Reversing sintering effect of Ni particles on $\gamma$-Mo$_2$N via strong metal support interaction

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Reversing the thermal induced sintering phenomenon and forming high temperature stable fine dispersed metallic centers with unique structural and electronic properties is one of the ever-lasting targets of heterogeneous catalysis. Here we report that the dispersion of metallic Ni particles into under-coordinated two-dimensional Ni clusters over $\gamma$-Mo$_2$N is a thermodynamically favorable process based on the AIMD simulation. A Ni-4nm/$\gamma$-Mo$_2$N model catalyst is synthesized and used to further study the reverse sintering effect by the combination of multiple in-situ characterization methods, including in-situ quick XANES and EXAFS, ambient pressure XPS and environmental SE/STEM etc. The under-coordinated two-dimensional layered Ni clusters on molybdenum nitride support generated from the Ni-4nm/$\gamma$-Mo$_2$N has been demonstrated to be a thermally stable catalyst in 50 h stability test in CO$_2$ hydrogenation, and exhibits a remarkable catalytic selectivity reverse compared with traditional Ni particles-based catalyst, leading to a chemo-specific CO$_2$ hydrogenation to CO.
Sintering, the term referring to the high-temperature agglomeration of the fine-dispersed metal species in a heterogeneous catalyst\(^1\)–\(^4\), is a common phenomenon and one of the major reasons accounting for the deactivation of the working heterogeneous catalysts\(^5\)–\(^9\). From thermodynamic point of view, the surface free energy of the nanosized metal clusters rises significantly with the decreasing particle size, due to the enlarged ratio of the under-coordinated surface atoms in the entire particle\(^7\). As long as the thermal perturbation overcomes the adhesion barrier of the supported particles on the substrate, the highly mobile surface metal particles will tend to agglomerate to reduce the exposing metal surfaces and form larger particles\(^6\)–\(^8\).

To enhance the sintering-resistance ability of catalysts, a number of confinement strategies that encapsulate the metal particles within the pores/tunnels of the porous materials, such as carbon nanotubes\(^9\)–\(^10\), zeolites\(^11\)–\(^12\), and metal-organic frameworks\(^13\)–\(^15\) (MOFs) etc., have been proposed. The feasibility of these confinement methods have been widely demonstrated to prevent the migration and interparticle aggregation of metal particles. However, the undesirable activity loss and selectivity change caused by the mass transport limitation of the reactants and/or products are difficult to prevent in the confinement systems. Therefore, the concept of reversing the sintering of metal nanoparticles\(^16\)–\(^18\) which refers to the transformation of large particles with minimized exposing atoms into smaller ones highly exposed to the environment at high temperature and remain stable under reaction condition, appears to be another effective solution. In a recent study, a nitrogen doped carbon (CN) material derived from a MOF material was taken as the anchoring substrate and exhibited a strong capture ability to grasp the Pd atoms from 2 to 3 nm Pd-NPs. Under the strong coordinative interaction of the CN\(_x\) site with the Pd atoms, the gradual transformation of the Pd-NPs into single atoms at high temperature was observed\(^17\). The reverse sintering transformation from nanoparticles to single atoms was also confirmed in the systems of silver particles supported on Hollandite-type manganese oxide and Pt particles loaded on FeO\(_x\)\(^19\)–\(^21\). DFT calculations suggested that the reverse sintering effect requires the coordination of the metal-support bond significantly exceeded the internal metal-metal binding inside the particles, leading to a thermodynamically favorable redispersion of metal particles to the most stable single atomic dispersion geometry.

