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

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Abstract

Atomically dispersed metal catalysts maximize atom efficiency and display unique catalytic properties compared to regular metal nanoparticles. However, achieving high reactivity while still preserving high stability at high loadings remains as a grand challenge. Here we solve the challenge by synergizing strong metal-support interactions and spatial confinement, which enable to fabricate highly loaded (3.1 wt%), active and stable atomic Ni and dense atomic Cu grippers (8.1 wt%) on a graphitic C₃N₄ support. For semi-hydrogenation of acetylene in excess of ethylene, the fabricated catalyst shows 11 times higher activity than the atomic Ni alone, high ethylene selectivity (90%), and high stability against both sintering and coke formation for 350 h. Comprehensive microscopic and spectroscopic characterization and theoretical calculations reveal the active site of the bridging Ni confined in two hydroxylated Cu grippers, whose structure changes dynamically by breaking interfacial Ni-support bonds upon reactant adsorption and making these bonds upon product desorption. Such a dynamic effect confers high activity/selectivity and high stability, providing an avenue to rational design of efficient, stable, highly loaded, yet atomically dispersed catalysts.

Introduction

Supported atomically dispersed catalysts (SADCs) have recently drawn great attention in numerous reactions for their maximized atom efficiency¹⁻³. Exclusive site homogeneity, distinct energetics and spatial site confinement endow SADCs very attractive in high selectivity and alleviated coke formation in conversion of hydrocarbons⁴⁻⁶, sharply distinct from the low selectivity and heavy coke formation on metal nanoparticle (NP) catalysts⁷. However, owing to the drastically increased surface free energy, stability of the atomically dispersed metal species under reaction conditions, especially at high metal loadings has been the key issue to significantly limit the overall performance, restraining their practical applications⁸.

Realization of a highly-loaded and stable SADCs for hydrogenation reactions is particularly challenging, because atomically dispersed active metal species often show higher mobility in reducing environments⁹. For instance, in semi-hydrogenation of acetylene in excess ethylene, a crucial industrial process operated at a scale of billions of tons per annum to purify alkene streams^{10,11}, severe metal aggregations occurred even for low-loaded SADCs, which sequentially generated heavy coke formation, an even worse scenario to further accelerate catalyst deactivation to a short life time¹². Increasing metal-support interactions (MSIs)^{13,14} or confining the active metal species in restrained spaces (eg. micropores)¹⁵ are two widely adopted methodologies to achieve for higher stability. However, too strong MSI might over stabilize the active sites, hindering its activation to reactants/intermediates^{14,16}; confinement of the metal species in micropores might also limit mass transfers^{15,17}. Consequently, a seesaw relation between stability and activity have been often observed, obscuring the tremendous efforts for optimizing the catalytic performance of SADCs¹⁸⁻²⁰.

In this work, we report that the challenge can be solved by synergizing strong metal-support interactions (SMSIs) and spatial confinement to break the seesaw relationship between activity and stability of SADCs at high metal loadings. Specifically, strong Ni-N/C interaction and spatial confinement applied by dense atomic Cu grippers (8.1 wt%) on a graphitic C₃N₄ support are simultaneously utilized, endowing a great structural flexibility and reversible bond breakings and makings of the supported highly loaded (3.1wt%) atomic Ni upon reactant adsorption and product desorption, respectively. Such a dynamic effect not only facilitates the acetylene adsorption for high activity by achieving a full acetylene conversion at a moderate temperature of ~170 °C along with a high ethylene selectivity of 90%, but also ensures high thermal/chemical stability and unprecedented inhibition of coke formation by exhibiting an unprecedented long-durability of at least 350 h, far superior to the conventional atomically-dispersed Ni catalyst in terms of stability, activity, and selectivity.

Results

Synthesis and catalytic performance. G-C₃N₄, containing periodic triangular cavities with six coordinately unsaturated pyridinic nitrogen (N_{py}) atoms, provides a perfect platform for anchoring active and dense metal species^{21,22}. Computational screening was first conducted by density functional theory (DFT) calculations to identify the optimum candidates among group VIII and IB metals on g-C₃N₄. Ni and Cu were found to exhibit strong binding to g-C₃N₄ underneath along with low formation energy compared to the other metals (Supplementary Table 1), therefore 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 reactions^{23,24}, was employed to deposit Cu and Ni on g-C₃N₄ with near atomic precision^{25,26}. Atomically dispersed Cu grippers were first fabricated on g-C₃N₄ by Cu ALD (denoted as Cu₁/g-C₃N₄), and the atomic dispersion of the Cu grippers, even at a saturated loading of as high as ~ 11.2 wt.% by five Cu ALD cycles was confirmed by X-ray adsorption spectroscopy (XAS) and aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Supplementary Figs. 1a, 2-5 and Supplementary Table 2). At sub-saturation coverages of Cu, the open N_{py} atoms along with the neighboring Cu atoms together provide abundant anchor sites for guest atoms, analogous to that of stabilization of metal atoms by pincer ligands in organometallic chemistry²⁷. Next, Ni_γCu₁/g-C₃N₄ catalysts were synthesized by depositing Ni on sub-saturated Cu₁/g-C₃N₄ (γ is the atomic ratio of Ni to Cu) using NiO_x ALD; therein isolated Ni atoms were gripped and stabilized jointly by the open N_{py} sites through SMSIs and adjacent Cu atom grippers through spatial confinements, as seen in the schematic illustration and morphology in Supplementary Figs. 6 and 7, respectively. This is supported by the decrease of Ni loadings as increase of the number Cu ALD cycles, and the negligible Ni deposition on the saturated **Cu₁/g-C₃N₄ sample** (Supplementary Fig. 1b). For comparison, Ni₁/g-C₃N₄ SADCs were also fabricated by executing one cycle of NiO_x ALD directly on g-C₃N₄ (Supplementary Figs. 8-12 and Supplementary Table 3). HAADF-STEM showed that Cu₁/g-C₃N₄, Ni₁/g-C₃N₄, and Ni₁Cu_x/g-C₃N₄

catalysts were all atomically dispersed and thermally stable at 350 °C under H₂ (Supplementary Figs. 13-15), in line with the above theoretical predictions. Next, three samples, Cu₁/g-C₃N₄ (8.1 wt.%), Ni₁/g-C₃N₄ (3.1 wt.%) and Ni₁Cu₂/g-C₃N₄ with similar loadings of Cu and Ni (8.1 wt.% and 3.1 wt.%, a mole ratio of 2.4:1, respectively), were tested for catalytic hydrogenation.

