}_2$  and  $\text{Ga}_2\text{O}_3$  films grown on top. Error bars represent the standard deviations of oxide particle size as determined by

TEM. **c–e**, Representative AC-HAADF-STEM images of  $\text{Pd}_1/\text{ZnO}$ -1.9 nm (**c**),  $\text{Pd}_1/\text{ZnO}$ -8.5 nm (**d**) and  $\text{Pd}_1/\text{ZnO}$ -bulk (**e**). The white circles in **c–e** highlight  $\text{Pd}_1$  single atoms on  $\text{ZnO}$ . **f,g**, *In situ* DRIFTS CO chemisorption (**f**) and *In situ* XPS spectra (**g**) in the  $\text{Pd} 3d$  region of  $\text{Pd}_1/\text{MO}_x$  SACs. All samples were pre-reduced at 100 °C for 30 min with 10 vol%  $\text{H}_2/\text{Ar}$  before CO chemisorption and XPS measurements without exposure to air. Scale bars, 5 nm (**c,d**); 2 nm (**e**).

Next,  $\text{Pd}_1$  atoms were selectively deposited on  $\text{MO}_x$  particles using  $\text{Pd ALD}$  to obtain a series of  $\text{Pd}_1/\text{MO}_x$  SACs, in which the selective deposition was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (Supplementary Fig. 21).  $\text{Pd}_1$  atoms were also deposited on some bulk oxide supports ( $\text{Pd}_1/\text{MO}_x$ -bulk) for comparison. The  $\text{Pd}$  loadings in  $\text{Pd}_1/\text{MO}_x$  were all close to 0.1 wt% according to ICP-AES (Supplementary Table 2). Aberration-corrected high-angle annular dark-field scanning transmission electron

microscopy (AC-HAADF-STEM) confirmed the atomic dispersion of  $\text{Pd}$  without the presence of any visible clusters or nanoparticles in all these samples (Fig. 1c–e and Supplementary Figs. 22–26). DRIFTS of CO chemisorption also showed that all  $\text{Pd}_1/\text{MO}_x$ -y nm samples exhibited a single peak at 2,080–2,096 cm<sup>-1</sup>, assigned to linear CO on  $\text{Pd}_1$  atoms<sup>31</sup> (Fig. 1f), but with the absence of bridge-bonded CO (about 1,900–2,000 cm<sup>-1</sup>), further validating the atomic dispersion of  $\text{Pd}$ . We observed blueshifts of CO peak by a few wavenumbers in all sets

of Pd<sub>1</sub> SACs as the size of oxide supports decreased, suggesting that Pd<sub>1</sub> atoms on nanosized oxide particles were more electron deficient, weakening the Pd(4d)-CO(2π\*) bonding through π back-donation<sup>32</sup>. In situ XPS also demonstrated the shifts of Pd 3d peak to higher binding energies by about 0.3–0.9 eV across all sets of samples (Fig. 1g), confirming the increased electron deficiency of Pd<sub>1</sub> atoms. UV–Vis spectra also disclosed more significant changes of the ZnO band structures in Pd<sub>1</sub>/ZnO-1.9 nm and Pd<sub>1</sub>/ZnO-2.8 nm than that in Pd<sub>1</sub>/ZnO-bulk by Pd deposition (Supplementary Fig. 27). Consequently, the above results all indicate the greatly enhanced orbital hybridizations between Pd<sub>1</sub> and nanosized oxide particles.

The semi-hydrogenation of acetylene in excess ethylene, an industrial process for purifying alkene streams<sup>33</sup>, was used as a probe reaction to evaluate their performance. We found that at a high acetylene conversion of 90%, the ethylene selectivity of these catalysts all remained above 90%, except for slightly lower ethylene selectivity on Pd<sub>1</sub>/Ga<sub>2</sub>O<sub>3</sub>-film and Pd<sub>1</sub>/TiO<sub>2</sub>-film (Supplementary Figs. 28–32). However, the intrinsic activity in terms of turnover frequencies (TOFs) per Pd atom increased substantially as the oxide particle size decreased (Fig. 2a). For the set of Pd<sub>1</sub>/ZnO-y nm SACs, the TOF was approximately 25.6 min<sup>-1</sup> for Pd<sub>1</sub>/ZnO-1.9 nm at 80 °C, far superior to the conventional Pd<sub>1</sub>/ZnO-bulk catalyst (1.0 min<sup>-1</sup>) (Supplementary Fig. 28). A tremendous activity enhancement was also observed for Pd<sub>1</sub>/CoO<sub>x</sub>-y nm with the TOFs increased dramatically from 1.0 min<sup>-1</sup> to 22.6 min<sup>-1</sup> (Supplementary Fig. 29), whereas the sets of Pd<sub>1</sub>/NiO<sub>x</sub>, Pd<sub>1</sub>/Ga<sub>2</sub>O<sub>3</sub> and Pd<sub>1</sub>/TiO<sub>2</sub> catalysts showed relatively smaller activity enhancements (Supplementary Figs. 30–32).

Kinetic studies showed that the apparent reaction barriers ( $E_a$ ) decreased considerably for all sets of Pd<sub>1</sub> SACs as the oxide particle size decreased (Supplementary Fig. 33), verifying the remarkable activity improvement. It is worth noting that the activity of Pd<sub>1</sub>/ZnO-1.9 nm is far superior to those Pd<sub>1</sub> SACs reported in the literature<sup>34,35</sup> and in particular approximately 46 times greater than the benchmark Pd<sub>1</sub>/Ag/SiO<sub>2</sub> single-atom alloy catalyst<sup>35</sup> (Fig. 2b and Supplementary Table 3). More importantly, Pd<sub>1</sub>/ZnO-1.9 nm also exhibited excellent stability without any noticeable decrease in either activity or selectivity for at least 100 h (Fig. 2c). By contrast, Pd<sub>1</sub>/ZnO-8.5 nm and Pd<sub>1</sub>/ZnO-bulk both deactivated rapidly along with a continuous decrease in ethylene selectivity. HAADF-STEM imaging showed that Pd atoms remained atomically dispersed in the used Pd<sub>1</sub>/ZnO-1.9 nm and Pd<sub>1</sub>/ZnO-8.5 nm catalysts after the long-term reaction, whereas severe aggregations occurred in the used Pd<sub>1</sub>/ZnO-bulk catalyst (Supplementary Fig. 34). In situ thermogravimetric analysis under hydrogenation conditions showed that coke deposition, another key factor of catalyst deactivation<sup>33</sup>, was also negligible on Pd<sub>1</sub>/ZnO-1.9 nm, but substantially on Pd<sub>1</sub>/ZnO-8.5 nm and Pd<sub>1</sub>/ZnO-bulk (Supplementary Fig. 35). Pd<sub>1</sub>/ZnO-1.9 nm also showed enhanced activity and long-term stability in the selective hydrogenation of 1,3-butadiene (Supplementary Fig. 36), rendering this material promising for a wide range of selective hydrogenation reactions.

