Synergizing metal-support interactions and spatial confinement boosts dynamics of atomic nickel for hydrogenations

Jian Gu1,7, Minzhen Jian1,7, Li Huang2,7, Zhihu Sun2, Aowen Li3, Yang Pan2, Jiuzhong Yang1,2, Wu Wen2, Wu Zhou3,4, Yue Lin3,1, Hui-Juan Wang5, Xinyu Liu1, Leilei Wang1, Xianxian Shi1, Xiaohui Huang1, Lina Cao1, Si Chen1, Xusheng Zheng2, Haibin Pan2, Junfa Zhu3,4, Yue Lin2, Aowen Li3, Yang Pan2, Jiuzhong Yang1,2, Wei-Xue Li1,6, and Junling Lu1,6

Atomically dispersed metal catalysts maximize atom efficiency and display unique catalytic properties compared with regular metal nanoparticles. However, achieving high reactivity while preserving high stability at appreciable loadings remains challenging. Here we solve the challenge by synergizing metal-support interactions and spatial confinement, which enables the fabrication of highly loaded atomic nickel (3.1 wt%) along with dense atomic copper grippers (8.1 wt%) on a graphitic carbon nitride support. For the semi-hydrogenation of acetylene in excess ethylene, the fabricated catalyst shows extraordinary catalytic performance in terms of activity, selectivity and stability—far superior to supported atomic nickel alone in the absence of a synergizing effect. Comprehensive characterization and theoretical calculations reveal that the active nickel site confined in two stable hydroxylated copper grippers dynamically changes by breaking the interfacial nickel–support bonds on reactant adsorption and making these bonds on product desorption. Such a dynamic effect confers high catalytic performance, providing an avenue to rationally design efficient, stable and highly loaded, yet atomically dispersed, catalysts.

Supported atomically dispersed catalysts (SADCs) have recently drawn great attention in numerous reactions for their maximized atom efficiency1,2. Exclusive site homogeneity, distinct energetics and spatial site confinement make SADCs very attractive in high selectivity and alleviated coke formation in the conversion of hydrocarbons3–5, sharply distinct from the low selectivity and heavy coke formation on metal nanoparticle (NP) catalysts6. However, owing to drastically increased surface free energies, the stability of atomically dispersed metal species under reaction conditions, especially at high metal loadings, has been the key issue to substantially limit the overall performance, restraining their practical applications7.

Realization of a highly loaded and stable SADC for hydrogenation reactions is particularly challenging, because atomically dispersed metal species often show higher mobility in reducing environments8. For instance, in the semi-hydrogenation of acetylene in excess ethylene, a crucial industrial process operated at a scale of billions of tons per annum to purify alkene streams9,10, severe metal aggregation and heavy coke formation—an even worse scenario to further accelerating catalyst deactivation to a shorter lifetime11. Increasing metal-support interactions (MSIs)12,13 or confining active metal species in restrained spaces (for example, micropores)14,15 are two widely adopted methodologies to achieve higher stability. However, excessively strong MSIs might over-stabilize the active sites and cause low activity1,2,16; confinement of metal species in micropores might also limit mass transfers14,17. Consequently, a seesaw relation between stability and activity has been often observed, obscuring efforts for catalytic performance optimizations18–20.

In this work, we report that the challenge can be solved by synergizing MSIs and spatial confinement to break the activity-stability seesaw of SADCs at high metal loadings. Specifically, strong Ni–N/C interaction and spatial confinement by dense atomic Cu grippers (8.1 wt%) on a graphitic carbon nitride (g-C3N4) support are synergized to endow great structural flexibility of highly loaded (3.1 wt%) atomic Ni with reversible bond breakings and makings on reactant adsorption and product desorption, respectively. Such a dynamic effect not only facilitates acetylene adsorption for high activity but also ensures high thermal/chemical stability and unprecedented inhibition of coke formation.

Results

Synthesis and catalytic performance. As it contains periodic triangular cavities with six coordinately unsaturated pyridinic nitrogen (Npy) atoms, g-C3N4 provides a perfect platform for anchoring active and dense metal species19,20. Screening of metals among groups VIII and IB by density functional theory (DFT) calculations revealed that Ni and Cu atoms exhibit strong binding to g-C3N4 underneath...
along with low formation energy (Supplementary Table 1); therefore, they are the most promising candidates for highly loaded and stable metals on g-C3N4 with atomic dispersion.

Inspired by these results, atomic layer deposition (ALD), a gas-phase technique relying on sequential self-limiting molecular-level surface reactions23,24, was employed to deposit Cu and Ni with near-atomic precision25,26. Atomic Cu grippers were first fabricated on g-C3N4 by Cu ALD (denoted as Cu1/g-C3N4), as confirmed by X-ray absorption spectroscopy and aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), where the saturated loading was ~11.2 wt% (Supplementary Figs. 1a and 2–5 and Supplementary Table 2). Ni Cu1/g-C3N4 catalysts (y is the atomic ratio of Ni to Cu) were synthesized by depositing Ni on subsaturated Cu1/g-C3N4 using NiO ALD, as shown in the schematic and morphology in Supplementary Figs. 6 and 7, respectively. Therein, the Ni loadings decreased with an increase in Cu loadings (Supplementary Fig. 1b), which implies that at Cu subsaturation coverages, the open Npy sites along with neighbouring Cu atoms provide anchoring sites for guest atoms, analogous to pincer ligands in organometallic chemistry27. For comparison, Ni1/g-C3N4 SADCs were also fabricated by NiO ALD (Supplementary Figs. 8–12 and Supplementary Table 3). HAADF-STEM measurements showed that Cu1/g-C3N4, Ni1/g-C3N4, NiCu1/g-C3N4, and NiCu1/g-C3N4 were thermally stable at 350°C under H2 (Supplementary Figs. 13–15), in line with the above theoretical prediction.

Next, three samples, namely, Cu1/g-C3N4 (8.1 wt%), Ni1/g-C3N4 (3.1 wt%), and NiCu1/g-C3N4 (8.1 wt%), were evaluated in the selective hydrogenation of acetylene in excess ethylene. We found that compared with Cu1/g-C3N4 and Ni1/g-C3N4, NiCu1/g-C3N4 showed much higher activity by achieving 100% conversion at ~170°C (Fig. 1a). Importantly, the ethylene selectivity was as high as 90% even at full acetylene conversion (Fig. 1b), which is desirable for practical applications. The corresponding activity was 7.01 h−1 at 160°C, about 11 and 58 times higher than that of Ni1/g-C3N4 and Cu1/g-C3N4, respectively (Fig. 1c). Kinetics measurements further confirmed the activity trend (Supplementary Fig. 16).

