Grafting nanometer metal/oxide interface towards enhanced low-temperature acetylene semi-hydrogenation

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Metal/oxide interface is of fundamental significance to heterogeneous catalysis because the seemingly “inert” oxide support can modulate the morphology, atomic and electronic structures of the metal catalyst through the interface. The interfacial effects are well studied over a bulk oxide support but remain elusive for nanometer-sized systems like clusters, arising from the challenges associated with chemical synthesis and structural elucidation of such hybrid clusters. We hereby demonstrate the essential catalytic roles of a nanometer metal/oxide interface constructed by a hybrid Pd/Bi2O3 cluster ensemble, which is fabricated by a facile stepwise photochemical method. The Pd/Bi2O3 cluster, of which the hybrid structure is elucidated by combined electron microscopy and microanalysis, features a small Pd-Pd coordination number and more importantly a Pd-Bi spatial correlation ascribed to the heterografting between Pd and Bi terminated Bi2O3 clusters. The intra-cluster electron transfer towards Pd across the as-formed nanometer metal/oxide interface significantly weakens the ethylene adsorption without compromising the hydrogen activation. As a result, a 91% selectivity of ethylene and 90% conversion of acetylene can be achieved in a front-end hydrogenation process with a temperature as low as 44 °C.
Metal/oxide interface is of great fundamental and practical interest to heterogeneous catalysis, because it raises essential questions regarding the strong metal–support interaction and plays a pivotal role in several catalytic processes. From a structural perspective, a metal/oxide interface is constructed by components that significantly differ from each other in terms of chemical compositions, bonding characters, lattice parameters, and electric and mechanical properties, of which the adhesion structure and chemistry turn out to be a compelling research topic, while from a functional perspective, the chemical bonding and associated charge transfer at the metal/oxide interface allow the modulations of morphology, size, and electronic structures of metals to optimize the bonding strength of reaction intermediates for better catalytic performances. During the past few decades, considerable progress has been achieved in the structural elucidation and tuning of well-defined metal/oxide interfaces that usually adopt a bulk oxide support to facilitate the nucleation, adsorption, or deposition of metals. It is expected that a nanometer metal/oxide interface, perhaps formed by heterografting between metal and oxide clusters, would reinforce the structural and electronic effect to achieve better catalytic performance. However, due to the great challenges in the chemical synthesis and structural elucidation of such hybrid clusters, there are limited insights into the nanometer metal/oxide interface.

As a representative reaction where oxides supported metal catalysts are frequently used, the selective hydrogenation of acetylene to ethylene is subjected to an inherent trade-off between two essential requirements for both high catalytic activity and selectivity: the facile activation of hydrogen and the weak binding of ethylene. Despite the significant progress achieved by Pd-based catalysts, a simultaneous optimization of these two parameters is still challenging, especially in the front-end process where H$_2$ and C$_2$H$_4$ are in large excess. To reach this goal requires a sophisticated tuning of the geometric and electronic structure of Pd, which motivates people to engineer the metal/oxide interface. In most Pd/oxide catalysts, only Pd nanoparticles or isolated Pd atoms are loaded. Unfortunately, Pd nanoparticles are efficient to activate hydrogen at low temperatures, but their strong binding with ethylene favors sequential hydrogenation of ethylene to ethane. Isolated Pd site catalysts including Pd single-atom catalysts and Pd-based intermetallic compounds feature weak π-bonding with ethylene and thus good selectivity in the acetylene hydrogenation reaction, but their concomitant weakened hydrogen activation requires a relatively high reaction temperature (>100 °C) to achieve high conversion of acetylene, which potentially leads to a safety concern in the reactor beds. When Bi/Pd is reduced by the photo-generated electrons to produce Bi$^0$ clusters on TiO$_2$, Pd was deposited onto Bi/TiO$_2$ to form Pd/Bi/TiO$_2$. When Bi/TiO$_2$ and Pd/Bi/TiO$_2$ were exposed to the air, Bi was spontaneously oxidized into Bi$_2$O$_3$ because the Gibbs free energy of the reaction is minus. The synthetic procedure is schematically illustrated in Fig. 1a. Inductively coupled plasma–atomic emission spectroscopy (ICP-AES) suggests that the mass loading of Bi and Pd are 4.9 wt.% and 2.3 wt.%, respectively, close to the feeding ratio. Our previous study has proved that TiO$_2$ has a strong interaction with Bi$^+$, characterized by an unprecedented 1.5 eV upshift of Ti 2p. This interaction ensures the formation of highly dispersed Bi on TiO$_2$ during the following reduction of Bi$^{3+}$. As shown in Supplementary Fig. 1a, b, Bi species are uniformly dispersed on TiO$_2$ as ~1 nm clusters with a Bi loading up to 5 wt.%. Interestingly, close inspection of individual Bi cluster on the TiO$_2$ support by using aberration-corrected annular dark-field scanning transmission electron microscope (ADF-STEM) indicates that the Bi cluster has an ordered α-Bi$_2$O$_3$ structure with a highly distorted lattice, which exhibits relatively weak diffuse peaks in the fast Fourier transform (FFT; Fig. 1b). This is consistent with the literature result, which indicates that the mild oxidation of Bi$^0$ in the air is thermodynamically spontaneous and usually forms monoclinic α-Bi$_2$O$_3$ (monoclinic, P$_2_1$/c (14)). In addition to the intrinsic lattice distortion that blurs the image contrast, the beam-induced structural dynamics of the highly beam-sensitive Bi$_2$O$_3$ clusters may further introduce image blurring, mainly arising from the remarkable knock-on displacements and radiolysis. Despite these beam-induced effects, careful inspection on these ADF-STEM images allows the identification of local contrasts that closely resemble the projected structures and simulated ADF-STEM image of Bi$_2$O$_3$ along [100] (Fig. 1b). Specifically, the structural projection and simulated ADF-STEM image of ordered Bi$_2$O$_3$ feature a wave-shaped arrangement of Bi atomic columns from the [100] projection, while the experimental ADF-STEM image exhibits a similar contrast but with more lattice distortions (Fig. 1b). Accordingly, the FFT pattern of the experimental image exhibits rather diffuse spots compared with those in the FFT pattern of simulated image.