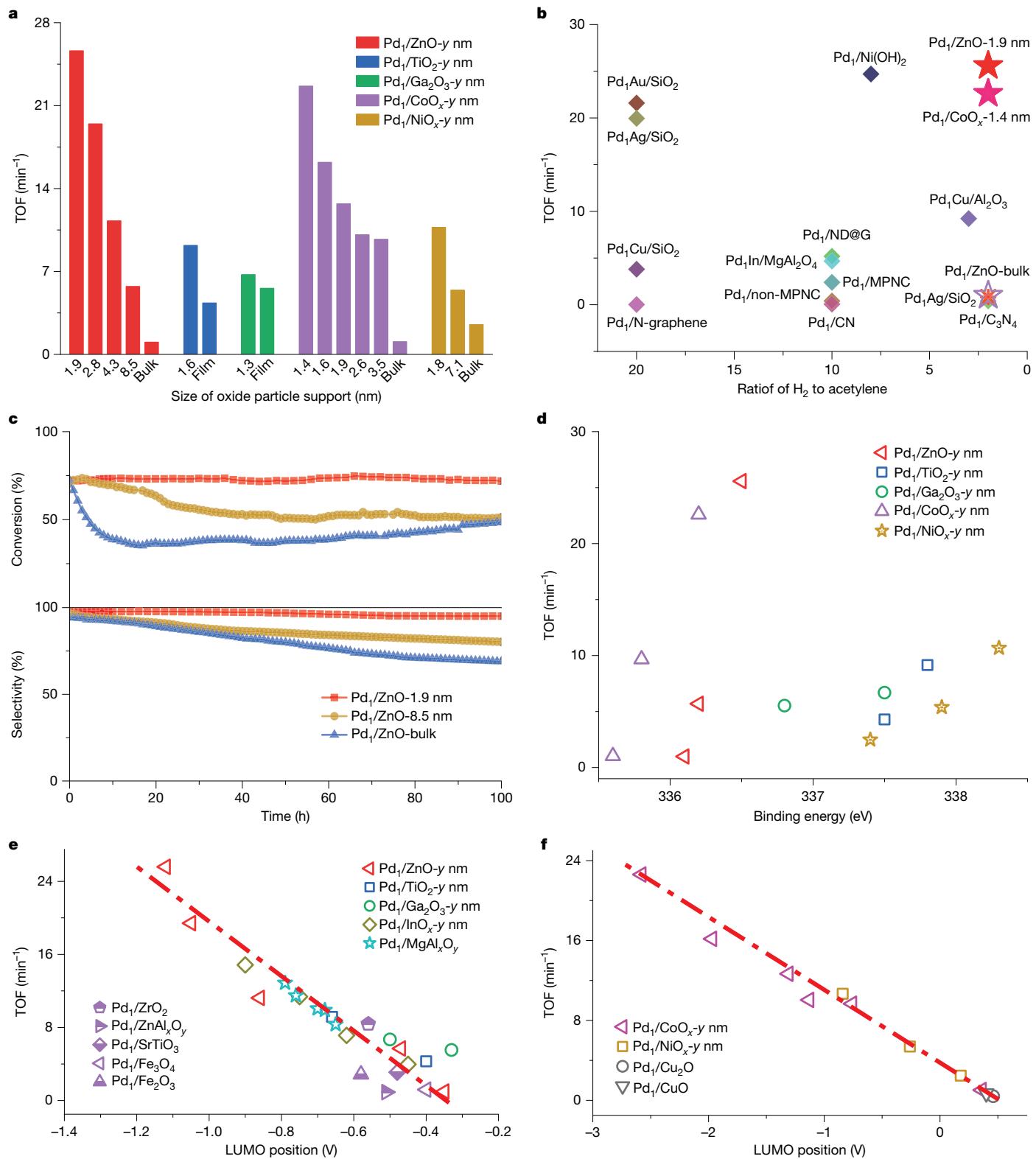
Correlation of the intrinsic activities with the properties of Pd<sub>1</sub> discloses that the activities of Pd<sub>1</sub>/MO<sub>x</sub> SACs showed a tight linear correlation with the Pd charge states in each series of samples (Fig. 2d), in line with the literature<sup>11,12,22</sup>. However, this relation failed when the activities of all sets of samples were compared. By contrast, their activities showed a linear scaling relationship with the LUMO positions of the n- and p-type oxide particle supports in Pd<sub>1</sub>/MO<sub>x</sub> (Fig. 2e,f). To confirm the above linear scaling, 16 more Pd<sub>1</sub> SACs on various bulk semiconducting supports (n-type: ZrO<sub>2</sub>, ZnAl<sub>x</sub>O<sub>y</sub>, SrTiO<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and MgAl<sub>x</sub>O<sub>y</sub> with different Al to Mg ratios, and InO<sub>x</sub> with varied sizes; and p-type: Cu<sub>2</sub>O and CuO) were further synthesized and evaluated (Supplementary Figs. 37–46). Their activities were again in a good fit of the above linear scaling, implying the essential role of the LUMO positions of oxide particles in governing the activity of Pd<sub>1</sub> SACs (Fig. 2e,f and Supplementary Figs. 42–46). This result is in line with the observation of a linear

correlation between the C–H activation energy and the surface reducibility of metal oxides in ref. 36, because the oxygen vacancy formation energy is probably associated with the LUMO position of oxide<sup>28,29</sup>. Here, compared with that for the p-type ones, a steeper slope for the n-type samples, along with relatively larger deviations from the fittings is noticed, which is probably caused by the perturbations from impurity energy levels that are close to the LUMOs of n-type semiconductors<sup>30</sup>. We also measured the LUMO positions of several representative supports using ultraviolet photoelectron spectroscopy (Supplementary Fig. 47 and Supplementary Table 4) and UV–Vis (Supplementary Figs. 9, 42–44). It again showed a similar linear scaling relationship, validating the above results (Supplementary Figs. 48 and 49 and Supplementary Tables 5 and 6).

H<sub>2</sub> activation is a crucial step in SAC-catalysed hydrogenation reactions<sup>11</sup>. We demonstrated that as the oxide particle size decreased, the H–D exchange rates over these Pd<sub>1</sub> SACs also increased greatly in the H–D exchange reaction (Fig. 3a), which was further confirmed by kinetic measurements (Supplementary Fig. 50). These results indicate that the drastic improvement in hydrogenation activity in Fig. 2a can be attributed to the facilitation of H<sub>2</sub> activation. More interestingly, a linear scaling relationship between the LUMO positions of either n- or p-type oxide supports and the activities of Pd<sub>1</sub> SACs was again established (Fig. 3b).

Temperature-programmed desorption (TPD) of H<sub>2</sub> on selected Pd<sub>1</sub>/ZnO-y nm showed that there were two H<sub>2</sub> desorption peaks located at 46 °C and 362 °C for Pd<sub>1</sub>/ZnO-bulk (Fig. 3c), assigned to chemisorbed H<sub>2</sub> on Pd<sub>1</sub> atoms and spillover H<sub>2</sub> on the ZnO support, respectively<sup>37</sup>; the latter case is further confirmed by the observation of noticeable surface hydroxyls formation after H<sub>2</sub> exposure using in situ XPS (Supplementary Fig. 51). As the size of ZnO decreased, the H<sub>2</sub> desorption peak from Pd<sub>1</sub> atoms gradually shifted to 87 °C. Meanwhile, the C<sub>2</sub>H<sub>2</sub> desorption temperature also shifted from 52 °C to 109 °C accordingly (Fig. 3d). Here the increased H<sub>2</sub> desorption temperature remained lower than that of C<sub>2</sub>H<sub>2</sub>, which is consistent with the decreased H<sub>2</sub> reaction order and negative C<sub>2</sub>H<sub>2</sub> reaction order on Pd<sub>1</sub>/ZnO-1.9 nm (Supplementary Fig. 52). The reduction of the underlying ZnO particle size to a few nanometres endows the Pd<sub>1</sub> atoms to be more electron deficient (Fig. 1f,g), which in turn enhances the adsorption of H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> on Pd. Moreover, we also noticed that the peak area of C<sub>2</sub>H<sub>2</sub> desorption on Pd<sub>1</sub>/ZnO-1.9 nm became substantially larger owing to additional C<sub>2</sub>H<sub>2</sub> adsorption on support (Supplementary Fig. 53). Nonetheless, ZnO-1.9 nm itself was inactive, and the H<sub>2</sub> spillover effect on activity was trivial (Supplementary Fig. 54).