Downsizing nanoparticles to cluster or even single atoms are highly desirable to maximize the metal utilization, and render the electronic properties of low-coordinated metals\(^22\)–\(^24\). In addition, the reverse sintering heterogeneous catalysts could even achieve extraordinary catalytic stability under the tough reaction conditions\(^17\),\(^25\). The main issue is the search for suitable hosting materials that possess stronger interaction with the active metal atoms than the metal lattice. Our expertise in molybdenum carbides and nitrides catalysts discloses the novelty of the molybdenum compounds as supports to a variety of metal species\(^26\)–\(^27\). The strong interaction between the supports and atomically dispersed species not only modulates atomic configurations of supported species, but also greatly modifies their catalytic activity. It inspires us to develop a universal method to design novel catalytic system via a controllable reverse sintering process. Herein, we present that the pre-synthesized 4 nm Ni nanoparticles loaded on the γ-Mo\(_2\)N were able to transform into under-coordinated rafted-like Ni clusters under the reductive thermal treatment. Static Density functional theory (DFT) calculations and the ab initio molecular dynamic (AIMD) simulations predict that the metallic Ni particles can be dispersed spontaneously on the surface of reduced γ-Mo\(_2\)N under the strong interaction between the Ni and γ-Mo\(_2\)N. In contrast, neither the NiO particles nor the Ni on the oxygen terminated γ-Mo\(_2\)N substrate was able to reversely sinter in the simulation. The redispersion processes were successfully monitored and confirmed by the in-situ characterizations of X-ray absorption fine structure spectroscopy (XAFS), ambient pressure X-ray photo electron spectroscopy (AP-XPS), and the environmental secondary electron/scanning transmission electron microscopy (ESE/STEM). The spontaneous dispersion of Ni nanoparticles to raft-like clusters also tuned the electronic properties of Ni species, endowing the Ni/γ-Mo\(_2\)N exceptional selectivity to CO and an excellent catalytic stability in the high temperature reaction.

Results

**AIMD simulations of Ni NPs structure evolution over γ-Mo\(_2\)N.** In the previous studies, we have discovered the existence of strong metal support interaction between metals and the transition metal carbides and nitrides\(^28\)–\(^30\). In all the studied systems, the catalysts exhibited several common properties, including the electron deficient supported metal centers (charge transfer from metal to support) and the capability of maintaining the fine dispersion of metal centers even after high temperature treatment in the activation atmosphere. Evoked by the SMSI effect in the TMCS/TMNs supported catalysts\(^31\), we focused our notice in verifying whether the molybdenum nitride as the alternative host material can spit metals from 3D nanoparticles to sub nanometer or 2D layers, even to single atoms, which is called the reversing sintering effect\(^17\). The AIMD simulation was applied to investigate the structural evolution of a Ni nanoparticle on the γ-Mo\(_2\)N support under thermal perturbation (Fig. 1 and Supplementary Movie 1–8). The temperature factor was set at 590 °C which is in accordance with the commonly used activation temperature of traditional Ni/γ-Mo\(_2\)N(C) catalysts\(^28\),\(^32\). The initial structure of the Ni/γ-Mo\(_2\)N model at 0 ps was constructed by 19-atom Ni particle placed on a Mo terminated γ-Mo\(_2\)N(111) surface, and after 30 ps relaxation the mean potential energies only slightly fluctuated, indicating that the energy and the structure were converged after 30 ps simulations (Supplementary Fig. 1). Due to the strong binding of the Ni with the γ-Mo\(_2\)N substrate, an instant collapse of the 3D structure of Ni particles was observed. Within 10 ps, the Ni atoms have spread into a raft-like monolayer on the γ-Mo\(_2\)N (Fig. 1a). The relative interface area of Ni\(_{19}\)/γ-Mo\(_2\)N(111) (Supplementary Fig. 2), increased dramatically to 4.5 times referring to the initial structure, indicating the dispersion of Ni on the γ-Mo\(_2\)N(111) support. No significant structure changes of the raft like particles occurred when the simulation time prolonged to 30 ps and the relative interface area was only slightly increased to 5 (Fig. 1d). In comparison, when the surface of molybdenum nitride was covered with oxygen, the NiO species were found to be incapable to spread into under-coordinated species and the relative interface area of Ni\(_{19}\)O\(_{19}\)/γ-Mo\(_2\)N(111) from initial structure to 30 ps kept ~1 (Fig. 1b, d), indicating the strong interaction between Ni and molybdenum nitride requires both materials under reduced state. Meanwhile, no obvious wetting phenomenon is observed on the Ni/CoO\(_2\) system (Fig. 1c), except for a small shape reconstruction from the cubie into hemispheric particles. A slightly interface area increase of Ni\(_{19}\)/CeO\(_2\)(111) was observed, which fluctuated ~1.5 (Fig. 1d). It can be seen from Fig. 1e that the relative energy change of the redispersive process of Ni on the γ-Mo\(_2\)N is ~9.0 eV. In contrast, the ΔE of the re-shape procedure in the Ni/CoO\(_2\) model is much smaller. Additionally, a Ni\(_{55}\) particle supported on a 8 × 8 supercell of Mo\(_2\)N(111) slab is also simulated for 30 ps (Supplementary Movie 7–8). It could be found that the configuration change of Ni\(_{55}\) on Mo\(_2\)N(111) is similar to Ni\(_{19}\) particle, the raft-like configuration is more favorable based on the energy profiles (Supplementary Fig. 3). This result suggests that the
morphology evolution trend is regardless to the size of supported Ni particles. The significant difference of the structure evolution of Ni particles on nitride and oxide supports is controlled by the thermodynamics of the Ni-γ-Mo2N and the Ni-CeO2 interfaces.