Remarkably, in addition to high thermal stability, NiCu1/g-C3N4 showed unprecedented chemical stability under hydrogenation conditions, without any visible decline in either activity or selectivity for at least 350 h at 160°C, and the used sample remained structurally intact (Fig. 1d and Supplementary Figs. 17–19). In sharp contrast, Ni1/g-C3N4 showed a slight activity increase approximately in the first six hours, and then rapidly deactivated with an activity loss of ~50% in about 50 h. X-ray diffraction (XRD) and HAADF-STEM measurements also revealed severe agglomeration of Ni atoms into Ni particles (Supplementary Figs. 19 and 20).

State-of-the-art in situ synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) revealed that besides C2 products, considerable gaseous C2–C5 species were produced from Ni1/g-C3N4 (Fig. 1e and Supplementary Fig. 21), indicating the facile formation of green oils. In contrast, no higher hydrocarbons formed on NiCu1/g-C3N4, except a trace amount of C2H4. Temperature-programmed desorption (TPD) SVUV-PIMS measurements of the two samples after 2 h of reaction further showed negligible accumulation of C4 species on Ni1/g-C3N4 (Fig. 1f and Supplementary Figs. 22 and 23), unambiguously confirming the complete inhibition of the formation of green oils on Ni1/g-C3N4. Coke formation was further quantitatively monitored by in situ thermogravimetric analysis (TGA) under hydrogenation conditions. After 12 h, the weight gain of Ni1/g-C3N4 was negligible, close to the thermal noise. However, Ni1/g-C3N4 showed a considerable weight increase by 7.6% (Fig. 1g), in line with the above SVUV-PIMS measurements. Meanwhile, the XRD data revealed the formation of graphitic coke on Ni1/g-C3N4 (Supplementary Fig. 19), but not for NiCu1/g-C3N4. Clearly, the capability of coke inhibition and long durability achieved on NiCu1/g-C3N4 is unprecedented, far superior to the benchmark catalysts reported in the literature (Table 1 and Supplementary Tables 4–6). Besides the above, NiCu1/g-C3N4 also exhibited extraordinary performance in the semi-hydrogenation of 1,3-butadiene in excess propene (Supplementary Fig. 24), rendering this material promising for wide applications.

**Structural characterization.** Statistical analysis of atomic-resolution STEM images of these samples found that there were mainly three structural motifs, namely, single atoms, linear trimers and triangular trimers (Fig. 2a and Supplementary Figs. 5, 7, and 12). For Cu1/g-C3N4, single atoms were the most populated (68%), followed by linear trimers (20%) and triangular trimers (12%) (Supplementary Fig. 25). Subsequent Ni deposition forms Ni1/g-C3N4, and linear trimers increased dramatically (71%) at the expense of single atoms (18%), while triangular trimers remained at ~11% (Fig. 2b). This suggests that most of the predepicted single Cu atoms were likely bridged by Ni atoms to form new linear trimers (Supplementary Fig. 6). Atomic-resolution electron energy-loss spectroscopy (EELS) elemental mapping of one linear trimer at a relatively low beam current to minimize electron-beam perturbations (Supplementary Fig. 26) further provided strong evidence of the linear Cu–Ni–Cu trimer structure, by identifying a Ni atom in the middle and two Cu atoms on the adjacent sides (Fig. 2c,d). The overall lengths of the linear trimers were 5.66 ± 0.20 Å comprising two unequal atom–atom distances of 2.61 ± 0.14 and 3.04 ± 0.13 Å on average (Supplementary Fig. 7).

To confirm direct Cu–Ni interactions, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO chemisorption measurements were carried out. As shown in Fig. 2e and Supplementary Fig. 27, Cu1/g-C3N4 showed one dominant peak at 2,103 cm−1 and a weak shoulder at 2,123 cm−1, assigned to linear CO on isolated Cu+ ions and trimers, respectively. CO chemisorption on Ni1/g-C3N4 was negligible. Deposition of Ni atoms on Cu1/g-C3N4 gradually diminished the intensity of the CO peak, strongly verifying the direct Cu–Ni interactions. On Ni3.1%Cu1/g-C3N4 (the optimized Ni1Cu1/g-C3N4 sample), when considering the CuNi mole ratio of 2.4:1:0, the trivial CO peak strongly confirms that one Ni is approximately coordinated with two Cu atoms but without forming Ni particles/clusters, in line with the formation of NiCu1 linear trimers (Supplementary Fig. 28). Analysis of the CO peak areas before and after Ni deposition reveals that NiCu1 linear trimers might be about 87% in NiCu1/g-C3N4, agreeing well with the STEM statistics (Fig. 2b). A control experiment of depositing Ni on a Cu1/g-C3N4 sample at low Cu loading revealed that a high density of Cu1 atoms is essential to form Ni1Cu2 linear trimers (Supplementary Fig. 29).

CH3 and C2H2 TPD were also applied to probe direct Ni–Cu interactions. We found that the main C2H2 desorption peak of Ni1Cu1/g-C3N4 was located at 107°C, sharply different from that of Cu1/g-C3N4 (146°C) and Ni1/g-C3N4 (82°C), further supporting the formation of NiCu1 linear trimers (Supplementary Fig. 30). Meanwhile, the tailing CH2 desorption peak of Ni1Cu1/g-C3N4 (146°C) coincided with that of Cu1/g-C3N4, suggesting the coexistence of isolated Cu atoms. Quantitative analysis of the TPD spectrum reveals that the percentage of NiCu1 linear trimers is about 74% (Fig. 2b), close to the STEM statistics (71%). Analysis of C2H2 TPD showed the same result. Considering the negligible activity of Cu1/g-C3N4, Ni1/g-C3N4 and Ni1%Cu0.5%/g-C3N4 below 170°C (Fig. 1a and Supplementary Fig. 29), the exceptional performance of Ni1Cu1/g-C3N4 should come solely from the prevailing linear trimers.

In situ X-ray photoemission spectroscopy (XPS) showed that the Cu2p3/2 binding energy was invariant at 933.2 eV, irrespective of
the treatments—an indication of the +1 oxidation state (Fig. 2f and Supplementary Fig. 31), which is in line with the DRIFTS CO chemisorption data (Fig. 2e). The Ni2p 3/2 binding energy located at 855.8 eV, close to that of Ni(OH)2 (ref. 31). Along with this, considerable hydroxyl-type oxygen, with O 1s at 531.4 eV, was found. Quantitative XPS analysis showed that the stoichiometric ratio between O and Ni was about 2:1. Taken together, these results suggest that the active linear trimers are Ni1(OH)2Cu2 complexes formed under the reaction conditions.