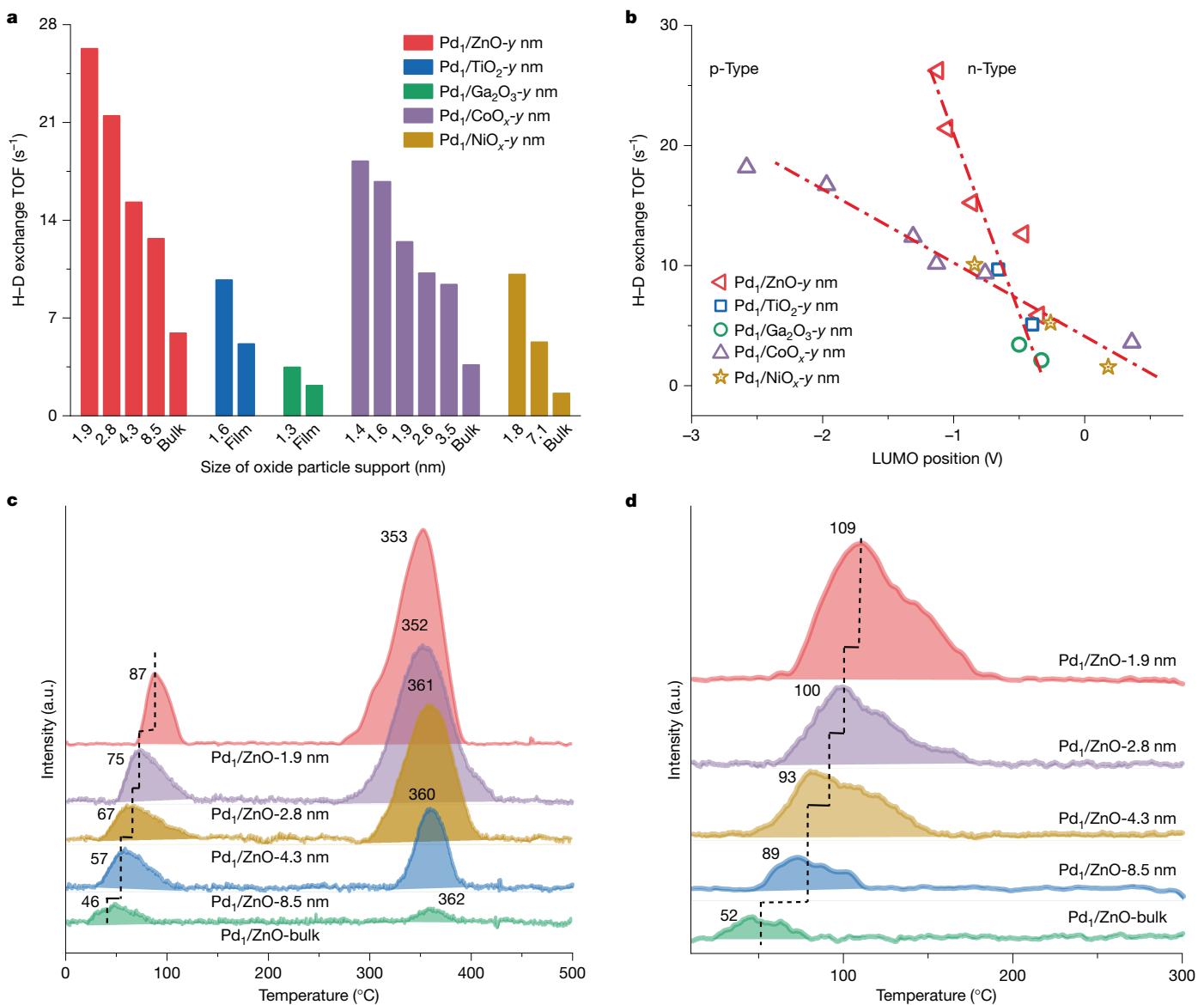
To understand the linear scaling relationship as well as improved stability, density functional theory (DFT) calculations were further performed on the Pd<sub>1</sub>/ZnO system, in which ZnO slab and clusters with different numbers of units (ZnO-x, where x is the number of units) and all nonpolar (10̄10̄) surface exposed were calculated to represent the ZnO bulk and particles with different sizes. Calculations using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional show that the HOMO position of freestanding Pd<sub>1</sub> atom is located at -4.08 eV (Fig. 4a), whereas the LUMO and HOMO of ZnO slab are located at -5.46 eV and -5.68 eV, respectively (Supplementary Fig. 55). As ZnO particle size is reduced to ZnO-30, the LUMOs sharply climb to -4.32 eV, whereas their HOMOs decline, which together broaden the band gap, consistent with the experimental results (Fig. 1b). It is worth noting that the PBE functional might have considerably underestimated the band gap, although the trend of changes in the LUMO positions can be reliable and further corroborated by calculations using a high-level screened hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional (Supplementary Table 7). The reduction of ZnO particle size largely narrows the energy gap between the LUMO of ZnO and the HOMO of freestanding Pd atom. According to the FMO theory<sup>24,25</sup>, this would substantially intensify orbital couplings between these two to lead to a high stability (Fig. 1a).



**Fig. 2 | Catalytic performance of Pd<sub>1</sub>/MO<sub>x</sub> catalysts.** **a**, Intrinsic activities of Pd<sub>1</sub>/MO<sub>x</sub> catalysts at 80 °C in the semi-hydrogenation of acetylene in excess ethylene. **b**, Comparison of the activities of Pd<sub>1</sub>/ZnO-1.9 nm and Pd<sub>1</sub>/CoO<sub>x</sub>-1.4 nm with those of conventional Pd-based SACs reported in the literature at 80 °C. **c**, Acetylene conversion and ethylene selectivity as a function of time during long-term stability tests of Pd<sub>1</sub>/ZnO-1.9 nm, Pd<sub>1</sub>/ZnO-8.5 nm and Pd<sub>1</sub>/ZnO-bulk.

The optimized structures of Pd<sub>1</sub> on ZnO show preferential anchoring of Pd<sub>1</sub> atoms at Zn vacancies with three Pd–O coordinations (Supplementary Fig. 56 and Supplementary Table 8), evidenced by X-ray

absorption spectroscopy (Supplementary Fig. 57 and Supplementary Table 9) and high-resolution HAADF-STEM measurements (Supplementary Fig. 22). The adsorption of Pd<sub>1</sub> on nanosized ZnO is



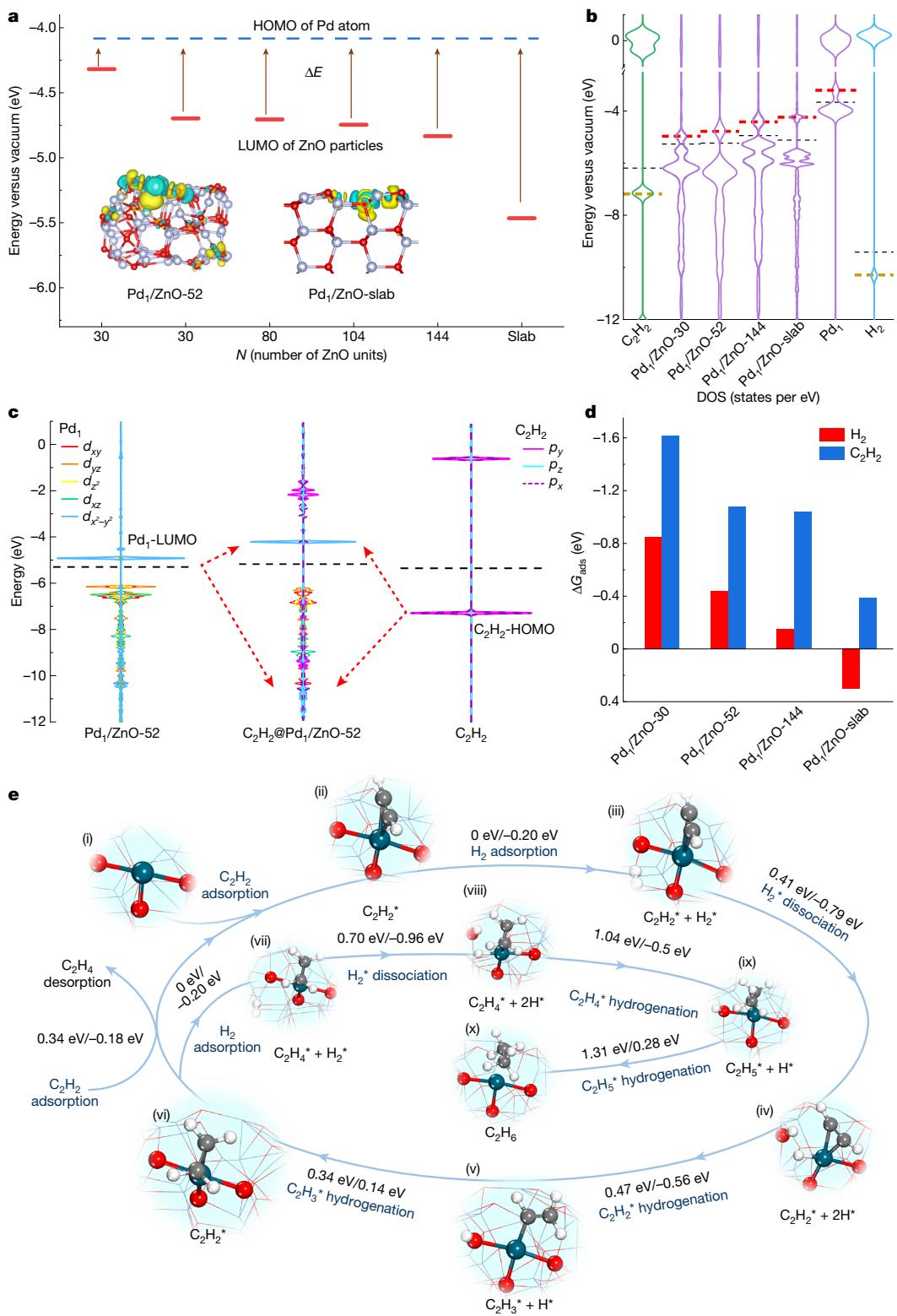
**Fig. 3 | Chemical properties of Pd<sub>1</sub>/MO<sub>x</sub> SACs.** **a**, The H–D exchange rates of Pd<sub>1</sub>/MO<sub>x</sub> SACs at 80 °C. **b**, Linear scaling relationships between the H–D exchange activity and the LUMO positions of n- and p-type semiconducting oxide supports. **c,d**, TPD curves of H<sub>2</sub> (**c**) and acetylene (**d**) over various Pd<sub>1</sub>/ZnO-y nm catalysts.

