Reversing sintering effect of Ni particles on γ -Mo₂N via strong metal support interaction

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Article

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Abstract

The reverse sintering effect of Ni particles under thermal treatment has been observed in the Ni/ γ -Mo₂N catalysts. The ab initio molecular dynamic simulation has demonstrated the redispersion of metallic Ni particles into under-coordinated two-dimensional Ni clusters over γ -Mo₂N is a thermodynamically favorable process. Utilizing pre-synthesized 4 nm Ni nanoparticles as the loaded particles, a Ni-4nm/ γ -Mo₂N model catalyst was synthesized and used to 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 theoretical and experimental studies both confirmed the reverse sintering effect in the Ni- γ -Mo₂N system is driven by the strong metal-support interaction between Ni and γ -Mo₂N. The potential application of the reverse sintering effect in heterogeneous catalysis has been realized using the high temperature favored CO₂ hydrogenation reaction. The under-coordinated two-dimensional layered Ni clusters on molybdenum nitride support generated from the Ni-4nm/ γ -Mo₂N has been demonstrated to be a thermally stable catalyst in 50 h stability test, and exhibits a remarkable catalytic selectivity reverse compared with traditional Ni based catalyst, leading to a chemo-specific CO₂ hydrogenation to CO.

Introduction

Sintering, the term referring to the high-temperature agglomeration of the fine-dispersed metal species in a heterogeneous catalyst¹⁻⁴, is a common phenomenon and one of the major reasons accounting for the deactivation of the working heterogeneous catalysts^{5, 6}. 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 particle⁷. 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, 14} (MOFs) etc., have been proposed. The feasibilities 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 system. Therefore, the concept of reversing the sintering of metal nanoparticles¹⁵⁻¹⁷ which refers to the transformation of large particles into fine clusters and single atoms at high temperature, 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 2–3 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 observed¹⁶. 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 Fe₂O₃¹⁸⁻²⁰. 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 re-dispersion 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^{7, 21, 22}. In addition, the reverse sintering heterogeneous catalysts could even achieve extraordinary catalytic stability under the tough reaction conditions¹⁶. 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^{23, 24}. 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 -Mo₂N were able to transform into under-coordinated rafted-like Ni clusters under the reductive thermal treatment. Density functional theory (DFT) calculations and the ab initio molecular dynamic (AIMD) simulation predict that the metallic Ni particles can be dispersed spontaneously on the surface of reduced γ -Mo₂N under the strong interaction between the Ni and γ -Mo₂N. In contrast, neither the NiO particles nor the Ni on the oxygen terminated γ -Mo₂N 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 scanning transmission electron microscopy/secondary electron (ESTEM/ESE). The spontaneous dispersion of Ni nanoparticles to raft-like clusters also tuned the electronic properties of Ni species, endowing the Ni/ γ -Mo₂N exceptional selectivity to CO and an excellent catalytic stability in the high temperature reaction.

Results And Discussions

In the previous studies, we have discovered the existence of strong metal support interaction between metals and the transition metal carbides and nitrides^{25–27}. 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^{28, 29}, 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 effect¹⁶. The AIMD simulation was applied to investigate the structural evolution of a Ni nanoparticle on the γ -Mo₂N support under thermal perturbation (Fig. 1 and Video S1-S6). The temperature factor was set at 590°C which is in accordance with the commonly used activation temperature of traditional M/ γ -Mo₂N(C) catalysts^{25, 30}. The initial structure of the Ni/ γ -Mo₂N model at 0 ps was constructed by 19-atom Ni particle placed on a Mo terminated γ -Mo₂N(111) surface. Due to the strong binding of the Ni with the γ -Mo₂N substrate, an instant collapse of the 3D structure of Ni particles was observed. Within 3ps, the Ni atoms have spread into a raft-like monolayer on the γ -Mo₂N (Fig. 1a). No significant structure changes of the raft like particles occurred as the simulation time prolonged. 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 (Fig. 1b), indicating the strong interaction between Ni and molybdenum nitride requires both materials under reduced state. Meanwhile, no wetting phenomenon is observed on the Ni/CeO₂ system (Fig. 1c), except for a small shape reconstruction from the cubic into hemispheric particles. It can be seen from Fig. 1d that the relative energy change of the redispersion process of Ni on the γ -Mo₂N is about – 18.0 eV. In contrast, the ΔE of the re-shape procedure in the Ni/CeO₂ model is only – 3.0 eV. The significant difference of the structure evolution of Ni₁₉ particles on nitride and oxide supports is controlled by the thermodynamics of the Ni- γ -Mo₂N and the Ni-CeO₂ interfaces.