Selective hydrogenation of acetylene in excess ethylene was conducted in a quartz tube plug-flow reactor. We found that Cu₁/g-C₃N₄ was nearly inactive and reached a maximum acetylene conversion of only 10% with a low ethylene selectivity of ~60% at 214 °C (Fig. 1a, 1b). The Ni₁/g-C₃N₄ catalyst performed slightly better, achieving 33% conversion and ~85% ethylene selectivity at 260 °C. Surprisingly, the Ni₁Cu₂/g-C₃N₄ catalyst showed a much higher activity, 100% conversion at ~170 °C. Importantly, the ethylene selectivity was at least as high as 90% even at the full acetylene conversion, which is vital for the practical removal of acetylene impurity from ethylene down to a few parts per million (ppm) without consuming the ethylene²⁸. The corresponding activity was 7.01 h⁻¹ at 160 °C, which is about 11 and 58 times higher than that of Ni₁/g-C₃N₄ and Cu₁/g-C₃N₄, respectively (Fig. 1c). Though Cu alone was much less active with poor ethylene selectivity, its presence in Ni₁Cu₂/g-C₃N₄ promoted both activity and selectivity. This was further confirmed by

the corresponding kinetics measurements with less amounts of catalysts, where apparent activation energies were 45.1, 86.5, and 132.9 kJ/mol for Ni₁Cu₂/g-C₃N₄, Ni₁/g-C₃N₄, and Cu₁/g-C₃N₄, respectively (Supplementary Fig. 16).

Remarkably, in addition to high thermal stability, the Ni₁Cu₂/g-C₃N₄ catalyst showed an 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 increase of acetylene conversion in the first ~ 6 h, and then deactivated rapidly with an activity loss of ~50% in about 50 h at temperatures of 200 °C (Fig. 1d). The initial increase of acetylene conversion is likely due to agglomeration of Ni atoms into Ni particles under reaction conversions as evidenced by X-ray diffraction (XRD) and HAADF-STEM measurements (Supplementary Figs. 19 and 20).

To check for the possible formation of green oils, the dominant form of coke in this reaction²⁹⁻³³, highly sensitive state-of-the-art *in situ* synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) measurements were employed to detect the volatile green oils at the reactor outlet. We found that besides C₂ species, there were considerable gaseous C₃-C₈ species produced on Ni₁/g-C₃N₄ (Fig. 1e and Supplementary Fig. 21), indicating the facile formation of green oils. In contrast, there was no higher hydrocarbons observed except a trace amount of C₄H₈ on Ni₁Cu₂/g-C₃N₄, confirming unambiguously the complete inhibition of formation of green oils. After executing 2 h of reaction, temperature-programmed deposition (TPD) measurements using SVUV-PIMS were further conducted to analyze the possible accumulation of green oils on these two samples. Again, there were only trace amount of C₄₊ species found on Ni₁Cu₂/g-C₃N₄, and in sharp contrast, C₃-C₁₇ species were all heavily

present on Ni₁/g-C₃N₄ (Fig. 1f and Supplementary Figs. 22 and 23). Compared to those *in situ* SVUV-PIMS measurements in Fig. 1e, considerable increase of C₇₊ species on Ni₁/g-C₃N₄ during TPD measurements is attributed to their low vapor pressures, which endow them more prone to accumulate on the catalyst.

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

Catalysts	Morphology	Total transition metal loadings (wt.%)	Ethylene selectivity (%) ^a	TOS (h)	Average deactivation rate ^b (%/h)	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 ³¹
Ni SAs/N-C	Single ions	1.5	90	18	0.61	N.A. ^e	Ref ³⁴
Cu ₁ /ND@G	Single ions	0.2	98	60	0	N.A. ^e	Ref ¹⁰
0.5Cu/Al ₂ O ₃	Single ions	0.5	91	40	0	Yes	Ref ³⁵
Pd ₁ /ND@G	Single ions	0.11	90	30	0	N.D. ^f	Ref ³⁶
ISA-Pd/MPNC	Single ions	0.043	82	20	0.05	N.A. ^e	Ref ³⁷
AgPd _{0.01} /SiO ₂	SAAs ^c	4.91	80	24	0.25	N.A. ^e	Ref ³⁸
AuPd _{0.01} /SiO ₂	SAAs ^c	4.92	70	24	0.71	Yes	Ref ³⁹
NiGa	IMC ^d	10.0	75	24	0.04	Yes	Ref ⁴⁰
Ni ₃ Ga/MgAl ₂ O ₄	IMC ^d	2.0	77	24	0.16	Yes	Ref ⁴¹
Al ₁₃ Fe ₄	IMC ^d	N.A. ^e	82	20	0.55	Yes	Ref ⁴²
PdZn	IMC ^d	N.A. ^e	91	20	0.20	Yes	Ref ⁴³
Nano-GaPd ₂	IMC ^d	N.A. ^e	72	20	0.25	Yes	Ref ⁴⁴
pre-NiCu/MMO	Bimetallic NPs	19.7	70	16	1.56	Yes	Ref ⁴⁵
NiIn/SiO ₂	Bimetallic NPs	8.0	35	10	6.91	Yes	Ref ⁴⁶

^aEthylene selectivity was determined at near 100% acetylene conversion; ^bThe average deactivation rate was determined by the decrease of acetylene conversion divided by TOS; ^csingle-atom alloys; ^dintermetallic compound; ^enon-available; ^fnon-detectable.

Coke formation under hydrogenation conditions was further monitored by *in situ* thermogravimetric analysis (TGA). After 12 h, the weight-gain of Ni₁Cu₂/g-C₃N₄ was negligible, close to the thermal noise. Whereas, the Ni₁/g-C₃N₄ catalyst showed a considerable weight increase by 7.6% (Fig. 1g), in line with the above SVUV-PIMS measurements. X-ray diffraction (XRD) revealed graphitic coke formed on the used Ni₁/g-C₃N₄ (Supplementary Fig. 19), but not on the used Ni₁Cu₂/g-C₃N₄. Clearly, the capability of coke-inhibition and long-durability achieved on the Ni₁Cu₂/g-C₃N₄ catalyst are unprecedented, far superior to the benchmark catalysts of metal single-atoms, intermetallic compounds, and NPs reported in literature (Table 1 and Supplementary Tables 4-6). Such simultaneous achievement of complete coke-inhibition, high activity, high ethylene selectivity, as well as outstanding thermal and chemical stability by Ni₁Cu₂/g-C₃N₄ was also found in semi-hydrogenation of 1,3-butadiene in excess propene (Supplementary Fig. 24), rendering this material promising for wide applications.