Followed by the secondary deposition of Pd, the clusters of Bi$_2$O$_3$ intergrown with Pd particles can be found according to the low-magnification ADF-STEM images (Supplementary Fig. 1). Besides, Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$ exhibits no signals for Pd in the X-ray diffraction (XRD) patterns (Fig. 2a) while photo-deposited Pd/TiO$_2$ with an identical Pd loading (2.5 wt.%) shows a characteristic Pd(111) diffraction peak at 40.1°, suggesting that pre-deposited Bi$_2$O$_3$ clusters assist in the high dispersion of Pd species in Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$. According to the literature, the pre-deposited component with high work function can serve as a sink of photo-generated electrons, which preferentially reduce the second metal on the surface of the pre-deposited metal. By fixing the loading of Bi at 5.0 wt.%, we can also fabricate Pd$_{0.8}$/Bi$_2$O$_3$/TiO$_2$ (Supplementary Fig. 2), Pd$_{0.2}$/Bi$_2$O$_3$/TiO$_2$, and Pd$_{0.2}$/Bi$_2$O$_3$/TiO$_2$ with high dispersion of Pd (Pd/Bi$_2$O$_3$/TiO$_2$, x represents Pd-to-Bi molar ratio). In contrast, when we increase Pd/Bi ratio to...
to 3.0, the excess Pd also deposits directly on TiO₂. As a result, Pd nanoparticles are obtained (~6.7 nm, Supplementary Fig. 3).

Taking all above results together, Pd species are most likely deposited on the existing Bi₂O₃ clusters although the discrimination between Pd and Bi₂O₃ components is not straightforward by STEM imaging due to their small size and irradiation vulnerability. The nanoscopic elemental distribution can be mapped by a Super-X energy dispersive X-ray spectroscope (EDS) system with superior sensitivity. As shown in Fig. 1e and Supplementary Fig. 4, elemental mappings of Pd and Bi components suggest that

**Fig. 1 Microstructure of Pd₁₀/Bi₂O₃/TiO₂.** a Schematic illustration of the synthetic procedures. b–d STEM images of Bi₂O₃/TiO₂ (b) and Pd₁₀/Bi₂O₃/TiO₂ (c, d). The insets from upper to lower and left to right: HRSTEM images, projected structural models, simulated ADF-STEM images, FFTs from dashed circular regions in HRSTEM images, and FFTs from simulated ADF-STEM images, respectively. e Elemental mapping of Pd₁₀/Bi₂O₃/TiO₂.
their spatial distribution in most cases are correlated. In other words, these clusters are bicomponent with segregated Pd- and Bi-containing hemi-clusters, which unambiguously confirm the Pd-grafted Bi$_2$O$_3$ hybrid cluster structure. Careful inspection on several representative ADF-STEM images of Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$ (Fig. 1c, d and Supplementary Fig. 5) allows the discrimination of Pd- and Bi-containing hemi-clusters from their distinct contrasts for adjacent clusters. The hemi-clusters featuring less bright contrast (marked by circle) are directly attached to brighter ones assigned to Bi$_2$O$_3$ hemi-clusters, further confirming that Pd is grafted onto the surface of Bi$_2$O$_3$ clusters. Notably, most such Pd clusters are identified to bond and hybridize with Bi$_2$O$_3$ clusters without any fixed orientation relationship or facet preference, probably due to the ultra-small size and large strain of the clusters. Two representative atomic-resolution ADF-STEM images of Pd–Bi$_2$O$_3$ nanoclusters with well-resolved Pd- and Bi-containing hemi-clusters are shown in Fig. 1c, d, of which the image contrasts and FFT patterns closely resemble the simulated ones of artificially constructed hybrid cluster models with different orientation relationships between two types of hemi-clusters made of Pd and α-Bi$_2$O$_3$ structures, respectively. The above observations unambiguously validate the proposed Pd–Bi$_2$O$_3$ hybrid structural model. Quite rarely, such Pd clusters are observed to directly nucleate onto the TiO$_2$ substrate.