In order to test the theoretical prediction of AIMD results, a model catalyst composed with the pre-synthesized Ni nanoparticles (4 nm)³¹ 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 reagents³¹. The loading of Ni on the support is controlled at ~ 2wt%, and further confirmed by ICP-OES. The TEM image of the as-synthesized Ni NPs demonstrated that the average size is about 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. It can be seen from the STEM and 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 influences 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 around 360°C based on the QXANES measurement (Fig. 3a, left panel). The sample was fully reduced to Ni (0) state at around 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-590 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 support²⁵. 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 about 31% of the total Mo species observed.

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 positively²⁵, 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 charge transfer phenomenon has also been confirmed by the DFT calculations, as shown in Fig. 3c and 3d. The electron transfer from Ni to nitride occurred and the electron density at the Ni-nitride interface increased significantly. The Ni atoms closed to the molybdenum nitride were generally under electron deficient state. The formation of the 2D Ni raft-like clusters has maximized this electron interaction, hence the average electron deficiency per Ni atom in the layered Ni structure will be significantly larger than the Ni particles.

Furthermore, *in-situ* X-ray adsorption fine structure³² (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 minutes. 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 (Table S1, Figure S1 and S2), 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 about 2.49 Å, corresponding to a typical metallic Ni-Ni coordination. In addition, a Ni-N coordination peak appeared at 1.90 Å in the R space spectrum was identified as the Ni-N coordination (C.N._{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 simulation (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 simulation presented.

The spectroscopic evidence has given a detailed description on the electronic properties and coordination environment changes of the reverse-sintering of supported 4nm Ni particles over the molybdenum nitride surface. Electron microscopy is expected to directly monitor the structure evolution of the 4nm 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 supports^{33,34}. In this work, the relatively 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 substrate²⁵. 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 1Å)³⁵. 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 support³⁶. 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 (Figure S3). On the SE images, the supported nanoparticles showed an irregular polygon shape (about 5–7 nm) with clear edge (Fig. 5). No significant morphology change was observed with the time evolution at 400 °C (Fig. 5a and b). The detailed analysis of the fast Fourier transformation (FFT) of SE and BF images of the Ni-4nm/ γ -Mo₂N at 400 °C were shown in Fig. 6a

and 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 around 2.0 Å, which is the bare support. While region 2 is confirmed unexpectedly as Ni₄N particles (d-spacing 2.6 Å, Figure S4) 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 and 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 (Video S7). The FFT patterns of SE and STEM (Fig. 6c and d) further confirmed the thermal induced redispersion phenomenon. The SE FFT pattern at region III showed a typical Ni₄N features with d-spacing around 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 (Figure S5), 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 (Figure S6)

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 Ni₄Nm/ γ -Mo₂N model surface (Fig. 6e, Video S8-9). The spherical Ni₄N turns directly into layered structure with maximized Ni-N-Mo bonding with in 5 ps time evolution. The relative stabilization energy is calculated as 26.8 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.

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 methane³⁷⁻³⁹. Ever since the discovery of the CO₂ methanation by Sabatier and coworkers in 1902⁴⁰, Ni has been considered to be the typical inexpensive metal for this hydrogenation conversion process. Mechanism 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^{38, 41}. Indeed, when using the activated Ni-4nm/CeO₂ as the catalyst, the selectivity of methane was over 70% at 400 °C (CO₂ conv. ~8%), and ~60% at 500 °C (CO₂ conv. ~12%). While in comparison, the production of methane has been significantly suppressed on the activated Ni-4nm/ γ -Mo₂N catalyst. 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). 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 hrs. Neither the CO₂ conversion decay nor the decreasing on the selectivity of CO has been observed (Fig. 7d). The completely selectivity reversion of the Ni/ γ -Mo₂N 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. 6e). 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. Comparing the fresh catalyst with the Ni-4nm/ γ -Mo₂N-590 catalyst, the hydrogen evolution rate increased by about 10 times (Figure S7). 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 catalyst has a positive effect on the chemoselective hydrogenation of CO₂ to CO. Compared with the Ni-4nm/CeO₂ reference catalyst (CO Sel.%~29%), the activated Ni-4nm/ γ -Mo₂N catalyst exhibited over 96% CO selectivity at an even higher CO₂ conversion. This reverse transformation in the catalytic performance compared with traditional Ni based catalysts can accounts with the dispersion and wetting phenomena of Ni nanoparticle on γ -Mo₂N, which serves as an excellent example of the potential application of reverse sintering effect in the high temperature favorable reactions.