Observation of reverse sintering on Ni/γ-Mo2N model catalyst.

In order to test the theoretical prediction of AIMD results, a model catalyst composed with the pre-synthesized Ni nanoparticles (4 nm) and γ-Mo2N was prepared. The Ni particles were synthesized using the high temperature liquid phase synthesis method with oleylamine and tributylphosphine as the capping reagents. The loading of Ni on the support is controlled at ~2 wt%, and further confirmed by ICP-OES. The TEM image of the as-synthesized Ni NPs demonstrated that the average size is ~4.0 nm with a narrow size distribution and sphere-like shape (Fig. 2a), but the Ni NPs were partially oxidized after deposited onto the passivated FCC structured γ-Mo2N support (Fig. 2b). The HAADF-STEM images of the fresh 2%Ni-4 nm/γ-Mo2N catalyst were also collected along with the EDX elemental mapping images that the supported Ni appeared at the surface of γ-Mo2N and maintained their original size and shape (Fig. 2c, d).

The prepared model catalysts were used to track the thermal influence on the morphology of the 4 nm supported Ni particles using combination studies of a various of in-situ characterization methods. Both Ni-4nm/γ-Mo2N and Ni-4nm/CeO2 catalysts were treated under the reductive atmosphere during a temperature-programmed heating experiment from room temperature to 590 °C. The spectroscopic studies of in-situ quick X-ray adsorption near edge spectroscopy (QXANES) and the ambient pressure X-ray photoelectron spectroscopy (AP-XPS) were performed at the Ni K edge or Ni 3d region to confirm the chemical state and the electronic structure of the supported Ni species (Fig. 3). When the sample was treated in the flow of N2-H2 mixture, a gradual reduction of the sample started at ~360 °C based on the QXANES measurement (Fig. 3a, left panel). The sample was fully reduced to Ni (0) state at ~480 °C judging from the edge position and “white-line” profiles. With the further thermal treatment, an unusual intensity increasing emerged at the...
“white-line” of Ni-4nm/γ-Mo2N catalyst (Fig. 3a, right panel), which was probably due to the electron synergistic effect. The higher intensity of the Ni K edge “white-line” signal indicated that the electron density at the Ni site was weakened due to the charge redistribution from Ni to the molybdenum nitride support28. The electron structure change of the Ni-4nm/γ-Mo2N catalysts was further monitored by the surface sensitive AP-XPS technique (Fig. 3b). In the fresh sample, an obvious oxidation layer can be observed at the γ-Mo2N surface. The Mo (V) and Mo (VI) species were ~31% of the total Mo species. Meanwhile, most of the Ni species was NiO and only a small amount of Ni(0) species could be seen. After the activation, the signals of molybdenum nitride increased and the reduction of the supported Ni occurred. With the increasing temperature, the Ni(0) binding energy of Ni-4nm/γ-Mo2N-520 shifted ~0.4 eV positively28, which is probably related to the charge transfer from Ni species to the γ-Mo2N supports, in good agreement with the changing of “white line” of QXANES characterization. The N 1s XPS peak overlaps with the Mo 3d/3p, N 1s, and C 1s XPS regions were collected at each temperature after an hour treatment. The C 1s photoemission line with the surface carbon feature (284.8 eV) was used for the binding energy calibration.