Structural characterization. To identify the active sites and reveal the structure-activity relationships of the $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ catalyst, a number of atomic-resolution STEM images of these samples at different locations were collected. Statistical analysis indicates that there were mainly three structural motifs, namely, single atoms, linear trimers and triangular trimers with distinct composition and populations, respectively (Fig. 2a, Supplementary Figs. 5, 7, and 12). For $\text{Cu}_1/\text{g-C}_3\text{N}_4$, the single atoms were the most populated at 68%, followed by the linear trimers at 20% and the triangular trimers at 12% (Fig. 2b). Subsequent Ni deposition forms $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$, and the linear trimers increased dramatically to 71% in expense of the single atoms to 18%, while the triangular trimers remained $\sim 11\%$. This suggests that most of the pre-deposited single Cu atoms might be bridged by added Ni atoms to form new linear trimers (Supplementary Fig. 6). The overall lengths of the linear trimers were 5.66 ± 0.20 Å composing by two unequal atom-atom distances of 2.61 ± 0.14 and 3.04 ± 0.13 Å in average (Fig. 2c and Supplementary Fig. 7). Since there were no triangular trimers observed in $\text{Ni}_1/\text{g-C}_3\text{N}_4$ (86% of the single atoms and 14% of the linear trimers, Supplementary Fig. 12), the triangular trimers in $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ are the triangular trimers from $\text{Cu}_1/\text{g-C}_3\text{N}_4$ and compose Cu only. Considering the negligible activity of $\text{Cu}_1/\text{g-C}_3\text{N}_4$ and $\text{Ni}_1/\text{g-C}_3\text{N}_4$ below 170 °C, the exceptional overall performance of $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ should come solely from the new and prevailing linear trimers, which was extremely stable, even after 350 °C reduction and the long-term reaction test (Supplementary Figs. 15 and 18).

In situ X-ray photoemission spectroscopy (XPS) revealed the composition and chemical state of the $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ catalyst, in particular the active linear trimers. Figure 2d shows XPS spectra of the $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ catalyst in the Cu 2p, Ni 2p and O 1s regions after reduction at 350 °C for 2 h followed by exposing to the reaction gas at 160 °C for another 1 h. Irrespective of the treatments, the Cu 2p_{3/2} binding energy was invariant at 933.2 eV, an indication of 1⁺ oxidation state^{27,47} (Fig. 2d and Supplementary Fig. 25). The Ni 2p_{3/2} binding energy was located at 855.8 eV, close to that of $\text{Ni}(\text{OH})_2$ ⁴⁸. Along with this, considerable hydroxyl-type oxygen, with O 1s at 531.4 eV was found. Since there were only trace of oxygen in $\text{g-C}_3\text{N}_4$ and $\text{Cu}_1/\text{g-C}_3\text{N}_4$, the OH groups in $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ were accompanied along with the Ni (Supplementary Figs. 25 and 26). Quantitative XPS analysis showed that the stoichiometric ratio between O and Ni was about 2:1. Taken together the results suggest that the active linear trimers are $\text{Ni}_1(\text{OH})_2\text{Cu}_2$ complexes formed under reaction conditions. While we noticed that exposing $\text{Ni}_1/\text{g-C}_3\text{N}_4$ catalyst to the reaction gas at 200 °C for another 1 h cause the formation of metallic Ni and NiO species (Supplementary Fig. 26), in line with the STEM observation (Supplementary Fig. 20).

To reveal the structure of the active $\text{Ni}_1(\text{OH})_2\text{Cu}_2$ complexes on $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ under reaction conditions, *in situ* XAS measurements were conducted (Supplementary Fig. 15). The extended X-ray absorption fine structure (EXAFS) curve of $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ after 350 °C hydrogen reduction ($\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4\text{-R}$) exhibited a Ni K-edge spectrum with one main peak at 1.41 Å and a weak peak at 2.21 Å (Fig. 2e). The main peak was assigned to Ni-O/N/C scattering, by comparison to Ni foil, NiO, and nickel(II) phthalocyanine (NiPc). Furthermore, the EXAFS curve of $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ under the hydrogenation condition ($\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4\text{-H}$) is very close to that of $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4\text{-R}$, indicating little variation in local coordination of the active

$\text{Ni}_1(\text{OH})_2\text{Cu}_2$ complexes in presence of acetylene and ethylene. To get a better understanding of the weak feature at 2.21 Å, wavelet transform (WT) of the EXAFS spectrum was performed and showed that Ni-O/N/C and Ni-Cu coordination co-exists as evidenced by the shift of peak B toward to a higher k value relative to peak A (Supplementary Fig. 27). Quantitative EXAFS fitting produced coordination numbers (CNs) for the nearest Ni-O/N/C and the next-nearest Ni-Cu were 3.3 and 0.6 with bond distances of 1.95 and 2.90 Å, respectively (Supplementary Fig. 28 and Supplementary Table 7). Similarly, at the Cu K-edge, the $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4\text{-R}$ and the $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4\text{-H}$ appeared the same structure, the main peak at 1.47 Å was attributed to Cu-O/N/C coordination, and the weak peak 2.33 Å was assigned to Cu-Cu/Ni coordination according to the WT map. Quantitative EXAFS fitting gave CNs for the nearest Cu-O/N and the next-nearest Cu-Cu/Ni CNs of 1.7 and 0.5 with distances of 1.87 Å and 2.83 Å (Fig. 2f, Supplementary Fig. 29 and Supplementary Table 8).

Spectroscopic insight of the hydrogenation process. To further confirm the presence of hydroxyl groups in both $\text{Ni}_1/\text{g-C}_3\text{N}_4$ and $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$, and investigate their catalytic roles in hydrogenation, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were carried out by alternatively exposing these two catalysts to acetylene and hydrogen after reduction at 350 °C. We found that two negative peaks at 3562 and 3430 cm^{-1} on $\text{Ni}_1/\text{g-C}_3\text{N}_4$, assigned to Ni-OH groups⁴⁹, developed with time as exposing to acetylene at 160 °C (Fig. 3a). The consumption of hydroxyls may be attributed to their reaction with acetylene and Ni aggregations to Ni/ NiO_x particles (Supplementary Figs. 20 and 26). Meanwhile, the IR bands in the ranges of 3200-3300, 2900-3200 and 2800-2900 cm^{-1} gradually increased in intensity with time, which are assigned to the $\nu(\equiv \text{C-H})$ vibrations of gas phase acetylene, $\nu(\text{C-H})$ of chemisorbed acetylene, and $\nu(\text{CH}_3)$ of ethylidene/ethylidyne, respectively⁵⁰. Next, switching the gas to hydrogen declined the peaks of all C-H stretching, 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, but we noticed that the $\nu(\text{CH}_3)$ of ethylidene/ethylidyne peak intensity became more pronounced during the initial H_2 exposure in the second cycle, suggesting more ethane was formed in the second acetylene-hydrogen cycle.