To confirm the coordination environment of Pd clusters, X-ray absorption fine structure (XAFS) of Pd K-edge EXAFS for Pd/TiO$_2$, Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$, and oxidized Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$–ox (Fig. 2b–e) was performed, as shown in Fig. 2b–e. In the Fourier transformed extended X-ray absorption fine structure (FT-EXAFS) data of Bi L3-edge, it is important to note that a new coordination peak in R-space at about 2.6 Å is observed on Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$ (Fig. 2c), but it is totally absent on other samples containing Bi$_2$O$_3$ (i.e., Bi$_2$O$_3$ and Bi$_2$O$_3$/TiO$_2$). Considering that the only difference between Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$ and Bi$_2$O$_3$/TiO$_2$ is the secondary deposition of 2.3 wt.% Pd on Bi$_2$O$_3$/TiO$_2$, the peak at 2.6 Å should be contributed by the Bi–Pd interaction. Interestingly, the peak can be well fitted by a single Bi–Pd shell (Supplementary Fig. 6 and Supplementary Table 1), suggesting it is a characteristic peak of Bi–Pd coordination. To further prove this idea, the Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$–ox is mildly treated under air at 150 °C (denoted as Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$-ox) to oxidize Pd species while maintaining the structural integrity of Bi$_2$O$_3$ clusters. In Fig. 2e, Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$–ox shows clearly blue shift of the absorption edge position comparing with Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$, indicating the oxidation of Pd after the treatment. Meanwhile, the peak at ~2.6 Å of Bi L3-edge EXAFS diminishes significantly upon oxidation of Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$ (Fig. 2c). The fitting results reveal that the Bi–Pd CN is decreased from 2.9 for Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$ to 1.1 for Pd$_{1.0}$/Bi$_2$O$_3$/TiO$_2$–ox (Supplementary Table 1). Accordingly, this experiment identifies that the peak at 2.6 Å is
from Bi–Pd bond and in turn proves the Pd–Bi pairs across the interfaces of Pd/Bi2O3 hybrid clusters observed by ADF-STEM in Fig. 1c, d. The Bi–Pd interaction eventually changes the coordination environment of Pd in Pd1.0/Bi2O3/TiO2. As compared to Pd foil and Pd/TiO2, the significantly weaker and slightly broader coordination peak in the Pd K-edge EXAFS of Pd1.0/Bi2O3/TiO2 (Fig. 2b) implies a decreased CN of Pd–Pd pairs and distorted structure for the Pd clusters similarly as observed by STEM imaging33. The fitting of Pd K-edge EXAFS (Supplementary Fig. 7 and Supplementary Table 2) further confirms that the presence of Pd–Bi coordination (CN = 4.6) decreases the Pd–Pd CN from 10.0 for Pd/TiO2 to 4.7 for Pd1.0/Bi2O3/TiO2, which is consistent with Pd cluster structure observed by ADF-STEM. The Pd–Bi bond length obtained from the fitting of Pd K and Bi L3 edge is 2.79 ± 0.03 Å, suggesting the observed spatial correlation of Pd–Bi pairs arises from the direct bonding between Pd- and Bi-terminated clusters instead of the Pd–O–Bi moieties that attain a larger interatomic distance (~3.5 Å). Photo-deposition procedure is critical to ensure the formation of direct Pd–Bi bonding in Pd/Bi2O3 clusters as depicted in Fig. 1a. The particle size of Bi2O3 favors an oxygen termination. Pd supported on Bi2O3 would be in direct contact with O rather than Bi. We prepared a Pd/Bi2O3 sample by directly depositing Pd onto commercial Bi2O3 support. Interestingly, no characteristic peak at ~2.6 Å was observed in the Bi L3 EXAFS of Pd/Bi2O3, excluding the presence of Pd–Bi bond (Fig. 2c). In