To reveal the structure of the Ni1(OH)2Cu2 complexes in Ni1Cu2/g-C3N4, in situ X-ray absorption spectroscopy measurements were further conducted (Supplementary Fig. 15). At the Ni K edge,
the extended X-ray absorption fine-structure (EXAFS) curve of Ni$_1$Cu$_2/g$-C$_3$N$_4$ after 350 °C hydrogen reduction (Ni$_1$Cu$_2/g$-C$_3$N$_4$-R) was nearly identical to that under the hydrogenation condition (Ni$_1$Cu$_2/g$-C$_3$N$_4$-H) (Fig. 2g). The main peak at 1.41 Å was assigned to Cu–O/NC coordination with a CN of 1.7, and the weak peak at 1.96 Å was assigned to Cu–Cu/Ni coordination with a CN of 0.5 (Fig. 2h, Supplementary Fig. 33 and Supplementary Table 7). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32). Quantitative EXAFS fitting revealed that the coordination numbers (CNs) for the nearest Ni–O/N/C and Ni–Cu were 3.3 and 0.8 with bond distances of 1.96 and 2.90 Å, respectively (Supplementary Fig. 32).

### Table 1 | Catalytic performances of benchmark catalysts reported in the literature in the semi-hydrogenation of acetylene

| Catalysts | Morphology | Total transition metal loadings (wt%) | Ethylene selectivity (%)$^a$ | TOS (h) | Average deactivation rate (% h$^{-1}$) | Coke formation | Notes |
|-----------|------------|--------------------------------------|-------------------------------|--------|--------------------------------------|----------------|-------|
| Ni$_1$Cu$_2/g$-C$_3$N$_4$ | Trimeric ions | 11.2 | 90 | 350 | 0 | N.D.$^f$ | This work |
| Ni$_1/g$-C$_3$N$_4$ | Single ions | 3.1 | 85 | 50 | 0.71 | Yes | This work |
| Na-Ni@CHA | Single ions | 3.5 | 97 | 50 | 0.28 | Yes | Ref. 57 |
| Ni-SAs/N-C | Single ions | 1.5 | 90 | 18 | 0.61 | N.A.$^a$ | Ref. 58 |
| Cu$_2$/ND@G | Single ions | 0.2 | 98 | 60 | 0 | N.A.$^a$ | Ref. 59 |
| 0.5Cu/Al$_2$O$_3$ | Single ions | 0.5 | 91 | 40 | 0 | Yes | Ref. 60 |
| Pd$_2$/ND@G | Single ions | 0.11 | 90 | 30 | 0 | N.D.$^f$ | Ref. 61 |
| ISA-Pd/MPNC | Single ions | 0.043 | 82 | 20 | 0.05 | N.A.$^a$ | Ref. 62 |
| AgPd$_{30}$/SiO$_2$ | SAAs$^i$ | 4.91 | 80 | 24 | 0.25 | N.A.$^a$ | Ref. 63 |
| AuPd$_{30}$/SiO$_2$ | SAAs$^i$ | 4.92 | 70 | 24 | 0.71 | Yes | Ref. 64 |
| NiGa | IMC$^c$ | 10.0 | 75 | 24 | 0.04 | Yes | Ref. 65 |
| Ni$_1$Ga/MgAl$_2$O$_4$ | IMC$^c$ | 2.0 | 77 | 24 | 0.16 | Yes | Ref. 66 |
| Al$_2$Fe$_4$ | IMC$^c$ | N.A.$^a$ | 82 | 20 | 0.55 | Yes | Ref. 67 |
| PdZn | IMC$^c$ | N.A.$^a$ | 91 | 20 | 0.20 | Yes | Ref. 68 |
| Nano-GaPd$_2$ | IMC$^c$ | N.A.$^a$ | 72 | 20 | 0.25 | Yes | Ref. 69 |
| Pre-NiCu/MMO | Bimetallic NPs | 19.7 | 70 | 16 | 1.56 | Yes | Ref. 70 |
| NiIn$_1$/SiO$_2$ | Bimetallic NPs | 8.0 | 35 | 10 | 6.91 | Yes | Ref. 71 |

$^a$Ethylene selectivity was determined at near 100% acetylene conversion. $^b$The average deactivation rate was determined by the decrease in acetylene conversion divided by TOS. $^c$Single-atom alloys. $^d$Intermetallic compound. $^e$Not available. $^f$Not detectable.

### Spectroscopic insight into the hydrogenation process.

In situ DRIFTS measurements were carried out to investigate the catalytic roles of trimers in the reaction with acetylene and Ni aggregations to Ni/NiO particles (Supplementary Figs. 20 and 37). Meanwhile, IR bands in the ranges of 3,200–3,300, 2,900–3,200 and 2,800–2,900 cm$^{-1}$ gradually increased in intensity with time, assigned to the vibrations of gas-phase acetylene, $\nu$(C–H) of chemisorbed acetylene and $\nu$(CH$_3$) of ethylidene/ethylidyne, respectively (where $\nu$ represents stretching vibrations)$. Switching the gas to hydrogen, the peaks of all C–H stretching declined, indicating the formation of ethylene and ethane. However, the Ni–OH groups were not recovered. Repeating the above experiments for another acetylene–hydrogen cycle showed a similar result.

**Fig. 2** | Structural characterization. a, Representative HAADF-STEM image of Ni$_1$Cu$_2/g$-C$_3$N$_4$ with atomic resolution, where representative isolated trimers, linear trimers and linear trimers are highlighted by dashed yellow circles, red triangles and green rectangles, respectively. b, Statistics of single atoms, linear trimers and triangular trimers in Ni$_1$Cu$_2/g$-C$_3$N$_4$ using four different approaches, namely, HAADF-STEM, DRIFTS CO chemisorption, C=H TPD and C=H TPD. c, Intensity profile and atomic-resolution EELS elemental mapping of an individual linear trimer shown in the inset. d, Atomic-resolution EELS spectra collected at the corresponding positions in c, e. In situ DRIFTS spectra of CO chemisorption on Ni$_1$/Cu$_2$ g-C$_3$N$_4$ catalysts with different Ni loadings (%). The spectrum of CO chemisorption on Ni$_1$/Cu$_2$ g-C$_3$N$_4$ is also shown for comparison. f, In situ Cu$_2$P, Ni$_2$P and OIs XPS spectra of Ni$_1$Cu$_2/g$-C$_3$N$_4$ after treatments of 350 °C reduction and acetylene hydrogenation reaction at 160 °C. g, h. In situ $k^2$-weighted Fourier transform (FT) spectra of Ni$_1$Cu$_2/g$-C$_3$N$_4$ after reduction and under reaction conditions at the Ni (g) and Cu (h) K edges; references of Ni foil, NiO, NiPC, Cu foil, Cu$_2$O and CuPc are also presented for comparison. i, j. In situ DRIFTS of C$_2$H$_2$ hydrogenation on the
used Ni$_1$Cu$_2$/g-C$_3$N$_4$ catalyst showed an identical result with the fresh sample (Supplementary Fig. 39), validating the excellent stability.