Furthermore, in-situ X-ray adsorption fine structure34 (XAFS) of Ni K edge was carried out to evaluate the size of Ni domains and the surrounding coordination environment changes after the thermal treatments at 400 and 590 °C for 40 min. Figure 4a presents the Ni K edge XANES spectra of Ni-4nm/γ-Mo2N and...
Ni-4nm/CeO₂ catalysts after 590 °C reduction. Compared with the Ni and NiO standards, the Ni-4nm/CeO₂-590 catalysts exhibited similar pre-edge and near edge features with the Ni foil, indicating the supported Ni species were almost fully reduced after the high temperature reduction. In comparison, the pre-edge feature of Ni/γ-Mo₂N-590 catalyst is slightly weaker than the metallic standard and the XANES oscillation appeared at 8365 eV and higher energy regions cannot be described by neither the Ni (0) nor the NiO (Fig. 4a, the right panel). This phenomenon suggested the Ni formed a special electronic and coordination structure completely different from the metallic and oxide standards. The further EXAFS fitting of the steady state XAFS spectra was performed to reveal the detailed coordination structure of supported Ni species. The much stronger intensity of the Ni–Ni coordination peak of Ni-4nm/CeO₂ catalyst in R-space FT-EXAFS spectra than that of the Ni-4nm/Mo₂N catalyst were observed (Fig. 4b), indicating the size of Ni species on γ-Mo₂N is much smaller than that on the CeO₂ substrate. Indeed, based on the EXAFS fitting results (Supplementary Table 1 and Supplementary Figs. 4–5), the C.N.(Ni–Ni) of Ni-4nm/CeO₂-590 was 10.8. While the C.N.(Ni–Ni) of the Ni-4nm/γ-Mo₂N-590 was only 4. To track the temperature effect on the coordination shell of the Ni domains on the molybdenum nitride supports, the EXAFS spectra of Ni-4nm/γ-Mo₂N-400 at the different temperatures were also collected and presented in Fig. 4c. It suggested that the supported Ni was fully reduced after 400 °C reduction, as the major neighbor atoms of Ni was Ni atoms located at ~2.49 Å, corresponding to a typical metallic
Catalyst at 520 °C for 22 min. Different pretreatment temperature, the first Fourier spectrum was identified as 9 min and 520 °C for 9 min, 400 °C for 50 min, 500 °C for 9 min and 520 °C for 9 min, e-g high resolution images of selected region (marked as yellow circle in b-d, h high resolution images of Ni-4nm/γ-Mo2N catalyst at 520 °C for 22 min.

Ni–Ni coordination. In addition, a peak appeared at 1.90 Å in the R space spectrum was identified as the Ni–N coordination (C,Ni,Ni-N of 1.1). This feature confirmed that the metallic Ni particles were located on the N-interlayer which was predicted by the AIMD simulations (Fig. 1a). With the elevated temperature, a novel Ni–Mo bonding at 2.62 Å appeared in the Ni/γ-Mo2N-590 catalyst. These phenomena also indicated that the Ni has formed direct interaction with the molybdenum nitride support, confirming the similar structure variation as the AIMD simulations presented.

Environmental SE/STEM studies of the structure evolution. The spectroscopic evidence has given a detailed description on the electronic properties and coordination environment changes of the reverse sintering of supported 4 nm Ni particles over the molybdenum nitride surface. Electron microscopy is expected to directly monitor the structure evolution of the 4 nm Ni particles downsizing into the raft-like clusters. However, in conventional in-situ TEM/STEM experiments, thin and light supports, for instance, activated carbon, should be used or one has to find a proper orientation where electron beam is parallel to interface between nanoparticles and supports35,36. In this work, the relative lower Z-contrast of Ni particles than the Mo makes it difficult for the conventional environmental scanning transmission electron microscope (STEM) imaging techniques to distinguish the Ni from the γ-Mo2N substrate28. Moreover, it is hard to derive the surface information from the recorded 2D projection when samples were thick (above 100 nm) or in irregular shape.

The new electron microscopy technique of environmental probe-corrected scanning transmission electron microscope equipped with secondary electron detector was applied to achieve the simultaneous acquisition of SE image and STEM image (STEM-ADF, STEM-BF) with an atomic spatial resolution (below 1 Å)37. Utilizing the surface sensitive low energy secondary electron caused by interaction between the primary beam and object, SE images showed a powerful ability to analyze surface morphology on bulk materials, regardless of the thickness and Z contrast of the metal on the support38. With the assistance of the SE-STEM method, we managed to observe the structural evolution of Ni particles on γ-Mo2N directly in-situ during the high temperature treatment under the designated atmosphere.