this study, photo-deposition procedure ensures the Pd cluster deposited on reduced Bi0 clusters and allows the formation of Pd–Bi bonding during the synthesis as depicted in Fig. 1a. The Pd–Bi bond preserves during the mild oxidation of Bi to Bi2O3 at room temperature (RT) that occurred after the deposition of Pd onto Bi2O3, as evidenced by the characteristic Bi–Pd peak in Bi L3 EXAFS (Fig. 2c). More interestingly, 36% of this peak preserves even after oxidation in air at a higher temperature of 150°C (Pd1.0/Bi2O3/TiO2-ox). These results clearly indicate the good stability of Pd1.0/Bi2O3/TiO2 downshift slightly to lower BE although the particle size of Pd generally upshifts Pd 3d signals of Pd/TiO2 and Pd1.0/Bi2O3/TiO2 locate at ~334.9/340.0 eV, which are characteristic of Pd31. It is important to note that, due to the differences in the extra-atomic relaxation of metal particles of different sizes, decreasing the particle size of Pd generally upshifts Pd 3d to higher binding energy (BE)32. In this study, the Pd 3d peaks of Pd1.0/Bi2O3/TiO2 show a marked red-shift of the absorption edge energy and decrease in the white line intensity. This indicates the electron-richness of Pd atoms in Pd1.0/Bi2O3/TiO2 compared to those in Pd foil and Pd/TiO2, which most likely arises from the Bi2O3-to-Pd intra-cluster electron transfer. Moreover, Pd1.0/Bi2O3/TiO2 shows a much weaker Pd L3 white line intensity at ~3173 eV than Pd/TiO2 (Supplementary Fig. 10), which indicates an enhanced d-band filling. Such phenomenon is similarly predicted by the Bader charge analysis over Pd8 clusters supported by the Bi2O3 cluster as shown in Supplementary Fig. 11. It is quite surprising to observe such an enhanced d-band filling and associated negative shift of d-band center away from the Fermi level for nanometer-sized Pd clusters, because the strong “size effect” of most supported metals usually leads to a decreased d-band filling and thus positive shift of d-band center toward Fermi level for smaller nanoparticles39. Actually, this has become a limiting factor for applying supported metal nanoparticles in the selective acetylene hydrogenation reaction due to the strong adsorption of ethylene molecules on electron-deficient metals and results in over-hydrogenation. The metal termination of Bi2O3 observed here at the Pd–Bi interface of the hybrid cluster could lead to a strong downshift of its surface conduction band. Similar results were also reported in metal–metal interface of Pd/MgO, Pd/ZnO, Ru/MgO, and Au/TiO238,40–42. Electrons transferred from terminated magnesium or zinc to adsorbed Pd can also result in negatively charged Pd. This charge transfer was ascribed to the band filling modification and the orbital hybridization between substrate and metal atoms40. Specifically, for Pd deposited on magnesium termination, the surface Mg conduction band is shifted toward higher energy and is emptied, while the Pd d band is shifted in the opposite direction and becomes filled. Similar band filling modification and orbital hybridization might also apply to Pd–Bi2O3 system. This allows the Bi2O3-to-Pd intra-cluster electron transfer through direct Pd–Bi bonding across the interface, which leads to a greater filling of high-lying d bands in Pd clusters and largely circumvented over-hydrogenation.
problem. It is important to note that the charge transfer between Pd and Bi is localized in the Pd–Bi interface. Considering the relatively higher concentration of Bi2O3 compared with Pd, the signal of electron-deficient Bi is likely overwhelmed by the signal of unaffected Bi2O3 and is therefore not observed by XPS and XANES.