**Theoretical insights into Ni$_1$ and Ni$_1$Cu$_2$ catalysts.** Based on the above structural characterization and extensive DFT calculations, the Ni–Cu complex is identified as a chain-like Cu–OH–Ni–OH–Cu structure (Fig. 4a), whereas the Ni species in Ni$_1$/g-C$_3$N$_4$ after reduction forms the Ni$_1$(OH)$_2$ complex (Supplementary Fig. 40 and Supplementary Table 9). For the former one, the Ni atom bonds to Npy and C of g-C$_3$N$_4$ underneath, and is confined by Cu atoms from two sides via the bridging OH group; the Cu atoms are

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**Fig. 3 | In situ DRIFTS investigation of C$_2$H$_2$ hydrogenation.** a, b. In situ DRIFT spectra over Ni$_1$/g-C$_3$N$_4$ (a) and Ni$_1$Cu$_2$/g-C$_3$N$_4$ (b) catalysts after alternatively exposing to C$_2$H$_2$ and H$_2$ for different times with two consecutive C$_2$H$_2$ and H$_2$ cycles. The shaded regions with different colours highlight the variations in the peak position and intensity. Conditions: 0.03 g catalyst; 160 °C; 0.5% C$_2$H$_2$ or 5% H$_2$ in Ar; total flow, 6 ml min$^{-1}$.
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Further fastened $\text{g-C}_3\text{N}_4$ via a strong $\text{Cu}–\text{N}_\text{py}$ bond. Optimized bond lengths of Ni–O/N/C bond and Cu–O/N bond are in excellent agreement with the EXAFS data (Supplementary Table 10). The overall length of the optimized complex (5.84 Å) and two unequal Ni–Cu distances (2.74 and 3.10 Å) also perfectly agree with the STEM data (Supplementary Fig. 25). There is substantial charge accumulation between the Ni–C/N bonds and between the Cu–C/N bonds, while considerable charge transferring from Ni/Cu to high-lying OH groups (Fig. 4a and Supplementary Fig. 41); therefore, the characteristic covalent bond and ionic bond coexist between Ni/Cu(OH) and the $\text{g-C}_3\text{N}_4$ support, as well as in Ni(OH)/$\text{g-C}_3\text{N}_4$. Impressively, the formation of Ni/Cu linear trimer is energetically favourable, exothermic by 0.79 eV (Supplementary Fig. 42), manifesting the driving force for the linear trimer formation (Supplementary Fig. 6).

Different chemical stability of Ni$_1$/g-C$_3$N$_4$ and Ni$_1$Cu$_1$/g-C$_3$N$_4$ stems from the distinct structure change induced by stronger C$_2$H$_4$ adsorption, as found by DFT calculations and TPD measurements (Supplementary Fig. 30 and Supplementary Table 11). We found that acetylene adsorption on Ni$_1$/g-C$_3$N$_4$ has a modest barrier of 0.62 eV and exothermic by 0.69 eV (Fig. 4b), while simultaneously breaking one Ni–N/C support bond. The one Ni–N/C support bond left can be further broken only with a barrier of 0.66 eV. In other words, the Ni(OH)/C$_2$H$_4$ complex is rather mobile on g-C$_3$N$_4$, which would facilitate its aggregation to form Ni NPs, as found by STEM and XPS measurements (Supplementary Figs. 20 and 37). Obviously, strong Ni–support interaction alone is not sufficient to stabilize the Ni(OH)$_2$ complexes, although the bonding by the two Ni–N bonds (~2.93 eV) is considerably strong.

Acetylene adsorption on Ni$_1$/g-C$_3$N$_4$ and Ni$_1$Cu$_1$/g-C$_3$N$_4$ stems from the distinct structure change induced by stronger C$_2$H$_4$ adsorption, as found by DFT calculations and TPD measurements (Supplementary Fig. 30). The optimized structure indicates that although acetylene adsorption breaks two interfacial Ni–N/C support bonds with practically no barrier, spatial confinement by two atomic Cu grippers from both sides through two bridging hydroxyls endows the breakages of the Cu–O support bond extremely endothermic by more than 4 eV, ensuring the high chemical stability of this catalyst during acetylene hydrogenation. Meanwhile, the two new Ni–C bonds formed with adsorbed C$_2$H$_4$ retain the overall CN of the Ni atom before and after acetylene adsorption (Fig. 4b and Supplementary Video 1), which is in good agreement with the X-ray absorption fine-structure (XAFS) data (Fig. 2g and Supplementary Table 12). Therefore, the resulting dynamics of Ni atoms via synergizing MSIs and spatial confinements ensures not only a facile structural transformation by breaking the Ni–N/C bonds to enhance acetylene adsorption but also a high chemical/thermal stability of SADCs free from aggregations (Supplementary Fig. 43).

 Atomically dispersed and stable Ni atoms are beneficial to suppress C–C bond breaking and creating the prerequisite for the formation of graphitic coke and green oils due to the limited sites available (Fig. 4c and Supplementary Table 12). For instance, the cleavage of adsorbed acetylene is highly endothermic because of the absence of sites accommodating the broken CH$_2$ fragments. Moreover, after the preferential adsorption of acetylene at the Ni atom, the additional adsorption of acetylene or ethylene is only possible at the Cu sites with a weak binding energy of ~0.55 and ~0.51 eV, respectively, but will desorb at temperatures above room temperature. As a result, the formation of graphitic coke and green oils is prohibited on Ni$_1$Cu$_1$/g-C$_3$N$_4$, which is in excellent agreement with the in situ SVUV-PIMS and TGA measurements (Fig. 1e–g).

Optimized potential energy surface for the hydrogenation of acetylene over the Ni$_1$(OH)$_2$Cu$_1$ complex is shown in Fig. 4d and Supplementary Figs. 44–46. Acetylene is expected to be dominant on the Ni sites during hydrogenation, owing to its much stronger adsorption (~1.00 eV) than H$_2$ (~0.07 eV) (Supplementary Table 11). After acetylene adsorption, the proton in one bridging OH tends to directly attack the adsorbed acetylene with a barrier of 1.23 eV to form C$_2$H$_3^*$ (here * denotes surface species; Fig. 4d(i),(ii)). Next, hydrogen adsorbs on the Ni sites and effortlessly dissociates with one H atom in addition to C$_2$H$_3^*$ to form C$_2$H$_4^*$, and the other one bonds to the Ni site (Fig. 4d(iii),(iv)). After that, the C$_2$H$_4^*$ species rearranges and the H atom transfers to the bridging O from Ni to regenerate the bridging OH with a low barrier of 0.81 eV. Compared with the sequential high hydrogenation barrier of 1.38 eV from ethylene to ethane, weakly bonded ethylene with a value of ~0.67 eV boosts the desorption rate of ethylene—a key step for the high selectivity of Ni$_1$Cu$_1$/g-C$_3$N$_4$ which is in line with the catalytic results shown in Fig. 1. Obviously, the participation of bridging hydroxyls in the hydrogenation reaction suggested by DFT is in good agreement with the DRIFTS results (Fig. 3).