In the case of $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$, two negative peaks at 3595 and 3453 cm^{-1} of Ni-OH, along with positive $\nu(\equiv \text{C-H})$ vibrations of gas phase acetylene (3200-3300 cm^{-1}), $\nu(\text{C-H})$ of chemisorbed acetylene (2900-3200 cm^{-1}), emerged as exposing to acetylene at 160 °C (Fig. 3b). Next, switching the gas to hydrogen recovered the Ni-OH group, and declined all C-H stretching. Repeating the experiments for another acetylene-hydrogen cycle showed identical results. Consumption and regeneration of Ni-OH groups during sequential acetylene and hydrogen exposures is in sharp contrast with that of $\text{Ni}_1/\text{g-C}_3\text{N}_4$, implying that Ni-OH group is present in $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$, and participates into the hydrogenation reaction. Interestingly, we noticed that there was lack of any features in the range of 2800-2900 cm^{-1} , suggesting that much less ethane was formed on $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$, in an excellent agreement with the high ethylene selectivity as shown in Fig. 1b.

Theoretical insight of Ni₁ and Ni₁Cu₂ catalysts. Based on the above structural characterization and extensive DFT calculations, the NiCu complexes on g-C₃N₄ is identified as a chain-like Cu-OH-Ni-OH-Cu structure (Fig. 4a and Supplementary Fig. 30), whereas the Ni species in Ni₁/g-C₃N₄ after reduction is Ni₁(OH)₂ complexes (Supplementary Fig. 31 and Supplementary Table 9). For the former one, the Ni atom bonds to N_{py} and C of g-C₃N₄ underneath, confined by Cu atom from two sides through bridging OH group; the Cu atom grippers are further fastened on g-C₃N₄ through strong Cu-N_{py} bond. Optimized bond lengths of the Ni-O/N/C bond and Cu-O/N bond are an average of 1.95 and 1.87 Å with corresponding CNs of 4 and 2 (Supplementary Table 10), respectively, in excellent agreement with EXAFS. The overall length of the optimized complexes (5.84 Å) and two unequal Ni-Cu distances (2.74 and 3.10 Å) also agree perfectly with STEM (Fig. 2c). Charge density difference shows that there is significant 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. 32). Simultaneous presence of characteristic covalent bond and ionic bond manifest clearly the so-called SMSI between Ni₁Cu₂(OH)₂ and g-C₃N₄ support, which was found in Ni₁(OH)₂/g-C₃N₄ as well.

As shown above, Ni₁/g-C₃N₄ and Ni₁Cu₂/g-C₃N₄ exhibited sharply different chemical stability under the hydrogenation condition, although both are stable in H₂. Different chemical stability after introduction of acetylene and ethylene stems from the distinct structure change induced by their stronger adsorption to both Ni₁/g-C₃N₄ and Ni₁Cu₂/g-C₃N₄ than H₂, as found by DFT calculations and the corresponding TPD measurement (Supplementary Fig. 33 and Supplementary Table 11). It is found that acetylene adsorption on Ni₁/g-C₃N₄ goes through a modest barrier of 0.62 eV with an exothermic adsorption energy of 0.69 eV (Fig. 4b). At the meanwhile, one Ni-N/C support bond is broken, and there is only one Ni-N/C support bond left between the Ni(OH)₂-C₂H₂ complex and the g-C₃N₄ support underneath, which can be broken further with a barrier of 0.66 eV only. In other words, the Ni(OH)₂-C₂H₂ complex formed is rather mobile on Ni₁/g-C₃N₄, and this would facilitate its aggregation and subsequent formation of Ni NPs, as found by STEM and XPS in acetylene hydrogenation (Supplementary Figs. 20 and 26). The formed Ni particles, owing to the presence of large Ni assemblies, in turn dramatically promotes the heavy coke formation (Fig. 1e-g), thus endowing rapid catalyst deactivation to a short catalyst life time (Fig. 1d). Obviously, SMSI alone is not sufficient to stabilize the Ni(OH)₂ complexes, although the corresponding bonding by the two Ni-N bonds (-2.93 eV) is considerable strong.

Acetylene adsorption on Ni₁Cu₂/g-C₃N₄ is stronger with an exothermic energy of 1.00 eV from DFT, and corresponding TPD measurement indeed found a higher desorption temperature than that on Ni₁/g-C₃N₄ (Supplementary Fig. 33). Optimized structure indicates that though acetylene adsorption breaks two interfacial Ni-N/C support bonds with practically no barrier, there are two new Ni-C bonds with adsorbed C₂H₂ formed (Fig. 4b and Supplementary Video 1). As a result, the overall coordination number of the Ni atom before and after acetylene adsorption does not change, a fact of that agrees excellently with invariant XAFS curve in both acetylene hydrogenation and pure hydrogen conditions (Fig. 2e, and Supplementary Table 10). Nonetheless, spatial confinement by the two atomic Cu grippers from both

sides through two bridging hydroxyls endows the breakages of Cu-O support bond extremely endothermic by more than 4 eV, ensuring a high chemical stability of this catalyst during acetylene hydrogenation. Resulted dynamics of the Ni atoms from synergizing SMSI and spatial confinements ensures not only a facile structural transformation by breaking the Ni-N/C bonds to enhance the adsorption of acetylene, but also a high chemical/thermal stability of SADCs free from aggregation (Supplementary Fig. 34).

Atomically dispersed and stable Ni atoms is beneficial to suppress the C-C bond breaking and making necessarily for formation of graphitic coke and green oils due to the limited sites available (Fig. 4c, and Supplementary Table 12). For instance, cleavage of adsorbed acetylene is highly endothermic because of the absence of sites accommodating the broken CH^* fragments. Moreover, after adsorption of acetylene preferentially at the top of the Ni atom, 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 (RT). As a result, formation of graphitic coke and green oils is prohibited on $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$, in an excellent agreement with the *in situ* SVUV-PIMS and TGA measurements (Fig. 1e-g).

Beside high stability and high coking-resistance, characteristic dynamics of Ni atoms from SMSI and spatial confinement also renders this material with high activity and selectivity (Supplementary Fig. 34 and Supplementary Video 1). Optimized potential energy surfaces for hydrogenation of acetylene over the $\text{Ni}_1(\text{OH})_2\text{Cu}_2$ complex are shown in Fig. 4d (also seen the details in Supplementary Figs. 35-37). Acetylene is expected to be dominant on the Ni sites during hydrogenation, because acetylene (-1.00 eV) adsorption on the Ni site is much stronger than that of H_2 (-0.07 eV) (Supplementary Fig. 33, and Supplementary Table 11). After acetylene adsorption, the proton in one bridging OH tends to attack the adsorbed acetylene directly with a barrier of 1.23 eV to form C_2H_3^* (here * denotes surface species, Fig. 4d, i and ii). Next, hydrogen adsorbs on the Ni sites and dissociates effortlessly with one H atom addition to C_2H_3^* to form C_2H_4^* , and the other one bonding to the Ni site (Fig. 4d, iii and iv). After that, the C_2H_4^* specie 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 to 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 a high selectivity of $\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$, in line with the catalytic results in Fig. 1. Obviously, the bridging hydroxyls participation into the hydrogenation reaction suggested by DFT consists very well with the DRIFTS results (Fig. 3).