The unique atomic and electronic structures of heterografted Pd cluster further result in its largely modulated gas adsorption behaviors compared with other supported Pd metals, which can be investigated by the in situ diffuse reflectance infrared Fourier transform spectroscopy using CO as the probe molecule. As shown in Fig. 2f, signals at 2089 and 2059 cm−1 for linear- and bridge-bonded CO34 over Pd/TiO2 redshift to 2076 and 2055 cm−1 for those over Pd1.0/Bi2O3/TiO2, suggesting a strengthened π-back donation of metal d-electrons to π*-orbitals of CO over Pd1.0/Bi2O3/TiO2 and a downshift of d-band center44. This result is well consistent with the XPS and XANES results. It is noteworthy that signals for bridge-bonded CO (1996 and 1948 cm−1) are observed over Pd/TiO2 but invisible over Pd1.0/Bi2O3/TiO2, likely arising from combined size and electronic effects. Specifically, the downshifted d-band center weakens the adsorption strength of CO on Pd44. More importantly, the small size and large structural distortion of Pd clusters disfavor the bridge adsorption mode of CO molecules due to the low average CN and broad distance distribution of Pd–Pd pairs.

Catalytic performance in acetylene hydrogenation. With the unique hybrid cluster structure and Bi2O3-to-Pd intra-cluster electron transfer, Pd1.0/Bi2O3/TiO2 readily serves as a model catalyst to demonstrate the essential catalytic role of a nanometer metal/oxygen interface. The catalytic properties were evaluated in selective hydrogenation of acetylene with excess ethylene, mimicking the front-end condition. In this condition, the thermodynamically favored over-hydrogenation of ethylene with the large excess hydrogen generally leads to an unsatisfied C2H4 selectivity at high C2H2 conversion, accompanied by a thermal runaway. To overcome this problem, a small amount of CO is usually added in the feed stream to reduce the reaction rate so as to improve the C2H4 selectivity10. At very low CO levels, high C2H4 selectivity and C2H2 conversion are difficult to achieve simultaneously. In this study, no CO is added in the feed stream. Both Pd/TiO2 and well-established Pd3.0Ag0.5Al2O3 catalysts30,45 were evaluated for comparison with Pd1.0/Bi2O3/TiO2. The composition and synthesis procedure of the PdAg/Al2O3 catalyst is the same as OleMax@251, a widely used industrial catalyst for acetylene hydrogenation45. The carbon balances are all >99%. Negligible oligomers were formed during the hydrogenation process, likely due to the short contact time and high concentration of hydrogen. According to the literatures, the large excess of hydrogen would change the adsorption modes of C2H2 and C2H4 from C-CH2 vinylidene and C-CH3 ethylidyne to weak π-bonded C2H2 and C2H446,47. As a result, the possible reaction between vinylidene and acetylene to form C4 species as well as the hydrocarbon isomerization and decomposition are suppressed.

Figure 3a plots the C2H4 selectivity as a function of C2H2 conversion on various catalysts. Consistent with the literature results30, the C2H4 selectivity drops rapidly on well-established Pd3.0Ag0.5Al2O3 catalyst once the C2H2 conversion exceeds 40%. On the contrary, Pd1.0/Bi2O3/TiO2 and Pd0.2/Bi2O3/TiO2 catalysts preserve very high selectivity toward C2H4 at much higher C2H2 conversions. Figure 3b compares the C2H4 selectivity at 95% C2H2 conversion. Interestingly, all catalysts except Pd1.0/Bi2O3/TiO2 and Pd0.2/Bi2O3/TiO2 exhibit negative selectivity toward C2H4 due to the over-hydrogenation of ethylene to ethane. Specifically, Pd1.0/Bi2O3/TiO2 exhibits much higher selectivity than 2.3 wt.% Pd/TiO2 regardless of the same Pd loading. In addition, we also synthesized Bi1.0/Pd/TiO2 (x = 0.5, 1, x is the molar ratio of Bi to Pd) by photo-depositing Bi onto 2.3 wt.% Pd/TiO2. Interestingly, both Bi0.5/Pd/TiO2 and Bi1.0/Pd/TiO2 exhibit 100% conversion of C2H2 and negative selectivity toward ethylene (−123% for Bi0.5/Pd/TiO2 and −143% for Bi1.0/Pd/TiO2) at RT. These results suggest that a simple site blocking mechanism cannot explain the beneficial effect of Bi in this study. PdBi/TiO2 composed of PdBi IMC (Supplementary Fig. 9) shows 100% conversion of C2H2 and negative selectivity toward ethylene (−1319%) at RT. The strong exothermic effect of unselective acetylene hydrogenation eventually leads to a runaway temperature up to 58.5 °C. These results exclude PdBi IMC as the active site for Pd1.0/Bi2O3/TiO2 and further indicates the critical role of the nanometer Pd/Bi2O3 interface in the catalytic selectivity of Pd. It is important to highlight that 91% selectivity of C2H4 with 90% conversion of C2H2 is achieved by Pd1.0/Bi2O3/TiO2 at a temperature as low as 44 °C (Fig. 3c). Such an excellent low-temperature performance of acetylene hydrogenation has never been reported previously, suggesting the unique structural and catalytic properties of Pd1.0/Bi2O3/TiO2. Moreover, the C2H2 conversion and C2H4 selectivity remain almost constant over 24 h operating at 40 °C (Fig. 3d). XRD and XAFS also confirm that Pd/Bi2O3 hybrid cluster structure is still maintained (Fig. 2), demonstrating a good long-term stability of Pd1.0/Bi2O3/TiO2.