considerably stronger than on ZnO-slab (Supplementary Table 10). Charge density difference analysis further illustrates markedly stronger orbital couplings along with greater charge transfer from Pd<sub>1</sub> atom to nanosized ZnO in Pd<sub>1</sub>/ZnO-x (Fig. 4a (inset) and Supplementary Figs. 58 and 59), consistent with the DRIFTS CO chemisorption and XPS results (Fig. 1f,g). These results verify the high stability of Pd<sub>1</sub>/ZnO-1.9 nm. When electrons are transferred from Pd to ZnO, the original HOMO of freestanding Pd<sub>1</sub> atoms becomes an unoccupied or partially occupied state (or LUMO) of anchored Pd<sub>1</sub> atoms in Pd<sub>1</sub>/ZnO. Therefore, intensifying Pd<sub>1</sub>-ZnO orbital coupling would enhance charge transfer and cause a greater downshift and broadening of Pd energy levels (Supplementary Fig. 60 and Supplementary Note), which in turn leads to the lowering of the LUMO position of anchored Pd<sub>1</sub> atoms. Deconvoluted partial density of states (PDOS) analysis demonstrates this gradual decline for Pd<sub>1</sub>/ZnO-x (mainly contributed by the  $d_{x^2-y^2}$  orbitals of Pd) with the reduction of ZnO particle size (Fig. 4b and Supplementary Fig. 61), analogous to the ligand effect in homogeneous catalysts<sup>38</sup>.

Regarding the M<sub>1</sub>-adsorbate orbital interactions, we show that the lowered LUMO of Pd<sub>1</sub> atoms on nanosized ZnO exhibits smaller energy

gaps with the HOMOs of C<sub>2</sub>H<sub>2</sub> (mainly contributed by the  $p_y$  and  $p_x$  orbitals of C<sub>2</sub>H<sub>2</sub>) and H<sub>2</sub> molecules (Fig. 4c), which could reinforce the Pd<sub>1</sub>-adsorbate orbital overlapping and enhance their adsorption according to the FMO theory<sup>24,25</sup> (Fig. 4c). As the ZnO particle size decreases from ZnO-slab to ZnO-30, the adsorption energies of H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> on Pd<sub>1</sub> increase substantially from 0.30 eV to -0.84 eV and from -0.38 eV to -1.61 eV, respectively (Fig. 4d), in line with the TPD results (Fig. 3c,d).

Next, we calculated the energy profiles for H<sub>2</sub> activation and C<sub>2</sub>H<sub>2</sub> hydrogenation on Pd<sub>1</sub>/ZnO-52 (the size of ZnO-52 is close to that in Pd<sub>1</sub>/ZnO-1.9 nm) and Pd<sub>1</sub>/ZnO-slab. We demonstrate that compared with Pd<sub>1</sub>/ZnO-slab, Pd<sub>1</sub> in Pd<sub>1</sub>/ZnO-52 draws more electrons from the bonding orbitals of H<sub>2</sub> molecule owing to the increased electron deficiency (Supplementary Fig. 62), which enhances its adsorption (-0.43 eV) and facilitates sequential H–H bond activation (energy barrier of 0.46 eV versus 1.03 eV; Supplementary Fig. 63), consistent with the H–D exchange results (Fig. 3a). In C<sub>2</sub>H<sub>2</sub> hydrogenation (Fig. 4e, Supplementary Fig. 64 and Supplementary Tables 11 and 12), we show that on Pd<sub>1</sub>/ZnO-52, C<sub>2</sub>H<sub>2</sub> first adsorbs on the Pd<sub>1</sub> atom (Fig. 4e, i, ii). Then, H<sub>2</sub> approaches the Pd<sub>1</sub> and dissociates heterolytically with a low



**Fig. 4 | Theoretical insight into orbital coupling on activity in Pd<sub>1</sub>/ZnO SACs.** **a**, Calculated LUMO positions of ZnO particles with different sizes (red horizontal solid line) and the HOMO of unsupported Pd<sub>1</sub> atom (blue dashed horizontal line) relative to vacuum. Shiny brown arrows highlight the energy discrepancies ( $\Delta E$ ) between the ZnO LUMOs and the Pd<sub>1</sub> HOMO. The insets in **a** show the charge density difference of Pd<sub>1</sub> atoms in Pd<sub>1</sub>/ZnO-52 and Pd<sub>1</sub>/ZnO-slab, in which the yellow and cyan regions represent electron accumulation and electron depletion, respectively. The isosurface value is 0.002e Bohr<sup>-3</sup> (ref. 3). **b**, PDOSs of unsupported and ZnO-x-supported Pd<sub>1</sub> with varying ZnO sizes. The PDOSs of C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub> in the gas state are also given here for comparison.