Conclusions

In summary, we have reported that synergizing SMSI and spatial confinement through the Cu atomic grippers boosts dynamics of high loaded atomic Ni on a $\text{g-C}_3\text{N}_4$ support for efficient hydrogenations. Such dynamic and synergetic effects enable not only exceptionally high stability against both sintering and coke formation in hydrogenation of acetylene and 1,3-butadiene, but also lead the active sites highly adaptable for both reactant adsorption and product desorption, thus boosting an activity, 11 times higher

than the conventional $\text{Ni}_1/\text{g-C}_3\text{N}_4$ catalyst, and high ethylene selectivity. This is the first example of synthesis of dynamically confined SADCs using an atom-by-atom fabrication approach, shedding light on how rational design of highly-active and stable catalysts can achieve practical application in selective chemical reactions. This work might bridge and inspire the heterogeneous catalysis community and organometallic community to develop new structures of advanced catalysts for large-scale industrial processes in the near future.

Methods

Materials. Copper(II) hexafluoroacetylacetonate hydrate ($\text{Cu}(\text{hfac})_2$), formalin (37% formaldehyde in aqueous solution), and bis(cyclopentadienyl) nickel(II) (NiCp_2) were all bought from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Urea (99%), Cu_2O (99.9%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%), NaBH_4 (99%), CuO (99%), CaCl_2 (99%) and NiO (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nickel(II) phthalocyanine (NiPc), copper(II) phthalocyanine (CuPc), and $\text{Ni}/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst (Ni loading 66 wt.%) were all bought from Alfa Aesar Co., Ltd. Lindlar Pd catalyst ($\text{Pd-PbO}/\text{CaCO}_3$) was purchased from TCI (Shanghai) Development Co., Ltd. All chemicals were used as received without further purification.

Ultrahigh purity N_2 (99.999%), O_2 (99.999%), H_2 (99.999%), Ar (99.999%), and the gas mixtures include: 10% O_2 in Ar, 10% H_2 in Ar, 0.5% C_2H_2 , 5% H_2 , 25% C_2H_4 in Ar, 1.2% 1,3-butadiene, 12% H_2 in Ar were all provided by Nanjing Special Gases.

Synthesis of $\text{g-C}_3\text{N}_4$ support. Urea **was placed in a crucible and heated** to 600 °C for 4 h in static air with a ramp rate of 5 °C min^{-1} . 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 $\text{g-C}_3\text{N}_4$ support was finally obtained.

Synthesis of $\text{Cu}_1/\text{g-C}_3\text{N}_4$ catalysts. Cu ALD was carried out on a viscous flow stainless steel tube reactor system (ACME (Beijing) Technology Co., Ltd) at 300 °C using $\text{Cu}(\text{hfac})_2$ and formaldehyde as precursors. Ultrahigh purity N_2 (99.999%) was used as a carrier gas at a flow rate of 60 $\text{mL} \cdot \text{min}^{-1}$. The $\text{Cu}(\text{hfac})_2$ precursor container was heated to 65 °C to reach a sufficient vapor pressure. The inlet manifold was held at 100 °C to avoid precursor condensation. The timing sequence was 300, 300, 40, and 180 s for $\text{Cu}(\text{hfac})_2$ exposure, N_2 purge, formaldehyde exposure, and N_2 purge, respectively. One, two, and ten cycles of Cu ALD were performed on $\text{g-C}_3\text{N}_4$ to obtain $\text{Cu}_1(5.1\%)/\text{g-C}_3\text{N}_4$, $\text{Cu}_1(8.1\%)/\text{g-C}_3\text{N}_4$, and $\text{Cu}_1(11.4\%)/\text{g-C}_3\text{N}_4$ catalysts, respectively. When the $\text{Cu}(\text{hfac})_2$ exposure time was reduced to 150 s, one cycle of Cu ALD on $\text{g-C}_3\text{N}_4$, yielded a Cu loading of 2.7%, which was denoted as $\text{Cu}_1(2.7\%)/\text{g-C}_3\text{N}_4$.

Synthesis of $\text{Ni}_1/\text{g-C}_3\text{N}_4$ and **$\text{Ni}_1\text{Cu}_2/\text{g-C}_3\text{N}_4$ catalysts.** NiO_x ALD was carried out on the $\text{g-C}_3\text{N}_4$ support at 240 °C using NiCp_2 and ozone as precursors. The NiCp_2 precursor container was heated to 90 °C to achieve a sufficient vapor pressure. The inlet manifold was held at 115 °C to avoid precursor condensation on the inner walls. The timing sequence was 1260, 200, 1260, and 200 s for the NiCp_2

exposure, N₂ purge, O₃ exposure, and N₂ purge, respectively. Different NiCp₂ exposure time (from 100 to 1260 s) was performed on g-C₃N₄ to obtain a series of Ni single-atom catalysts with different Ni loadings (denoted as Ni₁(x%)/g-C₃N₄, x is the Ni loading). NiO_x ALD was also carried on the Cu₁(5.1%)/g-C₃N₄ and Cu₁(8.1%)/g-C₃N₄ samples. The resulting samples were denoted as Ni₁Cu₁/g-C₃N₄ and Ni₁Cu₂/g-C₃N₄, respectively.

Synthesis of Ni_{NPS}/g-C₃N₄ catalyst. The g-C₃N₄ supported Ni particle catalyst (Ni_{NPS}/g-C₃N₄) was synthesized using the precipitation deposition method. Briefly, 1 gram of as-prepared g-C₃N₄ support was immersed into 50 mL water, then stirring for 10 min at room temperature. Next, 198 mg of Ni(NO₃)₂·6H₂O was slowly added into the solution and stirred for 1 h. Afterward, an aqueous solution of NaBH₄ (0.54 mol L⁻¹, 10 mL) was added dropwise and stirred overnight. The solids were separated by filtration, washed thoroughly with H₂O and dried overnight at 70 °C. Finally, the dried material was reduced at 350 °C for 2 h in 10% H₂/Ar to obtain the Ni_{NPS}/g-C₃N₄ catalyst.