As shown in Fig. 5a, the γ-Mo2N support is highly porous, and the supported nanoparticles were well dispersed on the surface of the γ-Mo2N at 400 °C in the simulated activation atmosphere. The corresponding BF and ADF-STEM did not show useful information since the support is too thick (Supplementary Fig. 6). On the SE images, the supported nanoparticles showed an irregular polygon shape (~5–7 nm) with clear edge (Fig. 5). No significant morphology change was observed with the time evolution at 400 °C (Fig. 5a, b). The detailed analysis of the fast Fourier transformation (FFT) of SE and BF images of the Ni-4nm/γ-Mo2N catalyst at 400 °C were shown in Fig. 6a, b. Due to the penetration depth differences of secondary electron and traditional electron probes, the FFT patterns of SE and STEM reflect the structural information of the near surface species and the bulk of the sample respectively. As shown in the Fig. 6a, the region 1 shows a typical pattern of FCC structured γ-Mo2N with a d-spacing ~2.0 Å, which is the bare support. While region 2 is confirmed unexpectedly as Ni4N particles (d-spacing 2.6 Å, Supplementary Fig. 7) rather than the metallic Ni. This phenomenon suggested that the formation of Ni–N bonding changes the bulk structure of loaded Ni species. While the FFT of the BF image at region I is identical to the SE one, confirming the bulk phase of region 1 is the substrate. In contrast the features of both γ-Mo2N and Ni4N could be seen at region II in the FFT of STEM images, demonstrating the bulk of the catalyst below region II is composed by both the Ni4N particles and the nitride support. These results also demonstrate that the loaded Ni particles are 3D particles with considerable thickness at 400 °C.
With the elevated activation temperature, the supported nanoparticles on the surface begins to fade, or even disappear. The SE images of 520 °C (Fig.5d, g, h) proves that the pores in the γ-Mo2N substrate have disappeared, probably been covered by the loaded species, indicating the Ni has formed raft-like clusters and spread over the support (Supplementary Movie 9). The FFT patterns of SE and STEM (Fig. 6c, d) further confirmed the thermal induced redispersion phenomenon. The SE FFT pattern at region III showed a typical Ni4N features with d-spacing ~2.5 Å, suggesting the surface of region 3 is still covered by the Ni species. However, the STEM FFT pattern at the same region only showed features belong to γ-Mo2N, which demonstrates that the Ni particle is possibly too thin to generate diffraction patterns. Compared with the electron diffraction patterns collected at 400 °C, we could confirm that the Ni particles have been spread into 2D layers on the nitride substrate under the thermal treatment. The normalized intensity profiles of the 520 °C sample’s surface were much weaker than those of the 400 and 500 °C samples (Supplementary Fig. 8), which is another evidence that the Ni particles have reverse sintering at high temperature. The EDS mapping on STEM of ex-situ samples of Ni-4nm/γ-Mo2N-590 catalysts were also carried out to further confirm the spontaneous dispersion of Ni NPs on the γ-Mo2N (Supplementary Fig. 9).

As the SE-STEM characterization has confirmed the existence of Ni4N during the thermal treatment, it is important to further confirm whether the Ni4N is able to further reverse sintering to undercoordinated structures. The AIMD simulation has been done using the same setting to the Ni19/γ-Mo2N over a novel Ni4N (Ni20N5 cluster was truncated from bulk Ni4N(Pm3m)/γ-Mo2N model surface (Fig.6e and Supplementary Movie 10–11). The spherical Ni4N turns directly into layered structure with maximized Ni–N–Mo bonding with in 10 ps time evolution (Supplementary Fig. 10). The relative stabilization energy is calculated as 18 eV, even larger than the energy change of Ni19/γ-Mo2N system (Fig.6f), ensuring that the loaded Ni particles will be converted into layered structure under thermal perturbation.