The red and brown horizontal dashed lines indicate the LUMOs of unsupported and ZnO-x-supported Pd<sub>1</sub> and the HOMOs of C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>, respectively. **c**, PDOS analysis of orbital interactions between Pd<sub>1</sub>/ZnO-52 and C<sub>2</sub>H<sub>2</sub> molecule before and after adsorption. **d**, Calculated adsorption free energies of H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> on Pd<sub>1</sub>/ZnO-x with different ZnO particle sizes. **e**, Calculated Gibbs free energy profiles of selective hydrogenation of acetylene on Pd<sub>1</sub>/ZnO-52. The structures of the key steps and intermediates are shown, as well as the energy barriers (left of the slash) and reaction free energies (right of the slash) between the corresponding key steps. Here, Pd, O, C, H and Zn atoms are in cyan, red, grey, white and silver, respectively.

barrier of 0.41 eV (Fig. 4e, iii → iv). In the following, the two H\* (asterisk denotes surface species) sequentially attack C<sub>2</sub>H<sub>2</sub>\* to form C<sub>2</sub>H<sub>4</sub>\*, with barriers of only 0.47 eV and 0.35 eV, respectively (Fig. 4e, iv → vi). Next, C<sub>2</sub>H<sub>4</sub>\* desorbs easily with a low barrier of 0.34 eV with the assistance of competitive C<sub>2</sub>H<sub>2</sub> adsorption (Supplementary Fig. 65), evidenced by the slight increase in the C<sub>2</sub>H<sub>2</sub> reaction order after introducing ethylene to the reaction gas (Supplementary Fig. 52). Here the first addition of H\* to C<sub>2</sub>H<sub>2</sub>\* to form C<sub>2</sub>H<sub>3</sub>\* is the rate-limiting step. Further hydrogenation of C<sub>2</sub>H<sub>4</sub>\* to C<sub>2</sub>H<sub>6</sub>\* is highly unfavourable, with a considerably high barrier of 1.31 eV (Fig. 4e, vii → x). For Pd<sub>1</sub>/ZnO-slab, the hydrogenation of C<sub>2</sub>H<sub>2</sub> becomes considerably laborious (Supplementary Figs. 64, 66 and 67), in which the H\* attack of C<sub>2</sub>H<sub>2</sub>\* to form C<sub>2</sub>H<sub>3</sub>\* has a barrier as high as 0.84 eV. Microkinetic simulations further confirmed the much greater activity of Pd<sub>1</sub>/ZnO-52 than of Pd<sub>1</sub>/ZnO-slab (Supplementary Fig. 68), agreeing well with the experimental results (Fig. 2a). Here, the improved activity is mainly attributed to the greatly enhanced H<sub>2</sub> adsorption and activation (Fig. 2b, Supplementary Fig. 69 and Supplementary Table 13).

Notably, the variations in the Pd coordination structures (for example, Pd–O bond lengths and O–Pd–O bond angles), which are due to variations in the ZnO facet orientations and anchoring sites on the ZnO clusters, do not alter the above result (Supplementary Figs. 70 and 71 and Supplementary Tables 14 and 15). Hydroxyls and oxygen vacancies might also be present on ZnO surfaces but have a minor effect on the activity (Supplementary Figs. 72–75 and Supplementary Tables 16–20).

Calculations were also carried out on the Pd<sub>1</sub>/Ga<sub>2</sub>O<sub>3</sub> and Pd<sub>1</sub>/Co<sub>3</sub>O<sub>4</sub> systems. We show that the variation of Ga<sub>2</sub>O<sub>3</sub> size upshifts only its LUMO position slightly from -5.23 eV to -4.90 eV ( $\Delta(\text{LUMO}) = 0.33 \text{ eV}$ ), which causes minor changes in the adsorption of adsorbates on various Pd<sub>1</sub>/Ga<sub>2</sub>O<sub>3</sub> (Supplementary Figs. 76 and 77 and Supplementary Tables 21 and 22). By contrast, the upshift of the Co<sub>3</sub>O<sub>4</sub> LUMO is relatively large ( $\Delta(\text{LUMO}) = 0.78 \text{ eV}$ ), close to the change in the ZnO LUMO ( $\Delta(\text{LUMO}) = 1.14 \text{ eV}$ ) as its size decreases from the bulk to a Co<sub>11</sub>O<sub>13</sub> cluster, which further leads to considerably enhanced adsorption of adsorbates on Pd<sub>1</sub>/Co<sub>11</sub>O<sub>13</sub> (Supplementary Figs. 78 and 79 and Supplementary Tables 23 and 24). These calculation results agree well with the small activity improvement on the set of Pd<sub>1</sub>/Ga<sub>2</sub>O<sub>3</sub>-y nm SACs but large improvement on Pd<sub>1</sub>/CoO<sub>x</sub>-y nm (Fig. 2a), again unambiguously verifying the essential roles of the LUMO positions of semiconducting supports in single-atom catalysis.

Finally, to gain insight into the failure in the correlation of the activities with the Pd charge states across various supports (Fig. 2d), we further calculated the average ionicity of Pd–O bonds on several oxide supports according to natural bond orbital analysis<sup>39</sup>. We show that the ionicities of Pd–O bonds in average for Pd<sub>1</sub>/ZnO-52 and Pd<sub>1</sub>/ZnO-slab are rather close to each other, approximately 64.1% and 67.3%, respectively, but change substantially from one oxide to another, approximately 81.1%, 66.2%, 52.1%, 75.6%, 67.2% and 71.7% for Co<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, NiO, CuO and ZrO<sub>2</sub>, respectively (Supplementary Fig. 80 and Supplementary Table 25). It demonstrates that ionic and covalent bonding are capricious with the type of support, in line with the literature<sup>16</sup>, thus excluding the charge states of metal atom as a unified descriptor for the activity of SACs across various supports. In line with this observation, both experiments and theory demonstrate that although the higher charge state of Pd<sub>1</sub> atoms in Pd<sub>1</sub>/Ga<sub>2</sub>O<sub>3</sub> than that of Pd<sub>1</sub>/ZnO-1.9 nm (Figs. 1f,g, Supplementary Fig. 81 and Supplementary Table 26), Pd<sub>1</sub>/Ga<sub>2</sub>O<sub>3</sub> shows a considerably lower activity (Figs. 2d and 3a and Supplementary Figs. 50 and 82).

In summary, the identification of the measurable LUMO positions of both n- and p-type semiconducting supports as a universal descriptor for the predictable activity and stability of SACs substantiates the FMO theory experimentally. More importantly, these findings also open a new avenue with high practicability for screening proper

metal–support pairs for high activity and stability, particularly when powered by artificial intelligence<sup>40</sup>.

## Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41586-025-08747-z>.

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## Methods

### Preparation of the SiO<sub>2</sub> sphere substrate

SiO<sub>2</sub> spheres were prepared by the Stöber method<sup>41</sup>. Typically, 17.8 ml of ethyl silicate (TEOS), 5.4 ml of NH<sub>3</sub>·H<sub>2</sub>O, 360 ml of C<sub>2</sub>H<sub>5</sub>OH and 30 ml of H<sub>2</sub>O were added to a 500-ml beaker, and then, the solution mixtures were vigorously stirred at 25 °C for 24 h. Afterwards, the precipitate was centrifuged, washed with ethanol several times and dried at 70 °C overnight. Finally, the SiO<sub>2</sub> spheres were obtained by calcination at 800 °C under 10% O<sub>2</sub>/Ar at a flow rate of 40 ml min<sup>-1</sup> for 5 h in a tube furnace.

### Preparation of MgAl<sub>x</sub>O<sub>y</sub> and ZnAl<sub>x</sub>O<sub>y</sub> spinel supports

MgAl<sub>2</sub>O<sub>x</sub> spinel support was prepared by the coprecipitation method<sup>42,43</sup>. First, 3.85 g of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 11.25 g of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (molar ratio of Mg/Al = 0.5) were dissolved in 100 ml of deionized water at room temperature. Next, NH<sub>3</sub>·H<sub>2</sub>O was added dropwise to the mixed solution to adjust the pH value to 10 ± 0.5. The resulting suspension was vigorously stirred for 2 h and aged for another 2 h at 65 °C. After that, the precipitate was filtered, washed several times with deionized water, and then dried at 100 °C for 12 h. Finally, the precipitate was calcined at 800 °C for 5 h in a static air atmosphere to obtain MgAl<sub>2</sub>O<sub>x</sub> spinel. MgAl<sub>x</sub>O<sub>y</sub> with different ratios of Al to Mg were achieved by varying the amounts of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O during the synthesis process. The ZnAl<sub>x</sub>O<sub>y</sub> spinel support was synthesized using a similar procedure, except that Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was replaced by Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (ref. 44).

### Preparation of MO<sub>x</sub> nanoparticle supports

MO<sub>x</sub> particles were fabricated on an SiO<sub>2</sub> sphere substrate using ALD, which was performed in a viscous flow reactor (ALD-V401-PRO, ACME (Beijing) Technology) with an ultrahigh purity N<sub>2</sub> carrier gas at a flow rate of 200 ml min<sup>-1</sup> at a base pressure of 0.6 torr. The size of the MO<sub>x</sub> nanoparticles was tuned by varying the number of ALD cycles and deposition temperatures.