Conclusions

In summary, we have reported that synergizing MSIs and spatial confinement through Cu atomic grippers boosts the dynamics of highly loaded atomic Ni for efficient hydrogenations. Such dynamic and synergetic effects enable not only exceptionally high stability against both sintering and coke formation in the hydrogenation of acetylene but also lead the active sites to become highly adaptable towards both reactant adsorption and product desorption, thus boosting the activity (11 times higher than the conventional Ni$_1$/g-C$_3$N$_4$ catalyst) and ethylene selectivity. Compared with the literature$^{13,14}$, the synthesis of metal trimer catalysts using an atom-by-atom fabrication approach provides an avenue for the rational design of highly active and stable SADCs for practical application in selective chemical reactions.

Online content

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References

1. Wang, A. Q., Li, J. & Zhang, T. Heterogeneous single-atom catalysis. Nat. Rev. Chem. 2, 65–81 (2018).
2. Liu, L. & Corma, A. Metal catalysts for heterogeneous catalysis: from single atoms to nanoclusters and nanoparticles. Chem. Rev. 118, 4981–5079 (2018).
3. Marcinkowski, M. D. et al. Pt/Cu single-atom alloys as coke-resistant catalysts for efficient C–H activation. Nat. Chem. 10, 325–332 (2018).
4. Akri, M. et al. Atomically dispersed nickel as coke-resistant active sites for methane dry reforming. Nat. Commun. 10, 5181 (2019).
5. Kaiser, S. K. et al. Nanostructuring unkocks high performance of platinum single-atom catalysts for stable vinyl chloride production. Nat. Catal. 3, 376–385 (2020).
6. Barbier, J. Deactivation of reforming catalysts by coking—a review. Appl. Catal. 23, 225–243 (1986).
7. Gates, B. C., Flytzani-Stephanopoulos, M., Dixon, D. A. & Katz, A. Atomically dispersed supported metal catalysts: perspectives and suggestions for future research. Catal. Sci. Technol. 7, 4239–4275 (2017).
8. Yang, X. F. et al. Single-atom catalysts: a new frontier in heterogeneous catalysis. Acc. Chem. Res. 46, 1740–1748 (2013).
9. Huang, F. et al. Anchoring Cu species over nanodiamond-graphene for semi-hydrogenation of acetylene. Nat. Commun. 10, 4431 (2019).
10. Studt, F. et al. Identification of non-precious metal alloy catalysts for selective hydrogenation of acetylene. Science 320, 1320–1322 (2008).
11. Huang, X. et al. Enhancing both selectivity and coking-resistance of a single-atom Pd/C/Ni catalyst for acetylene hydrogenation. Nano Res. 10, 1302–1312 (2017).
12. Han, B. et al. Strong metal–support interactions between Pt single atoms and TiO$_2$. Angew. Chem. Int. Ed. 59, 11824–11829 (2020).
13. Lang, R. et al. Single-atom catalysts based on the metal–oxide interaction. Chem. Rev. 120, 11986–12043 (2020).
14. Liu, L. & Corma, A. Confining isolated atoms and clusters in crystalline porous materials for catalysis. Nat. Rev. Mater. 6, 244–263 (2021).

15. Fu, Q. et al. Interface-confined ferrous centers for catalytic oxidation. Science 328, 1141–1144 (2010).

16. Jones, J. et al. Thermally stable single-atom platinum-on-ceria catalysts via atom trapping. Science 353, 150–154 (2016).

17. Wei, S. et al. Direct observation of noble metal nanoparticles transforming to thermally stable single atoms. Nat. Nanotechnol. 13, 856–861 (2018).

18. Mitchell, S., Qin, R., Zheng, N. & Perez-Ramirez, J. Nanoscale engineering of catalytic materials for sustainable technologies. Nat. Nanotechnol., 16, 129–139 (2021).

19. Zhang, L., Zhou, M., Wang, A. & Zhang, T. Selective hydrogenation over supported metal catalysts: from nanoparticles to single atoms. Chem. Rev. 120, 683–733 (2020).

20. Li, Z. et al. Well-defined materials for heterogeneous catalysis: from nanoparticles to isolated single-atom sites. Chem. Rev. 120, 623–682 (2020).

21. Thomas, A. et al. Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts. J. Mater. Chem. B 8, 4893–4908 (2020).

22. Gao, G. P., Jiao, Y., Waclawik, E. R. & Du, A. J. Single atom (Pd/Pt) supported metal catalysts: from nanoparticles to single atoms. ACS Catal. 10, 91–144 (2020).

23. Lu, J. L., Elam, J. W. & Stair, P. C. Atomic layer deposition—sequential self-limiting surface reactions for advanced catalysts ‘bottom-up’ synthesis. Surf. Sci. Rep. 71, 410–472 (2016).

24. George, S. M. Atomic layer deposition: an overview. Chem. Rev. 110, 111–131 (2010).

25. Gould, T. D. et al. Synthesis of supported Ni catalysts by atomic layer deposition. J. Catal. 303, 9–15 (2013).

26. Huo, J. S., Solanki, R. & McAndrew, J. Characteristics of copper films produced via atomic layer deposition. J. Mater. Res. 17, 2394–2398 (2002).

27. Selander, N. & Szabo, K. J. Catalysis by palladium pincer complexes. Chem. Rev. 111, 2048–2076 (2011).

28. Borodziński, A. & Bond, G. C. Selective hydrogenation of ethyne in ethene-rich streams on palladium catalysts. Part 1. Effect of changes to the catalyst during reaction. Catal. Rev. 48, 91–144 (2006).

29. Liu, L., Zhao, C. & Li, Y. Spontaneous dissociation of CO2 to CO on defective regimes on palladium catalysts. Part 1. Surface structure and its effect on catalytic activity. J. Phys. Chem. C. 116, 7904–7912 (2012).

30. Huang, L., Peng, F. & Ohuchi, F. S. ‘In situ’ XPS study of band structures at CuO/TiO2 heterojunctions interface. Surf. Sci. 603, 2825–2834 (2009).

31. Biesinger, M. C., Payne, B. P., Lau, L. W. M., Gerson, A. & Smart, R. S. C. X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems. Surf. Interface Anal. 41, 324–332 (2009).