Declarations

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Contributions

D. M. and J. R. and L. L. designed the study. L. L. performed most of the reactions and data analysis. X. L. and F. Y. carried out the measurement and analysis of environmental SE/STEM images. J. L. and X. W. did the DFT calculation. N. R. and S. S. did the AP-XPS measurement. S. Y. and F. Z. did the *in-situ* XAFS measurement at APS. C. L. and S. Z. did the synthesis of uniform Ni-4nm particles. L. H. carried out the measurement of TEM and STEM. L. L., S. Y., J. R. and D. M. wrote the paper. All authors performed certain experiments, discussed and revised the paper.

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Financial and Non-Financial Competing Interest Statement

Declare no competing interest.

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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Figures

Figure 1

The structure evolution of Ni NPs on varied supports at 590°C in AIMD calculation. The structure evolution of (a) Ni₁₉ on γ-Mo₂N(111) support, (b) Ni₁₉O₁₉ on passivated γ-Mo₂N (O-Mo₂N(111)), (c) Ni₁₉ on CeO₂ support, (d) the free energy change in the redispersion process of Ni₁₉/γ-Mo₂N(111) and Ni₁₉/CeO₂.

Figure 2

The electron microscope images of the fresh Ni-4nm/γ-Mo₂N catalyst. (a) TEM image of the Ni-4nm suspension precursor; (b and c) STEM images of fresh Ni-4nm/γ-Mo₂N catalyst; (f) The EDS element mapping of fresh Ni-4nm/γ-Mo₂N catalyst.

Figure 3

In-situ QXANES characterization and AP-XPS spectroscopy of 4%Ni-4nm/γ-Mo₂N catalyst treated at different temperature. (a) QXANES, (b) AP-XPS profiles of Ni 2p and Mo 3d. The charge density difference of (c) Ni₁₉/γ-Mo₂N at 0 ps and (d) Ni₁₉/γ-Mo₂N (the red region reflects the electron deficiency, while the blue region represents the electron cumulation).

Figure 4

In-situ XAFS characterization of 2%Ni-4nm/ γ -Mo₂N pretreated at different temperatures of 400 and 590 °C in the atmosphere of H₂/N₂ at a ratio of 3:1 for 40 hours. (a) the evolution of Ni feature from Ni K edge XANES at different activated temperature, and the detailed comparison of XANES is presented at the right panel; (b) the EXAFS figures at R space of (b) 2%Ni-4nm/ γ -Mo₂N-590 and 2%Ni-4nm/CeO₂-590, and (c) 2%Ni-4nm/ γ -Mo₂N-400 and 2%Ni-4nm/ γ -Mo₂N-590; fitting details for Ni K-edge EXAFS spectra obtained for (d-f) 2%Ni-4nm/ γ -Mo₂N-400, and (g-h) 2%Ni-4nm/ γ -Mo₂N-590.

Figure 5

Environmental SE/STEM characterization. The evolution of Ni particles on the support of γ -Mo₂N in the flow of H₂/N₂ at a ratio of 3:1 under different pretreatment temperature, (a-d) large scale SE/STEM images of the Ni-4nm/ γ -Mo₂N catalyst at 400°C for 9min, 400°C for 50min 500°C for 9min and 520°C for 9min, (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 22min.

Figure 6

Comparison of high-resolution environmental SE and BF images. Corresponding FFT patterns of high-resolution (a, c) SE and (b, d) BF image from the selected area at (a, b) 400 °C and (c, d) 520 °C. Area 1, 2 and 3 marked in the SE images and the Area 1', 2' and 3' marked in the BF images are the at the same position of the catalysts. (e) The structure evolution of Ni₄N on -Mo₂N(111) in AIMD calculation; and (f) the interaction of the free energy change of the redispersion process of Ni₁₉/γ-Mo₂N(111) and Ni₄N/γ-Mo₂N(111).

Figure 7

The catalytic performances of the Ni-4nm/g-Mo₂N and Ni-4nm/CeO₂ catalysts in the CO₂ hydrogenation reactions. (a) the CO₂ conversion at different reaction temperature; (b) the CO₂ conversion and CO selectivity of Ni-4nm/g-Mo₂N catalyst at different

CO₂/H₂ ratio; (c) the CO₂ conversion and CO selectivity of 2, 4, 6% Ni-4nm/g-Mo₂N catalysts at different temperatures; (d) the comparison of the selectivities of Ni-4nm/g-Mo₂N and Ni-4nm/CeO₂ catalysts in the CO₂ hydrogenation; (e) the comparison of the stabilities of Ni-4nm/g-Mo₂N and Ni-4nm/CeO₂ catalysts in the CO₂ hydrogenation.

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