**Catalytic performance of Ni/γ-Mo2N in CO2 hydrogenation.** The special chemical properties of the under-coordinated Ni species derived from the strong interaction between supported Ni and the molybdenum nitride substrates have been utilized in the catalytic hydrogenation of carbon dioxide. It is a common sense
that the Ni-based catalysts were highly active in the methanation reactions of CO and CO2 with exclusive high selectivity to the product methane. Ever since the discovery of the CO2 methanation by Sabatier and coworkers in 1902, Ni has been considered to be the typical inexpensive metal for this hydrocarbonation conversion process. Mechanistic studies have confirmed that the domains of metallic Ni particles should be above 2 nm in order to achieve the optimal methane formation rate and efficiency. Single site Ni and sub-nm Ni sites are necessary to reverse the selectivity of Ni-based catalyst from CH4 to CO in CO2 hydrogenation. However, when the reaction temperature increased from 300 to 350 °C, the single site of Ni1/MgO was starting to aggregate to particles with the selectivity of CH4 appeared to 40%. Indeed, the production of methane has been significantly suppressed on the activated Ni-4nm/γ-Mo2N catalyst with highly dispersed Ni species. In the range from 250 to 500 °C, the selectivity of CH4 has never exceeded 3%, even at the low temperature region at which the reverse water-gas shift reaction is thermodynamically unfavorable. When the working temperature went above 400 °C, the CO2 was chemoselectively converted into CO (S(CO) > 99%) (Fig. 7a). While in comparison, when using the activated Ni-4nm/GeO2 as the catalyst, the selectivity of methane was over 70% at 400 °C (CO2 conv. ~8%), and ~60% at 500 °C (CO2 conv. ~12%). What’s more, the extraordinary selectivity toward CO remained above 95%, when decreasing the mass space velocity to 7500 ml/g/h (Fig. 7b) or tuning the CO2/H2 ratio (1:3 to 1:6) in the gas feed (Fig. 7c). Under a typical condition, the activated Ni-4nm/γ-Mo2N catalyst exhibited stable activity in the hydrogenation of CO2 for over 50 h. Neither the CO2 conversion decay nor the decreasing on the selectivity of CO has been observed (Fig. 7d). The completely selectivity changes of the Ni-4nm/γ-Mo2N to Ni-4nm/GeO2 catalysts suggested that the reverse sintering phenomenon induced by the strong interaction between the Ni and Mo2N was able to significantly change the intrinsic catalytic properties of Ni-based catalysts and prolong the stability of Ni catalysts (Fig. 6c and Supplementary Fig. 11). The reduced dimension and electronic deficiency of Ni species are the main reasons for the reduced Ni-4nm/Mo2N catalysts active for the RWGS reaction other than methanation. It has also been demonstrated the reverse sintering effect in the Ni/γ-Mo2N catalyst is able to enhance the water splitting activity by increasing the exposure of the active metal sites (Supplementary Fig. 12). Comparing the fresh catalyst with the Ni-4nm/γ-Mo2N-590 catalyst, the hydrogen evolution rate increased by ~10 times. Therefore, the reverse sintering effect can be used to maximize the dispersion and utilization efficiency of metals using simple treatments.

In conclusion, we have demonstrated using theoretical calculation and ab initio molecular dynamic simulation methods that the pre-synthesized 4 nm Ni particles are able to reverse sintering into under-coordinated Ni species after the high temperature activation procedure driven by the strong interaction between the γ-Mo2N and the Ni. The existence of both reduced Ni particles and the bare γ-Mo2N is important for the formation of the highly dispersed Ni species. In-situ structural characterizations have confirmed the dispersion of Ni occurred after the reduction of bulk phase Ni and the removal of surface passivated O-layer of γ-Mo2N. The reverse sintering effect for Ni-4nm/γ-Mo2N is important for the formation of the highly dispersed Ni species. In-situ structural characterizations have confirmed the dispersion of Ni occurred after the reduction of bulk phase Ni and the removal of surface passivated O-layer of γ-Mo2N. The reverse sintering effect for Ni-4nm/γ-Mo2N is important for the formation of the highly dispersed Ni species.
Methods