ZnO ALD was carried out using DEZ and H<sub>2</sub>O as precursors. The DEZ and H<sub>2</sub>O precursors were kept at room temperature. The ALD timing sequences were 100 s, 400 s, 140 s and 400 s for the DEZ exposure time, N<sub>2</sub> purge time, H<sub>2</sub>O exposure time and N<sub>2</sub> purge time, respectively. ZnO ALD was performed on the SiO<sub>2</sub> sphere substrate at 100 °C for 1, 2 and 3 cycles to obtain the ZnO-1.9 nm, ZnO-2.8 nm and ZnO-4.3 nm samples, respectively. ZnO-8.5 nm was obtained by performing ZnO ALD for 5 cycles at 150 °C.

TiO<sub>2</sub> ALD was carried out using TTIP and H<sub>2</sub>O as precursors. The TTIP precursor was heated to 65 °C to obtain sufficient vapour pressure, and H<sub>2</sub>O was kept at room temperature. The ALD timing sequences were 60 s, 300 s, 80 s and 300 s for the TTIP exposure time, N<sub>2</sub> purge time, H<sub>2</sub>O exposure time and N<sub>2</sub> purge time, respectively. To obtain the TiO<sub>2</sub>-1.6 nm and TiO<sub>2</sub>-film samples, TiO<sub>2</sub> ALD was performed on the SiO<sub>2</sub> sphere substrate at 150 °C for 1 and 5 cycles, respectively.

Ga<sub>2</sub>O<sub>3</sub> ALD was carried out using Ga(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>O as precursors, which were all kept at room temperature. The ALD timing sequences were 0.01 s, 480 s, 100 s and 480 s for the Ga(CH<sub>3</sub>)<sub>3</sub> exposure time, N<sub>2</sub> purge time, H<sub>2</sub>O exposure time and N<sub>2</sub> purge time, respectively. To obtain the Ga<sub>2</sub>O<sub>3</sub>-1.3 nm and Ga<sub>2</sub>O<sub>3</sub>-film samples, Ga<sub>2</sub>O<sub>3</sub> ALD was performed on the SiO<sub>2</sub> sphere substrate at 150 °C for 1 and 10 cycles, respectively.

CoO<sub>x</sub> ALD was carried out using CoCp<sub>2</sub> and O<sub>3</sub> as precursors. The CoCp<sub>2</sub> precursor was heated to 90 °C to obtain a sufficient vapour pressure. The ALD timing sequences were 200 s, 300 s, 200 s and 300 s for the CoCp<sub>2</sub> exposure time, N<sub>2</sub> purge time, O<sub>3</sub> exposure time and N<sub>2</sub> purge time, respectively. To obtain the CoO<sub>x</sub>-1.4 nm, CoO<sub>x</sub>-1.6 nm, CoO<sub>x</sub>-1.9 nm, CoO<sub>x</sub>-2.6 nm and CoO<sub>x</sub>-3.5 nm samples, CoO<sub>x</sub> ALD was performed on the SiO<sub>2</sub> sphere substrate at 200 °C for 1, 3, 5, 10 and 20 cycles, respectively.

NiO<sub>x</sub> ALD was carried out using NiCp<sub>2</sub> and O<sub>3</sub> as precursors. The NiCp<sub>2</sub> precursor was heated to 90 °C to obtain a sufficient vapour pressure.

The ALD timing sequences were 100 s, 300 s, 100 s and 300 s for the NiCp<sub>2</sub> exposure time, N<sub>2</sub> purge time, O<sub>3</sub> exposure time and N<sub>2</sub> purge time, respectively. To obtain the NiO<sub>x</sub>-1.8 nm and NiO<sub>x</sub>-7.1 nm samples, NiO<sub>x</sub> ALD was performed on the SiO<sub>2</sub> sphere substrate at 150 °C for 1 and 10 cycles, respectively.

InO<sub>x</sub> ALD was carried out using In(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>O as precursors. The In(CH<sub>3</sub>)<sub>3</sub> precursor was heated to 60 °C to obtain a sufficient vapour pressure, whereas H<sub>2</sub>O was kept at room temperature. The ALD timing sequences were 300 s, 480 s, 300 s and 480 s for the In(CH<sub>3</sub>)<sub>3</sub> exposure time, N<sub>2</sub> purge time, H<sub>2</sub>O exposure time and N<sub>2</sub> purge time, respectively. To obtain the InO<sub>x</sub>-1.3 nm, InO<sub>x</sub>-4.5 nm and InO<sub>x</sub>-film samples, InO<sub>x</sub> ALD was performed on the SiO<sub>2</sub> sphere substrate at 150 °C for 1, 5 and 10 cycles, respectively.

### Preparation of Pd<sub>y</sub>/MO<sub>x</sub>-y nm SACs

Pd<sub>y</sub>/MO<sub>x</sub>-y nm SACs were fabricated by depositing Pd exclusively on MO<sub>x</sub> nanoparticles but not on the SiO<sub>2</sub> sphere substrate using Pd ALD at 150 °C in the same ALD reactor using Pd(hfac)<sub>2</sub> and formalin as precursors. The Pd(hfac)<sub>2</sub> precursor was heated to 65 °C to obtain a sufficient vapour pressure. After temperature stabilization, one cycle of Pd ALD was conducted to prepare the Pd SACs. The ALD timing sequences were 30 s, 200 s, 30 s and 200 s for the Pd(hfac)<sub>2</sub> exposure time, N<sub>2</sub> purge time, formalin exposure time and N<sub>2</sub> purge time, respectively. The resulting samples were denoted as Pd<sub>y</sub>/MO<sub>x</sub>-y nm (where y represents the size of MO<sub>x</sub>). Pd ALD was also carried out on the bare SiO<sub>2</sub> spherical substrate under the same conditions to confirm the selective deposition of MO<sub>x</sub> nanoparticles.

### Preparation of Pd<sub>y</sub>/MO<sub>x</sub>-bulk and Pd<sub>y</sub>/MO<sub>x</sub> SACs

The synthesis of Pd<sub>y</sub> single atoms on conventional oxide and sulfide supports was similar to the above procedure of Pd<sub>y</sub>/MO<sub>x</sub>-y nm synthesis. The ZrO<sub>2</sub>, SrTiO<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> supports were calcined at 800 °C under 10% O<sub>2</sub>/Ar at a flow rate of 40 ml min<sup>-1</sup> for 5 h in a tube furnace before Pd ALD. The remaining samples, ZnO-bulk, CoO<sub>x</sub>-bulk, NiO<sub>x</sub>-bulk, InO<sub>x</sub>-bulk, MgAl<sub>x</sub>O<sub>y</sub>, ZnAl<sub>x</sub>O<sub>y</sub> and Fe<sub>3</sub>O<sub>4</sub>, were all directly used for Pd ALD without pretreatment.

### Characterization

The metal loadings of Pd SACs were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, iCAP7400, Thermo Fisher); therein, all the samples were dissolved in hot aqua regia. The XRD patterns were measured in the range of 10–80° on an X-ray diffractometer (TTR-III, Rigaku, Japan) equipped with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54,178 \text{ \AA}$ ). AC-HAADF-STEM images were recorded on a JEM ARM200F (JEOL) thermal-field emission microscope with a probe Cs-corrector operating at 200 kV. For the HAADF images, a convergence angle of about 23 mrad and a collection angle range of about 68–174 mrad were used for incoherent atomic number imaging. The MO<sub>x</sub> size distribution was obtained by counting more than 200 MO<sub>x</sub> nanoparticles from the STEM images at different locations using ImageJ software. The optical absorption and band gap energy of the sample at RT were characterized by an ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu DUV-3700).