32. Cao, L. et al. Identification of single-atom active sites in carbon-based cobalt catalysts during electrocatalytic hydrogen evolution. Nat. Catal. 2, 134–141 (2018).

33. Moon, J. et al. Discriminating the role of surface hydride and hydroxyl for acetylene semi-hydrogenation over ceria through in situ neutron and infrared spectroscopy. ACS Catal. 10, 5278–5287 (2020).

34. Tian, S. et al. Carbon nitride supported Fe3 cluster catalysts with superior performance for alkene epoxidation. Nat. Commun. 9, 2353 (2018).

35. Lu, Z. et al. An isolated zinc–cobalt atomic pair for highly active and durable oxygen reduction. Angew. Chem. Int. Ed. 58, 2622–2626 (2019).

36. Kwak, J. H. et al. Molecular active sites in heterogeneous Ir-La/C-catalyzed carbonation of methanol to acetates. J. Phys. Chem. Lett. 5, 566–572 (2014).

37. Chai, Y. et al. Acetylene-selective hydrogenation catalyzed by cationic nickel confined in zeolite. J. Am. Chem. Soc. 141, 9920–9927 (2019).

38. Dai, X. et al. Single Ni sites distributed on N-doped carbon for selective hydrogenation of acetylene. Chem. Commun. 53, 11568–11571 (2017).

39. Shi, X. X. et al. Copper catalysts in semihydrogenation of acetylene: from single atoms to nanoparticles. ACS Catal. 10, 3495–3504 (2020).

40. Huang, Y. et al. Atomically dispersed Pd on nanodiamond/graphene hybrid for selective hydrogenation of acetylene. J. Am. Chem. Soc. 140, 13142–13146 (2018).

41. Fang, Q. et al. Mesoporous nitrogen-doped carbon-nanosphere-supported single-atom Pd catalyst for highly efficient semi-hydrogenation of acetylene. Adv. Mater. 31, e1901024 (2019).

42. Pei, G. X. et al. Ag alloyed Pd single-atom catalysts for efficient selective hydrogenation of acetylene to ethylene in excess ethylene. ACS Catal. 5, 3717–3725 (2015).

43. Pei, G. X. et al. Promotional effect of Pd single atoms on Au nanoparticles supported on silica for the selective hydrogenation of acetylene in excess ethylene. New J. Chem. 38, 2043–2051 (2014).

44. Cao, Y. et al. Adsorption site regulation to guide atomic design of Ni–Ga catalysts for acetylene semi-hydrogenation. Angew. Chem. Int. Ed. 59, 11647–11652 (2020).

45. Liu, Y. et al. Intermetallic Ni,M (M = Ga and Sn) nanocystals: a non-precious metal catalyst for semi-hydrogenation of alkynes. Adv. Mater. 28, 4747–4754 (2016).

46. Armbrüster, M. et al. Al13Fe4 as a low-cost alternative for palladium in alkyn hydrogenation catalysis. ACS Catal. 10, 13142–13146 (2020).

47. Zhou, H. R. et al. PdZn intermetallic nanostructure with Pd–Zn–Pd ensembles for highly active and chemoselective semi-hydrogenation of acetylene. ACS Catal. 10, 13142–13146 (2020).

48. Armbrüster, M., Wowsnick, G., Friedrich, M., Heggen, M. & Cardoso-Gil, R. Synthesis and catalytic properties of nanoparticulate intermetallic Ga–Pd compounds. J. Am. Chem. Soc. 133, 9112–9118 (2011).

49. Liu, Y. N. et al. Layered double hydroxide-derived Ni–Fe3 for the selective hydrogenation of alkynes. Nat. Mater. 11, 690–693 (2012).

50. Zhou, H. R. et al. PdZn intermetallic nanostructure with Pd–Zn–Pd ensembles for highly active and chemoselective semi-hydrogenation of acetylene. ACS Catal. 6, 1054–1061 (2016).

51. Armbrüster, M., Wowsnick, G., Friedrich, M., Heggen, M. & Cardoso-Gil, R. Synthesis and catalytic properties of nanoparticulate intermetallic Ga–Pd compounds. J. Am. Chem. Soc. 133, 9112–9118 (2011).

52. Liu, Y. N. et al. Layered double hydroxide-derived Ni–Ca nanoalloy catalysts for semi-hydrogenation of alkynes: improvement of selectivity and anti-coking ability via alloying of Ni and Cu. J. Catal. 359, 251–260 (2018).

53. Chen, Y. J. & Chen, J. X. Selective hydrogenation of acetylene on SiO2 supported Ni-In bimetallic catalysts: promotional effect of In. Appl. Surf. Sci. 387, 16–27 (2016).
**Methods**

**Materials.** Copper(ii) hexafluorocacetonehydrate carbonate (Cu(hfac)2), formalin (37% formaldehyde in an aqueous solution) and bis(cyclopentadienyl) nickel(ii) (NiCp2) were bought from Shanghai Aladdin Bio-Chem Technology; Urea (99%), NiO (99%), CuO (99%), Ni(NO3)2·6H2O (99%), Cu(OH)2 (99%), CaCl2 (99%), NaBH4 (99%), Cu2O (99%), Ni(NO3)2·6H2O (99%), NaBH4 (99%), CuO (99%), CaCl2 (99%), and NiO (99%) were purchased from Sinopharm Chemical Reagent. Nickel(ii) phthalocyanine (NiPc), copper(ii) phthalocyanine (CuPc) and Ni/SiO2-Al2O3 catalyst (Ni loading, 66 wt%) were bought from Alfa Aesar. Lindlar Pd catalyst (Pd-PhO/CarC02) was purchased from TCI (Shanghai) Development. All the chemicals were used without further purification.

Ultrahigh-purity N2 (99.999%), O2 (99.999%), H2 (99.999%) and Ar (99.999%), as well as gas mixtures including 10% O2 in Ar, 10% H2 in Ar, 0.5% CH4, 5% H2, 25% C2H4 in Ar, 1.2% 1,3-butadiene and 12% H2 in Ar, were provided by Nanjing Special Gas.

**Synthesis of g-C3N4 support.** Urea was placed in a crucible and heated to 600 °C for 4 h in static air at a ramp rate of 5 °C/min. The resulting yellow material was milled into fine powders in a mortar. Next, the yellow powder was placed in an open ceramic container and heated at 550 °C for another 4 h. A light-yellow powder of g-C3N4 support was finally obtained.