DFT calculation. Ab initio molecular dynamic (AIMD) simulations were carried out using Vienna Ab initio Simulation Package (VASP)45,46 for 30 ps at a time step of 1 fs. The canonical ensemble (NVT) and Nosé–Hoover thermostats were set to 590 °C.7,48. The potential energies change suggested that all simulations reached equilibrium at last (Supplementary Fig. 1). The spin-polarized static DFT calculations were performed to get the relative energies of systems at different period among the AIMD simulations. The initial structures for static DFT calculations were from AIMD simulations and be converged to local minimization. In all simulations, the electron exchange and correlation energy was treated within the Perdew-Burke-Ernzerhof (PBE)49 functional of generalized gradient approximations (GGA).50 The electronic relaxation criterion is that the change in total energy between two successive steps should be <10 × 10−4 eV per atom and the forces were <0.05 eV Å−1. The interface area was calculated according to equation R1.

\[
R_{\text{interface}} \approx \frac{N_s}{N_M} \times S
\]

(1)

where \(N_s\) is the number of surface metal atoms (Mo or Ce) which connected to Ni, \(N_M\) is the total number of surface metal atoms of support, and \(S\) is the surface area. The relative interface area as a function to time is plotted, the initial interface area was taken as a benchmark as “1.” In calculations, the bulk structure of Mo2N is in accordance with previous study.45,48. For slab model, the Mo-terminated Mo2N(111) surface with (6 × 6) supercell was used, there are 108 Mo, 36 N, and 20 Ni atoms in Ni19/Mo2N(111) model. In Ni6N/Mo2N(111) model, supported Ni6N cluster was truncated from bulk Ni4N (Pm-3m), so there are 108 Mo, 41 N, and 20 Ni atoms in these three models. 36 Mo and 18 N atoms were fixed, while other atoms were relaxed. For CeO2 support, an O-terminated CeO2(111) surface with (5 × 5) supercell was used, it contains 50 Ce, 100 O, and 19 Ni atoms, where 25 Ce and 25 O atoms were fixed and others were relaxed.

Catalyst preparation

Material. Nickel acetylacetonate (Ni(acac)2, 95%), oleylamine (OAm, 70%), tributylphosphate (TBP, 97%), and ammonia molybdate ((NH4)6Mo7O24·4H2O) were purchased from Sigma-Aldrich and used without any further purification. Benzyl ether (BE, 99%) was bought from Acros Organics and used without any further purification. Isopropanol and hexane were purchased from Fisher (ACS Certified), distilled before use and kept with molecular sieves. All experiment was conducted under standard Schlenk line condition.

Synthesis of Ni-4nm. Ni(acac)2 (300 mg) was mixed with BE (60 ml) and OAm (8 ml) in a 95°C bath. The mixture was stirred under vacuum for 5 min and the reaction was switched to N2 atmosphere then. In all, 5 ml TBP was injected to the reaction flask. The mixture was further heated under vacuum at 100 °C for 1 h, generating a dark green transparent solution. The reaction flask was then filled with a N2 blanket and the green solution was heated to 230 °C at a heating ramp of 5 °C/min. The reaction was kept at 230 °C for 15 min at this temperature. All the product was transferred to N2-filled glovebox to avoid exposure to air. The product was purified with extra dry isopropanol and separated by centrifugation (9000g, 8 min). The purification was repeated two times and the product was then dispersed in extra dry hexane for further application.

Preparation of γ-Mo2N. First, MoO3 powders were synthesized by calcination of (NH4)6Mo7O24·4H2O at 773 K for 4 h. Then, the MoO3 powder was ground and the fine powder of MoO3 was transferred to a quartz tube and ammoniaized under the flow of pure NH3 (150 ml/min) at 973 K for 4 h (heating rate was set as 5 K/min). After cooling down to room temperature, the obtained γ-Mo2N catalyst was passivated with CO2 at room temperature overnight to protect the as-synthesized γ-Mo2N material from the pyrophoric oxidation when contacted with air.

The protocol of Ni/γ-Mo2N synthesis. The Ni-4nm/γ-Mo2N catalysts were synthesized by using incipient wet impregnation (IWI) of as-prepared homogeneous Ni-4nm hexane solution over the as-synthesized γ-Mo2N material. The slurry was then freeze-dried under stirring. The loading of Ni loading was set to ~2%. The catalyst was denoted as Ni-4nm/γ-Mo2N.