The variation of Pd-to-Bi ratio leads to an evolution of Pd/Bi2O3 hybrid clusters and major alteration of their catalytic performances in selective acetylene hydrogenation. Usually, the high Pd-to-Bi ratio results in the formation of Pd nanoparticles along with decreased Pd/Bi2O3 clusters, while low Pd-to-Bi ratio results in Pd single atoms. Here the reaction temperature (T90) and C2H4 selectivity at 90% conversion of acetylene are utilized to evaluate the catalytic performance of the samples. As shown in Fig. 3c, T90 increases along with the decrease of Pd-to-Bi ratio, implying that small Pd size is unfavorable to hydrogenation. Under an extreme condition when Pd is atomically dispersed (Pd-to-Bi ratio ≤ 0.1), a very high T90 (>90 °C) will be obtained, likely due to its poor ability of hydrogen activation21. In contrast, the moderate size of Pd in the hybrid clusters allows the efficient activation of hydrogen at much lower temperatures. All these catalysts exhibit quite high C2H4 selectivity. The Pd4.0/Bi2O3/TiO2 with an increased Pd-to-Bi ratio generates Pd nanoparticles and can even convert >90% of acetylene at RT. However, it suffers from the negative C2H4 selectivity at 90% conversion of acetylene. The above results experimentally confirm the trade-off between the conversion of acetylene and the selectivity of C2H4 upon the size effect of Pd, while an optimal catalytic performance is achieved over the Pd clusters stabilized by a nanometer metal–oxide interface.

The origin of such inherent trade-off in the catalytic performance of Pd lies in two aspects: the hydrogen activation and ethylene adsorption. It is generally accepted that the facile dissociative activation of hydrogen on Pd nanoparticles produces too much active H species, which migrate into the Pd lattice and generate β-hydride phase that leads to over-hydrogenation of ethylene43. Accordingly, a negative peak (55–75 °C, Fig. 3e) characteristic for the decomposition of β-hydride phase is observed from the temperature programmed reduction (TPR) profile of Pd/TiO2, which is, however, not observed from that of Pd1.0/Bi2O3/TiO2. These results are consistent with literatures that report high-coordinated Pd ensembles (the case of Pd/TiO2) as active sites for the formation of β-hydride43. As for Pd4.0/Bi2O3/TiO2, the Pd/Bi2O3 hybrid clusters feature a small Pd–Pd CN and nanometer Pd–Bi interface, which prevent the formation of β-hydride. The lack of β-hydride suppresses the over-hydrogenation of ethylene to ethane and therefore contribute to...
the high C₂H₄ selectivity. It is important to highlight that the reduced size of Pd cluster does not compromise the hydrogen activation and thus the catalytic activity. As a result, a low T₉₀ could be achieved on Pd₁.₀/Bi₂O₃/TiO₂ (Fig. 3c).

In addition to the formation of β-hydride, the adsorption behavior of ethylene is also strongly influenced by the Pd structures, which leads to different microcalorimetric profiles. Figure 3f shows the heat flow during the C₂H₄ pulse adsorption process as a function of time for Pd₁.₀/Bi₂O₃/TiO₂, Pd/TiO₂, and Bi₂O₃/TiO₂ at 40 °C. Obvious heat flow signals are observed on Pd/TiO₂ and Pd₁.₀/Bi₂O₃/TiO₂ but are absent on Bi₂O₃/TiO₂ and blank test, demonstrating that C₂H₄ is adsorbed on Pd instead of on Bi₂O₃. It is interesting to note that the amplitude of the heat flow signal of Pd₁.₀/Bi₂O₃/TiO₂ is much smaller than that of Pd/TiO₂. The calculated adsorption heat of Pd₁.₀/Bi₂O₃/TiO₂ (~5.9 kJ mol⁻¹) is significantly lower than that of Pd/TiO₂ (~234.5 kJ mol⁻¹), clearly indicating a much weaker ethylene adsorption on Pd₁.₀/Bi₂O₃/TiO₂. These observations can be attributed to the unique geometric and electronic structure of hybrid cluster, similar to the results reported in the alloying of Pd.⁵⁰,⁵¹ The low Pd–Pd coordination and the Bi₂O₃-to-Pd intra-cluster electron transfer likely change the adsorption configuration of C₂H₄ from stable ethylidyne to weak π-bonded C₂H₄ and promote the desorption of ethylene as the desired product. To confirm this hypothesis, we further performed the temperature programmed desorption of ethylene by monitoring the mass signal of m/e = 27 (Supplementary Fig. 12). According to the literature, the peak at ~65 °C could be assigned to weak π-bonded ethylene species, which readily desorb without decomposition. The peak centered at ~115 °C originates from di-σ-bonded ethylene, which undergoes decomposition followed by the recombination of surface hydrocarbon species and hydrogen to produce ethylene and ethane. Compared with Pd/TiO₂, Pd₁.₀/Bi₂O₃/TiO₂ exhibits a much weaker peak at ~115 °C but a significantly larger peak at 65 °C. These results confirm that the adsorption configuration of C₂H₄ is changed from the strong σ-bonding for Pd/TiO₂ to weak π-bonding for Pd₁.₀/Bi₂O₃/TiO₂.