**Synthesis of Cu/g-C3N4, NiO/g-C3N4 and NiCu/g-C3N4 catalysts.** Cu ALD was carried out on a viscous-flow stainless steel tube reactor system (ACME (Beijing) Technology) at 300 °C using Cu(hfac), and formaldehyde as the precursors. Ultrahigh-purity N2 (99.999%) was used as a carrier gas at a flow rate of 60 ml/min. The Cu(hfac), precursor container was heated to 90 °C to achieve a sufficient vapour pressure. The inlet manifold was held at 100 °C to avoid precursor condensation. The timing sequence was 300, 300, 40 and 180 s for Cu(hfac), exposure, N2 purge, formaldehyde exposure and N2 purge, respectively. One, two, and ten cycles of Cu ALD were performed on g-C3N4 to obtain Cu(3.1%)/g-C3N4, Cu(8.1%)/g-C3N4 and Cu(11.4%)/g-C3N4 catalysts, respectively. When the Cu(hfac), exposure time was reduced to 25 and 15 s, for principal Cd atoms on g-C3N4, Cu loadings of 0.5% and 2.7% were obtained, which were denoted as Cu(0.5%)/g-C3N4 and Cu(2.7%)/g-C3N4, respectively.

**NiO/g-C3N4 catalysts.** NiO ALD was carried out on the g-C3N4 support at 240 °C using NiCp2 and ozone as the precursors. The NiCp2, precursor container was heated to 90 °C to achieve a sufficient vapour pressure. The inlet manifold was held at 115 °C to avoid precursor condensation on the inner walls. The timing sequence was 1,260, 200, 1,260 and 200 s for NiCp2 exposure, N2 purge, O3 exposure and N2 purge, respectively. Different NiCp2 exposure times (from 100 to 1,260 s) were used on g-C3N4 to obtain a series of Ni single-atom catalysts with different Ni loadings (denoted as Ni(x)%/g-C3N4, where x is the Ni loading). NiO ALD was also carried on the Cu(8.1%)/g-C3N4 samples with different NiCp2 exposure times (from 200 to 1,260 s). The resulting samples were denoted as Ni(x)%/g-C3N4. NiO ALD was also carried on the Cu(8.1%)/g-C3N4 samples with different NiCp2 exposure times (from 200 to 1,260 s). The resulting samples were denoted as Ni(x)%/g-C3N4. NiO ALD was also carried on the Cu(8.1%)/g-C3N4 samples with different NiCp2 exposure times (from 200 to 1,260 s). The resulting samples were denoted as Ni(x)%/g-C3N4. NiO ALD was also carried on the Cu(8.1%)/g-C3N4 samples with different NiCp2 exposure times (from 200 to 1,260 s). The resulting samples were denoted as Ni(x)%/g-C3N4.

**Synthesis of Ni1/g-C3N4 and Ni1Cu2/g-C3N4 catalysts.** NiO, Cu(hfac)2, formalin and STEM measurements were performed on a JEM-ARM200F instrument (University of Science and Technology of China) at 200 keV. Meanwhile, energy-dispersive X-ray elemental mapping was also collected on the same equipment. Transmission electron microscopy (TEM) STEM measurements were performed on a JEM-ARM200F instrument equipped with a C3/C5 corrector, operated at 200 kV.

**Morphology and compositions.** Aberration-corrected HAADF-STEM measurements were taken on a JEM-ARM200F instrument (University of Science and Technology of China) at 200 keV. Meanwhile, energy-dispersive X-ray elemental mapping was also collected on the same equipment. Transmission electron microscopy (TEM) STEM measurements were performed on a JEM-ARM200F instrument operated at 200 kV.

**In situ XPS measurements.** In situ XPS measurements were conducted on the BL10B beamline photoemission end-station at the National Synchrotron Radiation Laboratory, Hefei, China. In brief, the beamline is connected to a bending magnet and covers photon energies from 100 to 1,000 eV. The end-station consists of four chambers, namely, analysis chamber, preparation chamber and sample handling chamber. High-pressure gas treatment of the sample was achieved through a high-pressure reactor, with a maximum current of 210 mA. A home-made reaction cell was used for the operando experiments, which allows exposing the sample to different pretreatment gases or reactions gases, as well as sample heating up to 400 °C. A home-made reaction cell was used for the operando experiments, which allows exposing the sample to different pretreatment gases or reactions gases, as well as sample heating up to 400 °C. A home-made reaction cell was used for the operando experiments, which allows exposing the sample to different pretreatment gases or reactions gases, as well as sample heating up to 400 °C. A home-made reaction cell was used for the operando experiments, which allows exposing the sample to different pretreatment gases or reactions gases, as well as sample heating up to 400 °C. A home-made reaction cell was used for the operando experiments, which allows exposing the sample to different pretreatment gases or reactions gases, as well as sample heating up to 400 °C. A home-made reaction cell was used for the operando experiments, which allows exposing the sample to different pretreatment gases or reactions gases, as well as sample heating up to 400 °C. A home-made reaction cell was used for the operando experiments, which allows exposing the sample to different pretreatment gases or reactions gases, as well as sample heating up to 400 °C. A home-made reaction cell was used for the operando experiments, which allows exposing the sample to different pretreatment gases or reactions gases, as well as sample heating up to 400 °C.
The amount of non-precious catalyst was 150 mg, which was diluted with 1 g of KCl; 50 m\(\times\)100 mm quartz chips. Before the reaction test, all the catalysts were reduced in 10\%\ H2 in Ar at 350 °C for 2 h. Then, the sample was cooled down to 25 °C in Ar. After that, the sample was exposed to 5\%\ H2O/Ar (6 ml min\(^{-1}\)) for 30 min until saturation and the spectra were continuously collected during this process. The CO chemisorption spectra were obtained by subtracting the CO chemisorption DRIFT spectrum of g-C\(_3\)N\(_4\) to remove the gas-phase CO.

As for in situ DRIFTS of C\(_2\)H\(_4\) or C\(_2\)H\(_2\) hydrogenation, the sample was first reduced in 10\%\ H2 in Ar at 350 °C for 2 h. Then, the sample was cooled down to 160 °C in Ar and kept for 30 min while the spectra were collected. After that, the experiments were repeated by sequentially exposing to C\(_2\)H\(_2\) and H\(_2\) for C\(_2\)H\(_2\) conversion and butene selectivity were calculated using the following equations, respectively:

\[
\text{Butene selectivity} (\%) = \frac{[\text{Butene}]_{\text{out}}}{[\text{Butene}]_{\text{in}} + [\text{Butene}]_{\text{out}}} \times 100
\]

In-situ DRIFTS. In situ DRIFTS was performed on a Thermo Nicolet iS10 FTIR spectrometer equipped with a mercury–cadmium–telluride detector at a resolution of 4 cm\(^{-1}\) and 128 scans. First, 30 mg of the sample was placed in a high-temperature cell (Harrick) with CaF\(_2\) windows. For in situ DRIFTS of CO chemisorption, the sample was first reduced in 10\%\ H2 in Ar at 350 °C for 2 h. Then, the sample was cooled down to 25 °C in Ar. After that, the sample was exposed to 10\%\ CO/Ar (30 ml min\(^{-1}\)) for 30 min until saturation and the spectra were continuously collected during this process. The CO chemisorption spectra were obtained by subtracting the CO chemisorption DRIFT spectrum of g-C\(_3\)N\(_4\) to remove the gas-phase CO.