The dispersion phenomena and mechanism of Ni-4nm/γ-Mo2N was investigated in the flow of the N2/H2 mixture (1:3 v/v, 32 ml/min) at a temperature ramp of 5 °C/min to 590 °C. The catalysts characterization

QXANES and XAFS. The in Situ Quick X-ray Absorption Near Edge Spectroscopy (QXANES) spectra was collected at ISS beamline of the Brookhaven National Laboratory (BNL), and X-ray Absorption Fine Structure Spectroscopy (XAFS) of the catalysts was collected at the 9-BM beamline of the Advance Photon Source (APS), Argonne National Laboratory (ANL). In the test, the powder samples were loaded in a Claussen Cell. The Ni K-edge XAFS spectra were collected in the fluorescence mode using a PIPS detector at BNL and four-channel vertex detector at APS, respectively. The activation processes for QXANES experiments is carried out in the flow of N2/H2 mixture (v/v = 1:3) at a temperature ramp of 2 °C/min to 590 °C. Each scan takes 1 min, and every 10 scans were merged together to get a spectrum. For the XAFS experiments, the activation processes were performed in the flow of N2/H2 mixture (v/v = 1:3) at a temperature ramp of 10 °C/min, but at the temperature of 400 °C and 590 °C is held for 40 min before collecting spectra. Each scan will take 20 min, and every three scans are merged to be one spectrum. The data pretreatment and extended X-ray absorption fine structure (EXAFS) fitting were performed using the fit2efl package52.

Ambient pressure X-ray photoelectron spectroscopy. AP-XPS spectra were collected by a SPECS AP-XPS chamber equipped with a PHOIBOS 150 EP MCD-9 analyzer with an energy resolution of 0.6 eV. The source of AP-XPS is the Mg Ka radiation (1253.5 eV). The C 1s photoemission line with the surface carbon feature (284.8 eV) was used for the binding energy calibration. The 2%Ni-4nm/Mo2N catalyst was pressed into a clean aluminum plate as XPS samples. Typically, the fresh sample was activated in the AP-XPS chamber by a 40 mTorr N2/H2 (1:3 v/v) mixture at 300, 400, 500, and 520 °C (the upper limit of the instrument) for 1 h. The spectra at the Ni 2p, Mo 3d/3p, O 1s, N 1s, and C 1s XPS regions were collected at each temperature after an hour treatment.

Electron microscopy. TEM, HAADF-STEM images and EDS mappings in Fig. 2 and Supplementary Fig. 4 were obtained using a FEI Talos F200X STEM microscope with a field-emission gun at 200 kV at CFN of Brookhaven National Lab.

Environmental SE-STEM. Environmental secondary electron scanning transmission electron microscopy (Environmental SE-STEM) experiments were carried out using a probe aberration corrected Hitachi HF-5000 equipped with a secondary detector, operated at 200 kV. The facility allows spontaneously record bright-field (BF), annular dark field (ADF), and secondary electron (SE) images under the STEM mode. By using the probe aberration corrector, it can get a resolution of 0.7 Å in ADF-STEM images and a resolution of below 1 Å in SE-STEM images. The sample was directly dispersed on the MEMS chip without any pretreatment. After inserting the heating holder equipped with the MEMS chip, a mixture of H2 and N2 with a molar ratio equal to 3:1 was introduced into the sample chamber and a total pressure of 2 Pa was maintained during the whole experiments. The sample was directly heated to 200 °C prior to the in-situ study. Once the sample was heated to the desired temperature, the following changes in morphology and structure of the samples was imaged.

Performance evaluation of CO2 hydrogenation. In a typical experiment, 10 mg of Ni-4nm/γ-Mo2N catalyst powder was mixed with 10 mg of pre-calcined SiO2 and loaded in a fixed-bed reactor. The sample was activated in a flow of a N2 and H2 mixture (1:3 v/v) at 590 °C for 2 h. After activation, the temperature of the reactor was changed to a designated temperature in the N2/H2 mixture and then switched to the reaction gas feed (CO2/H2/N2 1:3:1 v/v/v). The same procedures were performed for the reference catalysts. The products of the reaction were analyzed by online gas chromatography (GC, Agilent 7890) equipped with a thermal conductive detector (TCD) and a flammable ionization detector (FID). The N2 in the flow was used as the inner standard. The response factor of each reactant and product was calibrated using standard curve methods.

Data availability

The data that support the plots within this paper and other finding of this study are available from the corresponding author upon reasonable request.

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