Morphology and compositions. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (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) and STEM measurements were performed on another JEOL-2100F instrument operated at 200 keV. The Ni and Cu loadings of the catalysts were analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES). X-ray diffraction (XRD) spectra were recorded on a SmartLab™ 9kw Rotating Anode X-ray diffractometer.

***In situ* SVUV-PIMS Measurements.** To study the formation of green oils, *in situ* SVUV-PIMS measurements were conducted on the mass spectrometry end-station (BL04B) of the National Synchrotron Radiation Laboratory, Hefei, China⁵¹. In brief, 150 mg of Ni₁Cu₂/g-C₃N₄ or Ni₁/g-C₃N₄ catalyst was loaded in a fixed-bed flow reactor, which was connected to the SVUV-PIMS system⁵². The catalyst was first reduced in 10% H₂ in Ar at a flow rate of 50 mL min⁻¹ at 350 °C for 2 h, then cooled to 160 °C for Ni₁Cu₂/g-C₃N₄ and 200 °C for Ni₁/g-C₃N₄. After the sample temperature became stabilized, reaction gas consisting of 0.5% C₂H₂, 5% H₂, and 25% C₂H₄ balanced with Ar at a flow rate of 50 mL min⁻¹ was then introduced to the quartz-tube reactor at a total pressure of 2 Torr. The volatile components at the reactor outlet were ionized by the synchrotron VUV light, and the formed ions were analyzed by a homemade time-of-flight mass spectrometer at a photon energy of 12 eV. After 2 h of continuous data collection, the reaction gas was switched to pure Ar, then gradually increasing the sample temperature at a heating rate of 5 °C min⁻¹ to 300 °C, while the composition of accumulated green oils on two samples were analyzed by the online SVUV-PIMS spectrometer.

***In situ* TGA measurements.** *In situ* TGA measurements were performed on a TGA550 instrument (TA instruments) equipped with an evolved gas analysis (EGA) furnace to quantify the coke formation during

semi-hydrogenation of acetylene. After loading sample into the EGA furnace, the sample was heated to 350 °C with a heating rate of 3 °C min⁻¹ in 10% H₂/Ar (25 mL min⁻¹) and then maintained isothermally for 2 h to reduce the sample. Next, the sample was cooled to a specified temperature in argon (25 mL min⁻¹) and maintained isothermally for 1 h to stabilize the instrument. Next, acetylene hydrogenation gases consisting of 0.5% acetylene, 5% H₂, and 25% ethylene balanced in Ar was introduced to the sample at a flow rate of 25 mL min⁻¹ for about 12 h at the specified temperature. The change of the sample weight with time during acetylene hydrogenation was recorded. Here the temperatures for acetylene hydrogenation were 160, and 200 °C, for Ni₁Cu₂/g-C₃N₄, and Ni₁/g-C₃N₄ catalysts, respectively, to ensure a similar initial conversion for these samples.

***In situ* XPS measurements.** *In situ* XPS and Auger spectra measurements were conducted at the BL10B beamline photoemission end station at the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. In brief, the beamline is connected to a bending magnet and covers photon energies from 100 to 1000 eV. The end-station consists of four chambers, i.e., analysis chamber, preparation chamber, quick sample load-lock chamber and a high-pressure reactor. The analysis chamber, with a base pressure of <5×10⁻¹⁰ torr, is connected to the beamline and equipped with a VG Scienta R3000 electron energy analyzer and a twin anode X-ray source. The high-pressure reactor houses a reaction cell where the samples can be treated with different gases up to 20 bar and simultaneously heated up to 650 °C. After sample treatment, the reactor can be pumped down to high vacuum (<10⁻⁸ torr) for sample transfer.

In this work, after loading the as-prepared Ni₁Cu₂/g-C₃N₄ sample into the chamber, a set of XPS spectra in the Ni 2p, Cu 2p, N 1s, C 1s, and O 1s regions were first recorded without any treatment (denoted as Ni₁Cu₂/g-C₃N₄). Next, the sample was transferred back into the high-pressure reactor, and reduced in 10% H₂ in Ar at 350 °C for 2 h at the atmosphere pressure. Another set of XPS spectra were collected after transferred back to the analysis chamber. The reduced sample was denoted as Ni₁Cu₂/g-C₃N₄-R. Finally, the sample was exposed to the acetylene hydrogenation stream consisting 0.5% C₂H₂, 5% H₂, and 25% C₂H₄ balanced with Ar in the high-pressure reactor at 160 °C for another 1 h. Another set of XPS spectra were then collected after the hydrogenation reaction gas treatment without exposing to air, which was denoted as Ni₁Cu₂/g-C₃N₄-H. Similarly, XPS spectra of the Ni₁/g-C₃N₄ sample were also collected following the same procedure. The XPS spectra of the sample after reduction at 350 °C for 2 h and exposing reaction gas at 200 °C for another 1 h were denoted as Ni₁/g-C₃N₄-R and Ni₁/g-C₃N₄-H, respectively. The C 1s binding energy at 284.8 eV was used as an internal reference.

***In situ* XAFS.** *In situ* XAFS measurements at the Ni K edge (8333 eV) and the Cu K edge (8979 eV) were performed in a transmission mode with the Si(311) monochromator at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), China. The storage ring of SSRF worked at 3.5 GeV with a maximum current of 210 mA⁵³. A homemade 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.

Typically, the as-prepared Ni₁Cu₂/g-C₃N₄ sample was put into the reaction cell and purged with He for 10 min at room temperature, then XAFS spectra were recorded at both the Ni and Cu K edges (denoted as Ni₁Cu₂/g-C₃N₄). After that, the sample was reduced in 10% H₂ in He at 350 °C for 2 h. After cooling the sample to 160 °C in 10% H₂ in He, a XAFS spectrum was recorded at the Ni K edge and Cu K edge, which was denoted as Ni₁Cu₂/g-C₃N₄-R. Finally, the sample was exposed to the acetylene hydrogenation reaction stream consisting 0.5% C₂H₂, 5% H₂, and 25% C₂H₄ balanced with Ar at 160 °C for another 1 h, and XAFS spectra were recorded sequentially at the Ni and Cu K edges, which were denoted as Ni₁Cu₂/g-C₃N₄-H. Similarly, *in situ* XAFS measurements of Ni₁/g-C₃N₄ were also collected following the same procedure but only collecting XAFS spectra at the Ni K edge. The XAFS spectra of the sample after reduction at 350 °C for 2 h was denoted as Ni₁/g-C₃N₄-R.

The acquired EXAFS data were processed according to the standard procedures using the ARTEMIS module implemented in the IFEFFIT software packages. The EXAFS oscillation functions $\chi(k)$ were obtained by subtracting the post-edge background from the overall absorption spectra and then normalized with respect to the edge-jump step.