As for in situ DRIFTS of C\(_2\)H\(_4\) or C\(_2\)H\(_2\) hydrogenation, the sample was first reduced in 10\%\ H2 in Ar at 350 °C for 2 h. Then, the sample was cooled down to 160 °C in Ar and kept for 30 min while the spectra were collected. After that, the experiments were repeated by sequentially exposing to C\(_2\)H\(_4\) and H\(_2\) for C\(_2\)H\(_4\) hydrogenation or sequentially exposing to C\(_2\)H\(_2\) and H\(_2\) for C\(_2\)H\(_2\) hydrogenation. The total flow rate was 6 ml min\(^{-1}\). It should be noted that all the gases were passed through a calcium chloride filter at ~40 °C in the gas inlet line before the Harrick cell to remove trace water from the gas.

As for in situ DRIFTS of water adsorption, the sample was first reduced in 10\%\ H2 in Ar at 350 °C for 2 h. Then, the sample was cooled down to 25 °C in Ar. After that, the sample was exposed to 5\%\ H2O/Ar (6 ml min\(^{-1}\)) for 30 min until saturation, and the spectra were continuously collected during this process.

Catastic activity test. Selective hydrogenation of acetylene in excess ethylene was conducted in a fixed-bed flow reactor. The total flow rate was kept at 30 ml min\(^{-1}\), and the gaseous flow of 1\%\ C\(_2\)H\(_2\), 9\%\ C\(_2\)H\(_4\) (balance gas Ar) was introduced into the reactor at a flow rate of 30 ml min\(^{-1}\). After the reaction, the reactor was cooled down to room temperature in He: then, C\(_2\)H\(_2\) or C\(_2\)H\(_4\) gas was introduced into the sample until saturation. Subsequently, the sample was purged with He at 25 °C for 1 h and then the sample temperature was gradually increased at a heating rate of 10 °C min\(^{-1}\) in He from 25 to 300 °C while recording the TPD data.

TPD measurements. The C\(_2\)H\(_4\) and C\(_2\)H\(_2\) TPD experiments were performed on a Micromeritics AutoChem II chemisorption analyser, which was connected to a Pfeiffer OmniStar mass spectrometer. In a typical experiment, 50 mg sample was first reduced in 10\%\ H2/He at 350 °C for 2 h and then purged with He at 300 °C for 1 h. Next, the sample was cooled down to room temperature in He: then, C\(_2\)H\(_2\) or C\(_2\)H\(_4\) gas was introduced into the sample until saturation. Subsequently, the sample was purged with He at 25 °C for 1 h and then the sample temperature was gradually increased at a heating rate of 10 °C min\(^{-1}\) in He from 25 to 300 °C while recording the TPD data.

Computational methods and models. All the spin–polarized calculations were performed using DFT calculations implemented in the Vienna ab initio simulation package\(^\text{57}\). We described the electron–ion interaction using the projector augmented wave method\(^\text{59}\). The exchange–correlation interaction was described by the optB86b-vdW functional (ref. \text{16}). The Kohn–Sham equations were solved by using a plane-wave basis set with a kinetic energy cutoff of 400 eV. The convergence criterion for electronic self-consistent interactions is 10\(^{-6}\) eV. The geometries of bulk and surface were optimized by the conjugate gradient algorithm until the maximum force on any ion was less than 0.002 eV Å\(^{-1}\). All the transition states were determined by using the climbing image nudged elastic band method\(^\text{60}\) with confirmation of vibrational analysis. The transition states are optimized until all the forces are below 0.05 eV Å\(^{-1}\).

The g-C\(_3\)N\(_4\) was modelled by a (2\times2) supercell of a single-layer g-C\(_3\)N\(_4\), where all the atoms in the supercell were fully relaxed. A (3\times3\times1) Monkhorst–Pack \textit{k}-point mesh was used to sample the surface Brillouin zone. A 20 Å vacuum was introduced to avoid interaction from adjacent cells. The reaction energy and barrier are calculated as \(\Delta E = E_{\text{TS}} - E_{\text{init}}\), where \(E_{\text{TS}}\), \(E_{\text{init}}\) and \(E_{\text{final}}\) are the energies of the corresponding initial state, final state and transition state, respectively.

Data availability. Source data are provided with this paper. The data that support the findings of this study are available from the corresponding authors upon reasonable request.

References

51. de la Peña, F. et al. hyperspy/hyperspy: HyperSpy v.1.5.2 (Zenodo, 2019).
52. Zhou, Z. et al. The vacuum ultraviolet beamline/endstations at NSRL dedicated to combustion research. J. Synchrotron Rad. 23, 1035–1045 (2016).
53. Luo, L. et al. Gas-phase reaction network of Li/MgO-catalyzed oxidative coupling of methane and oxidative dehydrogenation of ethane. ACS Catal. 9, 2514–2520 (2019).
54. Yang, H. B. et al. Atomically dispersed Ni(111) as the active site for electrochemical CO2 reduction. Nat. Energy 3, 140–147 (2018).
55. Kresse, G. & Furthmuller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–50 (1996).
56. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).
57. Klimeš, J., Bowler, D. R. & Michaelides, A. Van der Waals density functionals applied to solids. J. Chem. Phys. 140, 140201 (2014).
58. Henkelman, G., Uberuaga, B. P. & Jonsson, H. A climbing image nudged elastic band method with confirmation of vibrational analysis. The transition states are optimized until all the forces are below 0.05 eV Å\(^{-1}\).

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Author contributions
J.L. designed the experiments and W.-X.L. designed the DFT calculations. J.G. performed the catalytic performance evaluation. S.W., L.H., Z.S., L.C. and S.C. performed the XAFS measurements. M.J. performed the DFT calculations. Y.Y., J.Y. and W.W. performed the SVUV-PIMS measurements. Y.L. conducted the HAADF-STEM measurements. A.L. and W.Z. performed the atomic-resolution EELS measurements. H.-J.W., J.Y. and W.W. performed the TEM measurements. X.S. and X.H. performed the TGA measurements. X.Z., H.P. and J.Z. performed the XPS measurements. J.L. and W.-X.L. co-wrote the manuscript, and all the authors contributed to the overall scientific interpretation and edited the manuscript. We gratefully thank P. C. Stair for his insightful suggestions and manuscript polishing.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to S.W., W.-X.L. or J.L.

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