**Reaction mechanism investigated by DFT calculations.** DFT calculations were performed to further provide insights into the molecular-level mechanisms of acetylene hydrogenation on experimental Pd₁.₀/Bi₂O₃/TiO₂ catalyst. Model of Bi₂O₃-supported Pd₈ cluster catalyst was built according to the experimental characterization results and the structure of which is shown in Fig. 4a (please see the details of model development in Supplementary Information). In this model, the size of Pd cluster on Bi₂O₃(100) is around 1.6 nm × 1.5 nm. In addition, this Pd cluster shows an average Pd–Pd CN of 4.0, which is close to the experimental values measured, i.e., 4.7 ± 0.5 (Supplementary Table 2). The Pd–Bi pair distribution function of the Pd₄ cluster structure is shown in Supplementary Fig. 13. In this figure, the dominant peak appears at ~2.75 Å, which is smaller that in
the PdBi intermetallic model (~2.91 Å, Supplementary Table 3). In addition, Bader charge analysis suggests that Pd atoms in PdBi IMC (average charge of $-0.36$ e) model are more electron-rich than those in Pd-Bi$_2$O$_3$ hybrid clusters model ($-0.21$ e). These results are well consistent with Pd K-edge XANES and Pd 3$d$ XPS shown in Supplementary Fig. 9, which therefore validate the reliability of the Pd$_8$ cluster model. The possibility of hydride formation over the Pd cluster was studied, and it was found that hydrogen atoms prefer to adsorb at surface Pd sites after optimization (Supplementary Fig. 14), suggesting that formation of Pd hydride from this cluster is difficult, which again agrees well with the results shown in Fig. 3e.

It was reported that C-CH$_2$ vinylidene and C-CH$_3$ ethylidyne are energetic stable and important spectator species in acetylene hydrogenation$^{53-55}$. However, in the front-end condition where H$_2$ is in large excess, vinylidene and ethylidyne are readily hydrogenated and are insignificant at steady-state conditions$^{10}$. Besides, the adsorption configurations of C$_2$H$_2$ and C$_2$H$_4$ also depend on the catalyst structure. For the Pd cluster structure studied in this work, it is found that the hydrogenation of CH≡CH to CHCH$_2$ has the lowest activation energy ($E_a$) of 0.74 eV compared with the dehydrogenation or hydrogen shift of CH≡CH (Supplementary Table 4). This strongly suggests that formation of CCH$_2$ would be unfavorable on the Pd cluster structure. Similarly, the hydrogenation of CHCH$_2$ to CH$_3$CH$_2$ has the lowest $E_a$ among all reactions starting from CHCH$_2$, again indicating that the spectator species CCH$_3$ is hard to form on Pd cluster model (please see Supplementary Information for details). To this end, the effects of these species are not discussed here.