In terms of the Ni K edge, fittings were done in the *R*-space within the *R*-range of 0.8 - 3.0 Å⁻¹ for *k*³-weighted $\chi(k)$ functions with Hanning windows (*dk* = 1.0 Å⁻¹), and a *k*-range of 2.3 - 10.4 Å⁻¹ was used, during curve fittings, the amplitude reduction factor *S*₀² was fixed at the value of 0.78 determined by fitting the data of Ni foil. In terms of the Cu K edge, the *R*-range of 1.1 - 3.0 Å⁻¹ and *k*-range of 2.9 - 12.4 Å⁻¹ were used, during curve fittings, the amplitude reduction factor *S*₀² was fixed at the value of 0.9 determined by fitting the data of Cu foil. Debye–Waller factors (*s*²), coordination numbers (*N*) and interatomic distances (*R*), energy shift (*DE*₀) were treated as adjustable parameters during the fitting process.

The yielded *R*-factors of all samples are not larger than 0.008, indicating the good fitting qualities.

Temperature-programmed desorption (TPD). The H₂, C₂H₂ and C₂H₄ TPD experiments were performed on a micromeritics AutoChem II chemisorption analyzer, which was connected to a Pfeiffer OminiSTAR 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 (RT) in He, H₂, C₂H₂ or C₂H₄ gas was then introduced to the sample until saturation. Next, purging the sample with He at 25 °C for 1 h, then gradually increasing the sample temperature at a heating rate of 10 °C min⁻¹ in He from 25 to 300 °C, while recording the TPD data.

***In situ* DRIFTS.** *In situ* DRIFTS were performed on a Thermo Nicolet iS10 FTIR spectrometer equipped with MCT detector at a resolution of 4 cm⁻¹ and 128 scans. 30 mg sample was first placed in a high-temperature cell (Harrick) with CaF₂ windows. 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. After that, the sample was exposed to 0.5% C₂H₂/Ar

(30 mL min⁻¹) for 30 min and the spectra were collected continuously during this process. Next, the gas was switched to 10% H₂ in Ar for 30 min, while recording the spectra. After that, the above experiments were repeated by sequentially exposing to C₂H₂ and H₂. It should be noted that all gases were passed through a calcium chloride filter at -40 °C in the gas inlet line before the Harrick cell to remove the trace water from the gas.

Catalytic 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. The amount of non-precious catalyst was 150 mg, which was diluted with 1 g of 200 mesh quartz chips. Prior to the reaction test, all catalysts were reduced in 10% H₂ in Ar at 350 °C for 2 h. Then the feed gas, consisting of 0.5% acetylene, 5% H₂, and 25% ethylene with Ar as the balance gas, was introduced to the reactor to start the reaction. Next, the acetylene conversion of all these catalysts was increased by increasing the reaction temperature. The reaction products were analyzed using an online gas chromatograph (A91, PANNA Instruments) equipped with a flame ionization detector and a capillary column (ValcoPLOT VP-Alumina-KCl, 50 m × 0.53 mm). The acetylene conversion and ethylene selectivity were calculated using the following equations (1) and (2), respectively:

$$\text{C}_2\text{H}_2 \text{ conversion (\%)} = \left(\frac{[\text{C}_2\text{H}_2]_{\text{in}} - [\text{C}_2\text{H}_2]_{\text{out}}}{[\text{C}_2\text{H}_2]_{\text{in}}} \right) \times 100 \quad (1)$$

$$\text{C}_2\text{H}_4 \text{ selectivity (\%)} = \left(1 - \frac{[\text{C}_2\text{H}_6]_{\text{out}} + 2[\text{C}_4]_{\text{out}}}{[\text{C}_2\text{H}_2]_{\text{in}} - [\text{C}_2\text{H}_2]_{\text{out}}} \right) \times 100 \quad (2)$$

[C₂H₂]_{in} and [C₂H₂]_{out} are the concentrations of acetylene at the inlet and outlet of reactor, respectively. [C₂H₆]_{out} and [C₄]_{out} is the concentrations of ethane and total C₄ products at the outlet of the reactor.

For the kinetic measurements, we reduced the amount of catalyst and increased the flow rate of reaction gas to ensure that the acetylene conversion was below 15%. TOFs of the non-precious catalysts were calculated using the following equation (3):

$$\text{TOFs} = \frac{\text{Mole of C}_2\text{H}_2 \text{ converted per hour}}{D \times n_{\text{metal}}} \quad (3)$$

Here, n_{metal} is the mole of Ni or Cu. For Ni₁Cu₂/g-C₃N₄, n_{metal} is the mole of Ni. D is the dispersion of metal nanoparticles or clusters/atoms, which is one for Ni₁/g-C₃N₄, Cu₁/g-C₃N₄, and Ni₁Cu₂/g-C₃N₄.

Semi-hydrogenation of 1,3-butadiene was also recorded on the same reaction test station and using the same gas chromatograph. The feed gas consists of 1.2% 1,3-butadiene, 12% H₂ with Ar as balance gas. Same pretreatment was performed on all catalysts prior to the reaction test. The 1,3-butadiene conversion and butenes selectivity were calculated using the following equations (4) and (5), respectively:

$$\text{1,3-butadiene conversion (\%)} = \frac{[1,3\text{-butadiene}]_{in} - [1,3\text{-butadiene}]_{out}}{[1,3\text{-butadiene}]_{in}} \times 100 \quad (4)$$

$$\text{Butenes selectivity (\%)} = \frac{[\text{Butenes}]_{out}}{[\text{Butenes}]_{out} + [\text{Butane}]_{out}} \times 100 \quad (5)$$

$[1,3\text{-butadiene}]_{in}$ and $[1,3\text{-butadiene}]_{out}$ are the concentrations of 1,3-butadiene at the inlet and outlet of reactor. $[\text{Butenes}]_{out}$ and $[\text{Butane}]_{out}$ are the concentrations of butenes and butane at the outlet of reactor, respectively.

Computational methods and models. All the spin-polarized calculations were performed using the DFT calculations as implemented in the Vienna ab initio Simulation Package (VASP)⁵⁴. We described the electron-ion interaction using the projector augmented wave (PAW) method⁵⁵. The exchange-correlation interaction was described by the optB86b-vdW functional⁵⁶. The Kohn-Shame equations were solved by using a plane-wave basis set with a kinetic energy cutoff of 400 eV. The convergence criteria for electronic self-consistent interactions is 10^{-4} eV. The geometries of bulk and surface were optimized by the conjugate gradient algorithm until the maximum force on any ion was less than 0.02 eV/Å. All the transition states were determined by using the climbing image nudged elastic band (CI-NEB) method⁵⁷ with confirmation of vibrational analysis. The transition states are optimized until all forces are below 0.05 eV/Å.