Mott–Schottky plot measurements were performed on a Zahner Zennium electrochemical workstation in a standard three-electrode system. The catalyst supports (20 mg) were first dispersed into a solution of 5 wt% Nafion (10  $\mu\text{l}$ ) and ethanol (1 ml). Then, the catalyst support suspension above (30  $\mu\text{l}$ ) was dropped onto the surface of the glassy carbon electrode (diameter = 5 mm) to obtain the working electrode. A Pt plate was used as the counterelectrode, and Ag/AgCl served as the reference electrode. A 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. The frequencies of the Mott–Schottky plot measurements were set as 300 Hz, 500 Hz, 1,000 Hz and 1,500 Hz. The LUMO position of the semiconductor is approximately equal to the flat-band potential determined by Mott–Schottky plots. Notably, there were

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trivial structural changes after the Mott–Schottky plot measurements (Supplementary Fig. 10).

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO chemisorption was performed on a Nicolet iS10 spectrometer equipped with a mercury cadmium telluride detector and a low-temperature reaction chamber (Praying Mantis Harrick). All samples were first reduced at 100 °C in situ for 30 min under 10% H<sub>2</sub>/Ar with a flow rate of 20 ml min<sup>-1</sup>. Then, the sample was cooled to 25 °C in Ar, and a background spectrum was taken before the catalyst was exposed to 10% CO/Ar at a flow rate of 25 ml min<sup>-1</sup> for 20 min until saturation. Subsequently, the catalyst was purged with pure Ar for 20 min to remove the gas phase CO, and the DRIFT spectrum was collected with 256 scans at a resolution of 4 cm<sup>-1</sup>.

X-ray absorption spectroscopy (XAS) at the Pd K-edge (24.35 keV) was performed at the beamline of the Materials Research Collaborative Access Team at Sector 10 of the Advanced Photon Source, Argonne National Laboratory. The Athena software package was used for the data analysis.

In situ XPS experiments were performed on a ThermoFisher instrument (ESCALAB XI+) equipped with a gas cell (Model HPGC 300, Fermi Instruments) directly mounted to the sample chamber at the Dalian Institute of Chemical Physics. The spectra were recorded using monochromated X-ray irradiation with Al K $\alpha$  ( $h\nu = 1,486.7$  eV) as the X-ray source. After reduction in 10% H<sub>2</sub>/Ar (the flow rate was 20 ml min<sup>-1</sup> and the total pressure was 1 bar) at 100 °C for 30 min in the high-pressure gas cell, the sample was directly transferred to the analysis chamber in UHV without exposure to air. All XPS spectra were recorded at room temperature under UHV conditions (about  $5 \times 10^{-10}$  mbar) and calibrated for the charging effect by considering the C1s peak at 284.6 eV and the Si 2p peak at 103.5 eV.

Ultraviolet photoelectron spectroscopy measurements were performed in a Thermo Scientific ESCALAB 250Xi instrument using a He discharge lamp (He:  $h\nu = 21.22$  eV). The data were acquired with a -10 eV bias during the ultraviolet photoelectron spectroscopy measurements, and Au foil (Alfa Aesar, 99.999%) was used as a reference. The work functions ( $\phi$ ) and HOMO and LUMO positions of these samples were calculated based on equations (1–3), respectively,

$$\phi = 21.22 \text{ eV} - (E_{\text{cutoff}} - E_F) \quad (1)$$

$$\text{HOMO position(vacuum level)} = -(VB - E_F + \phi) \quad (2)$$

$$\begin{aligned} \text{LUMO position(vacuum level)} \\ = \text{HOMO position(vacuum level)} + E_g \end{aligned} \quad (3)$$

where the Fermi edge ( $E_F$ ) starts at the cut-off of photoemission spectra near zero binding energy. The secondary electron emission cut-off energy ( $E_{\text{cutoff}}$ ) was calculated by the extremum in the first-order differential cut-off region. The valence band edge (VB) was calculated by the crossover point between the tangent of the photoemission spectra and the x-axis<sup>45</sup>. The band gap ( $E_g$ ) was determined by UV–Vis spectroscopy.

TPD of acetylene and H<sub>2</sub> was conducted on a Micromeritics Auto-Chem II chemisorption instrument connected to an online mass spectrometer (Pfeiffer OmniStar). Before the TPD measurements, all the samples were first reduced at 100 °C for 30 min under 10% H<sub>2</sub>/Ar at a flow rate of 20 ml min<sup>-1</sup>. Next, the sample was cooled to 10 °C in He, and C<sub>2</sub>H<sub>2</sub> was introduced to the sample for 30 min to ensure saturated adsorption. Subsequently, the sample was purged with He for 1 h to remove the weakly bonded and physically adsorbed C<sub>2</sub>H<sub>2</sub> on the sample. Next, the sample was gradually heated from 10 °C to 300 °C in He at a rate of 10 °C min<sup>-1</sup>, and the C<sub>2</sub>H<sub>2</sub> signal ( $m/z = 26$ ) was recorded by mass spectrometry. The procedure of H<sub>2</sub> TPD was similar to that of C<sub>2</sub>H<sub>2</sub> TPD, except that C<sub>2</sub>H<sub>2</sub> was replaced by H<sub>2</sub> and the temperature range of TPD was changed to 0–500 °C.

In situ thermogravimetric analysis measurements were performed on a TGA550 instrument (TA Instruments) equipped with an evolved gas analysis furnace to quantify coke formation during the semi-hydrogenation of acetylene. The sample was placed in an alumina crucible and heated at a rate of 3 °C min<sup>-1</sup> in 10% H<sub>2</sub>/Ar (20 ml min<sup>-1</sup>) from room temperature to 100 °C and kept for 30 min. Next, the sample was purged with Ar for 15 min before cooling to 80 °C. Then, the acetylene hydrogenation reaction gas, consisting of 1% acetylene, 2% H<sub>2</sub> and 50% ethylene with Ar as the balance gas, was introduced to the reactor for 25 h. The evolution of the sample weight during acetylene hydrogenation was then recorded.

## Catalyst evaluation

The semi-hydrogenation of acetylene in excess ethylene was carried out in a fixed-bed quartz tube reactor at atmospheric pressure. The amounts of Pd<sub>x</sub>/MO<sub>y</sub> catalysts were adjusted to maintain the same Pd content. The sample was diluted with 1.0 g of 60–80 mesh quartz chips to avoid any hot spots. Before the reaction test, all catalysts were reduced in situ in 10% H<sub>2</sub>/Ar at 100 °C for 30 min. Then, reaction feed gas, consisting of 1% acetylene, 2% H<sub>2</sub> and 50% ethylene with Ar as the balance gas, was introduced into the catalyst bed at a flow rate of 20 ml min<sup>-1</sup>. The reaction products were analysed using an online gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector and a capillary column (Rt-Alumina BOND/Na<sub>2</sub>SO<sub>4</sub>, 50 m × 0.53 mm). The acetylene conversion, ethylene selectivity and TOF were calculated using equations (4–6), respectively:

$$C_2H_2 \text{ conversion} = \left( \frac{[C_2H_2]_{\text{in}} - [C_2H_2]_{\text{out}}}{[C_2H_2]_{\text{in}}} \right) \times 100\% \quad (4)$$

$$C_2H_4 \text{ selectivity} = \left( 1 - \frac{[C_2H_4]_{\text{out}}}{[C_2H_2]_{\text{in}} - [C_2H_2]_{\text{out}}} \right) \times 100\% \quad (5)$$

$$TOF = \frac{[C_2H_2]_{\text{in}} \times C_2H_2 \text{ conversion}}{n_{\text{Pd}} \times 100\% \times 22.4 \times 10^{-3}} \quad (6)$$

Here, [C<sub>2</sub>H<sub>2</sub>]<sub>in</sub> and [C<sub>2</sub>H<sub>2</sub>]<sub>out</sub> are the concentrations of acetylene at the inlet and outlet of the reactor, respectively; [C<sub>2</sub>H<sub>4</sub>]<sub>out</sub> is the concentration of ethane at the outlet of the reactor; and  $n_{\text{Pd}}$  is the mole of Pd content. The molar volume of gas under standard conditions is  $22.4 \times 10^{-3}$  ml mol<sup>-1</sup>.