The energy profile of acetylene hydrogenation to ethane over this Pd cluster is shown in Fig. 4b, and the corresponding optimized configurations of surface intermediates and transition states are shown in Supplementary Fig. 15. Meanwhile, the energy profile on Pd(111) representing Pd foil is also shown in Fig. 4b for comparison. The calculated barriers are generally consistent with the reported values (Supplementary Table 5), demonstrating that our calculated results are reliable. In addition, we further calculated the vibrational frequency based on the transition state structures on Pd(111). All the transition states were characterized to possess only one imaginary frequency along the bond formation of hydrogenation reactions. These results further demonstrate the reliability of the constrained minimization method that we used in this work. As can be seen from Fig. 4b, the adsorption of C$_2$H$_2$ over Pd(111) and Pd$_8$ cluster is...
exothermic, and the transition state energies of C₂H₂ hydrogenation to C₂H₄ on both surfaces are below the energy of gaseous C₂H₂, suggesting that the hydrogenation processes should be facile. The semi-hydrogenation product C₂H₃ would either desorb from the surface or undergo further hydrogenation to ethane (C₂H₆). In Fig. 4b, the transition state energy of C₂H₄ hydrogenation on Pd₈ cluster is above the gaseous C₂H₄ energy, suggesting that desorption of C₂H₄ from the Pd₈ cluster may be favored compared with its further hydrogenation to C₂H₂. Herein, the difference between the barriers for further hydrogenation and desorption of ethylene can be used to estimate the possibility of selective C₂H₄ formation.⁵⁻⁶⁰ In this framework, a more positive value of \( E_{\text{hydro}} - E_{\text{ads,C₂H₂}} \), where \( E_{\text{hydro}} \) is the effective hydrogenation barrier of C₂H₄ to C₂H₂ and \( E_{\text{ads,C₂H₂}} \) is the absolute value of C₂H₂ adsorption energy, corresponds to higher C₂H₄ selectivity. The calculated values of \( E_{\text{hydro}} - E_{\text{ads,C₂H₂}} \) over Pd₈ cluster and Pd(111) are 0.53 and 0.31 eV, respectively, demonstrating higher C₂H₄ selectivity over the Pd₈ cluster than Pd(111), which is consistent with the experimental results. We further carried out electronic structure analysis to understand the weaker adsorption of reaction intermediates over the Pd cluster than Pd(111). In Fig. 4c, we plotted the density of states projected onto d-electrons of the surface Pd atom where C₂H₄ adsorbs over Pd(111) and Pd cluster, and the d-band center (\( \epsilon_d \)) were calculated to be −1.53 and −1.79 eV, respectively. According to the d-band center theory,⁶¹ the more negative \( \epsilon_d \) indicates weaker binding to adsorbates, which is in agreement with the trend of adsorption energies calculated for the reaction intermediates over Pd(111) and Pd cluster. In addition, the \( \epsilon_d \) of each Pd atom on Pd cluster was found to be correlated with \( E_{\text{ads,C₂H₂}} \) over Pd(111). The more negative \( \epsilon_d \) generally corresponds to weaker adsorption of C₂H₄. The most stable adsorption of ethylene, corresponding to the black solid square in Fig. 4d and *C₂H₄ in Fig. 4b, gives rise to the \( E_{\text{ads}} \) of −0.54 eV, which is slightly weaker than that over Pd(111), i.e., −0.57 eV. However, one can also see that C₂H₄ adsorbs much weaker at other Pd sites over the Pd₈ cluster (shown as black hollow squares), therefore Pd₈ cluster shows weaker adsorption on average compared with those sites over Pd(111) where all the surface sites are identical. C₂H₃ would be more likely to desorb from the Pd cluster, resulting in the high C₂H₄ selectivity observed.

Our findings demonstrate the essential catalytic roles of a nanometer metal/oxide interface in selective hydrogenation of acetylene. Pd₈-Bi₂O₃ hybrid clusters feature a small Pd–Pd CN and intra-cluster electron transfer, which enables a weak C₂H₃ adsorption without compromising the H₂ activation activity. The superior low-temperature catalytic performance of Pd₈-Bi₂O₃ nanocluster ensembles over Pd single atom and nanoparticles might open new opportunities for fundamental research of hybrid nanoclusters. Besides, the demonstrated stepwise photochemical strategy also provides a new path for fabricating hybrid nanoclusters and nanometer metal/oxide interface.
atoms of Bi$_2$O$_3$(100) component were fixed to simulate bulk structure of Bi$_2$O$_3$, while the other atoms were fully relaxed. The vacuum layer was set higher than 12 Å to avoid spurious interaction between adjacent slabs. The k-point grid used in the surface Brillouin zone was $1 \times 1 \times 1$ for all the calculations. More details about the structure development are provided in Supplementary Information (Supplementary Figs. 16 and 17).

**Data availability**

All the data supporting the findings of this study are available within the article and its Supplementary Information files or from the corresponding authors upon reasonable request. Source data are provided with this paper.

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Author contributions

J.F. and S.Z. designed the study. S.Z. and B.L. performed most of the experiments. W.Y., C.Z., Y.Z., and Y.W. performed the electron microscopy characterization. K.Y. and B.Y. finished the DFT calculations. L.M., Y.D., J.M., and Z.J. carried out the X-ray structure characterization and analysis. W.H. carried out the microcalorimetric measurements. Z.G. and Y.C. performed the in situ NAP-XPS studies. L.L., J.L., and L.X. performed the TPR and TPD measurements. S.Z., K.Y., J.R., B.Y., and Y.Z. wrote the paper. All authors interpreted the data and contributed to the preparation of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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