The g-C₃N₄ was modelled by a (2 × 2) supercell of a single layer g-C₃N₄, where all the atoms in the supercell were fully relaxed. A (3 × 3 × 1) Monkhorst-Pack 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 by $\Delta E = E_{FS} - E_{IS}$ and $E_a = E_{TS} - E_{IS}$, where E_{IS} , E_{FS} , and E_{TS} are the energies of the corresponding initial state, final state, and transition state, respectively.

The Gibbs free energy of CHCH and CH₂CH₂ gas species were corrected as equations (6):

$$G(T) = E_{DFT} + ZPE + U(T) - TS(T) + PV \quad (6)$$

Where E_{DFT} is the total energy from DFT at 0 K, ZPE is the zero-point energy. The temperature range was from 298.15 K to 573.15 K, the total pressure was 0.1 MPa, the partial pressures of CHCH and CH₂CH₂ were 0.5% and 25%, respectively, as the experimental reaction conditions.

The free energy of adsorbates at temperature T were estimated according to the harmonic approximation, and the entropy is evaluated using the following equation (7) and (8), respectively:

$$G(T) = E_{DFT} + ZPE + H(T) - TS(T) \quad (7)$$

$$S(T) = k_B \sum_i^{3N} \left[\frac{\varepsilon_i}{k_B T (e^{\varepsilon_i/k_B T} - 1)} - \ln (1 - e^{-\varepsilon_i/k_B T}) \right] \quad (8)$$

Where k_B is Boltzmann's constant, N is the number of atoms in the adsorbates.

Declarations

Competing interests

The authors declare no competing interests.

Author Contributions

J.L.L. designed the experiments and W.X.L. designed the DFT calculations; J.G. did the catalytic performance evaluation; S.Q.W., L.H., Z.H.S., L.N.C. and S.C. performed the XAFS measurements; M.Z.J. did the DFT calculations; Y.P., J.Z.Y. and W.W. performed the SVUV-PIMS measurements; Y.L. did the HAADF-STEM measurements; H.J.W., X.Y.L. and L.L.W. did the TEM measurements; X.X.S. and X.H.H. performed the TGA measurements; X.S.Z., H.B.P. and J.F.Z. performed the XPS measurements; J.L.L. and W.X.L. co-wrote the manuscript, and all the authors contributed to the overall scientific interpretation and edited the manuscript. All authors gratefully thank Prof. Peter C. Stair for his insightful suggestions and manuscript polishing.

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Additional information

Supplementary information is available in the online version of the paper.

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Figures

Figure 1

Catalytic performance of NiCu pincer complex catalyst. Acetylene conversion as a function of temperature (a) and ethylene selectivity as a function of acetylene conversion (b) over Ni₁Cu₂/g-C₃N₄, Cu₁/g-C₃N₄, and Ni₁/g-C₃N₄ catalysts. c, Activity of these three samples at 160 °C. d, Time-on stream (TOS) stability with the same initial conversion of 70% at different temperatures, inset shows the expanded conversion changes in the first 20 hours. Reaction conditions: 0.5% C₂H₂, 5% H₂, and 25% C₂H₄ balanced in Ar; the space velocity is 12000 ml g⁻¹ h⁻¹, the pressure is 0.1 MPa. e, Distributions of volatile C_n (n = 3, 4, 5...) gas-phase products at the reactor outlet during reactions on Ni₁Cu₂/g-C₃N₄ and Ni₁/g-C₃N₄ catalysts from in situ SVUV-PIMS measurements in the stable region. f, Distributions of desorption of accumulated C_n (n = 3, 4, 5...) green oils on these two samples in 2 h of reaction. g, In situ

TGA measurements of coke deposition on Ni₁Cu₂/g-C₃N₄ and Ni₁/g-C₃N₄ catalysts under reaction conditions at 160, and 200 °C, respectively.

Figure 2

Structural characterization. a, A representative HAADF-STEM image of Ni₁Cu₂/g-C₃N₄ with atomic resolution, where isolated atoms, triangular 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 Cu₁/g-C₃N₄, Ni₁Cu₂/g-C₃N₄ and Ni₁/g-C₃N₄. c, A representative intensity profile of an individual linear trimer at location 1 in a, and the statistical histogram of the distance between two adjacent atoms in linear trimers. d, In situ Cu 2p, Ni 2p, and O 1s XPS spectra of Ni₁Cu₂/g-C₃N₄ after treatments of 350 °C reduction and acetylene hydrogenation reaction at 160 °C. e, f, In situ k₃-weighted

FT spectrum of Ni₁Cu₂/g-C₃N₄ after reduction and under reaction conditions at the Ni (e) and Cu (f) K edges, the references of Ni foil, NiO, NiPc, Cu foil, Cu₂O, and copper(II) phthalocyanine (CuPc) were also presented for comparison.

Figure 3

In-situ DRIFT spectra investigation of C₂H₂ hydrogenation. In-situ DRIFT spectra over the (a) Ni₁/g-C₃N₄ and (b) Ni₁Cu₂/g-C₃N₄ catalysts after alternatively exposing to C₂H₂ and H₂ for different time with two C₂H₂ and H₂ cycles. The shaded regions with different colors highlight the variations in the peak position and intensity. Conditions: 0.03 g of catalyst, 160 °C, 0.5% C₂H₂ or 5% H₂ in Ar, total flow = 30 mL min⁻¹.

Figure 4

Theoretical insight of stability and hydrogenation mechanism. a, Top and side views and charge density difference of the DFT optimized structures of Ni₁Cu₂/g-C₃N₄ after reduction, where the Cu-Ni distances were highlighted. The orange, cyan, red, and white balls are copper, nickel, oxygen, and hydrogen atoms, respectively. b, Stability of Ni₁/g-C₃N₄ and Ni₁Cu₂/g-C₃N₄ upon C₂H₂ adsorption. Inserts show the side view of the structures of intermediates. c, Insight of C-C bond cleavage and Gibbs free energy of adsorption for acetylene or ethylene molecule on Ni₁Cu₂/g-C₃N₄ with pre-adsorbed acetylene at different temperatures in total pressure of 0.1 MPa, 0.5% C₂H₂, and 25% C₂H₄, respectively. d, Optimized potential energy surfaces of acetylene hydrogenation reaction over Ni₁Cu₂/g-C₃N₄ with energy reference of

acetylene and hydrogen molecule in gas phase. The dashed line represents the ethylene in gas phase. Inserts show the intermediate structures with side view.

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