Selective hydrogenation of 1,3-butadiene was also performed in a fixed-bed quartz tube reactor at atmospheric pressure. The reaction feed gas of the acetylene mixture gas was replaced by a mixture of 1,3-butadiene gas, which consisted of 1% 1,3-butadiene and 2% H<sub>2</sub> with Ar as the balance gas. The 1,3-butadiene conversion and butylene selectivity were calculated using equations (7) and (8), respectively:

$$C_4H_6 \text{ conversion} = \left( \frac{[C_4H_6]_{\text{in}} - [C_4H_6]_{\text{out}}}{[C_4H_6]_{\text{in}}} \right) \times 100\% \quad (7)$$

$$C_4H_8 \text{ selectivity} = \left( 1 - \frac{[C_4H_8]_{\text{out}}}{[C_4H_6]_{\text{in}} - [C_4H_6]_{\text{out}}} \right) \times 100\% \quad (8)$$

Here [C<sub>4</sub>H<sub>6</sub>]<sub>in</sub> and [C<sub>4</sub>H<sub>6</sub>]<sub>out</sub> are the concentrations of 1,3-butadiene at the inlet and outlet of the reactor, respectively; [C<sub>4</sub>H<sub>8</sub>]<sub>out</sub> is the concentration of butane at the outlet of the reactor.

## Kinetic measurements

Kinetic measurements were further performed in the same fixed-bed reactor. The amount of Pd catalyst was reduced to maintain the acetylene conversion below 20%. The apparent activation energies were determined on the same reaction system in the temperature range

between 60 °C and 120 °C with the same feed gas composition used for acetylene hydrogenation. To measure the H<sub>2</sub> reaction order, we kept the concentration of acetylene constant at 1% while changing the H<sub>2</sub> concentration from 2% to 9%. To measure the C<sub>2</sub>H<sub>2</sub> reaction order, we kept the concentration of H<sub>2</sub> constant at 6% while changing the C<sub>2</sub>H<sub>2</sub> concentration from 1% to 3%.

### H-D exchange reaction

The H–D exchange reaction was carried out in a fixed-bed quartz tube reactor at atmospheric pressure. The catalyst was diluted with 1 g of fine quartz chips, and the amount of catalyst was adjusted to keep the H<sub>2</sub> conversion below 20%. Before the H–D exchange reaction test, the sample was first reduced in 10% H<sub>2</sub>/Ar at 100 °C for 30 min. Next, a feed gas consisting of 10% D<sub>2</sub> and 10% H<sub>2</sub> with Ar as the balance gas was introduced to the sample at a total flow rate of 20 ml min<sup>-1</sup>. The reaction temperature was varied from 60 °C to 120 °C. The signals of H<sub>2</sub> (*m/z* = 2), HD (*m/z* = 3) and D<sub>2</sub> (*m/z* = 4) were recorded by online mass spectrometry (Pfeiffer OmniStar). The HD exchange activity and kinetic data were also calculated in the same way as those for acetylene hydrogenation.

### DFT calculations

All computations were carried out using the spin-polarized DFT method implemented in the Vienna ab initio Simulation Package (ref. 46). The projector-augmented-wave pseudopotential was used to treat the core electrons, whereas the Perdew–Burke–Ernzerhof exchange-correlation functional of the generalized gradient approximation (GGA) was used to describe the electron interactions<sup>47–50</sup>. Considering the systemic error of the GGA functional for describing the electronic structure of transition metal oxides, it is worth noting that the absolute energy level positions of the LUMO mentioned in the article might not be very accurate, whereas the trend of the energy-level position change with size can be informative and is what we are truly concerned with. A plane-wave cut-off energy of 500 eV was adopted for all calculations and both lattice constants along the periodic direction and atomic positions were optimized with the convergence of energy and force less than 10<sup>-5</sup> eV and |0.05| eV Å<sup>-1</sup>, respectively. The van der Waals interactions were described using the empirical correction in Grimme's scheme<sup>51</sup>. The study of charge transfer was completed by Bader charge analysis<sup>52</sup>. The adsorption energy of a gas molecule is defined as  $E_{\text{ads}} = E_{\text{mol}^*} - E_{\text{mol}} - E^*$ , where  $E_{\text{mol}}$ ,  $E^*$  and  $E_{\text{mol}^*}$  are the total energies of the gas molecule, the Pd<sub>1</sub>SAC and the adsorbate/SAC system, respectively. Moreover, the free energies of the reactant, product and reaction intermediates are defined as  $G = E_{\text{DFT}} + E_{\text{ZPE}} - TS$ , where  $E_{\text{DFT}}$ ,  $E_{\text{ZPE}}$  and TS represent the DFT-calculated electronic energy, zero-point energy and entropy of the system, respectively. The calculated finite-temperature entropy and zero-point energy (ZPE) are listed in Supplementary Table 12. The climbing image nudged elastic band (CI-NEB) method<sup>53</sup> was used to calculate the reaction activation energy barriers, with the transition states verified through a rigorous vibrational frequency analysis.

For the catalyst model, considering the consumption of computing resources and experimental characterization results, a series of approximately pie-shaped ZnO clusters (named ZnO-*x*, where *x* is the number of ZnO units in the chemical formula) mainly exposed to the (1010) surface was constructed to simulate different sizes of support particles. The ZnO-52 support, which has similar sizes to the experimental 1.9 nm particle, was selected as the model for the specific calculation of the reaction. The largest support was modelled by a (3 × 2) supercell of a seven-atomic-layer ZnO(1010) surface (named ZnO-slab), and the bottom three layers of atoms were fixed during optimization. A vacuum layer of more than 15 Å for all the models was used to avoid interactions between periodically repeated structures. Zinc vacancies on the ZnO surface were selected as the anchor sites for a single Pd atom, as shown in Supplementary Table 8.

Natural resonance theory analysis was conducted by using the Natural Bond Orbital (NBO 7.0) and Gaussian16 program package to evaluate the ionicity of surface Pd–O chemical bonds on various oxide supports<sup>54–56</sup>.

### Microkinetic simulations

Microkinetic simulations were performed by using the MKMCXX program<sup>57,58</sup>. The contributions of the elementary steps to the overall reaction were determined through the degree of rate control method<sup>59</sup>. For acetylene hydrogenation to ethylene from 340 K to 370 K on Pd<sub>1</sub>/ZnO-52 and Pd<sub>1</sub>/ZnO-slab, the gas phase contains a mixture of C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub> in a 1:2 molar ratio at a total pressure of 0.1 MPa, similar to the experimental conditions. For Pd<sub>1</sub>/ZnO-52, a gas phase with and without the presence of C<sub>2</sub>H<sub>4</sub> (C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub>:C<sub>2</sub>H<sub>4</sub> = 1:2:0 and C<sub>2</sub>H<sub>2</sub>:H<sub>2</sub>:C<sub>2</sub>H<sub>4</sub> = 1:2:10) was adopted to consider the impact of C<sub>2</sub>H<sub>4</sub> on the reaction kinetics. The reaction rates of each elementary reaction were calculated based on the surface coverages of the steady state. The reaction pathways, including the dissociation of H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>\* hydrogenation to C<sub>2</sub>H<sub>3</sub>\*, followed by C<sub>2</sub>H<sub>3</sub>\* to C<sub>2</sub>H<sub>4</sub>\* and the kick-off of C<sub>2</sub>H<sub>4</sub>\* by C<sub>2</sub>H<sub>2</sub>, were all considered in the kinetic calculations.

### Data availability

All data generated during this study are included in this published article (and Supplementary Information) or can be obtained from the authors upon reasonable request. Source data are provided with this paper.

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STEM and XPS measurements; M.S. performed the ICP measurements; X.S., L.J. and H.-L.J. conducted the Mott–Schottky curve measurements; M.P.L., A.C. and Z.F. carried out the XAS measurements; J.L., X.S., Q.G., B.Y., X.W. and Z.W. wrote the paper. All the authors contributed to the overall scientific interpretation and edited the paper.

**Competing interests** The authors declare no competing interests.

## Additional information

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