

Noble-Metal-Free Ni–W–O-Derived Catalysts for High-Capacity Hydrogen Production from Hydrazine Monohydrate

Qing Shi, Deng-Xue Zhang, Hui Yin, Yu-Ping Qiu, Liang-Liang Zhou, Chen Chen, Hui Wu, and Ping Wang*

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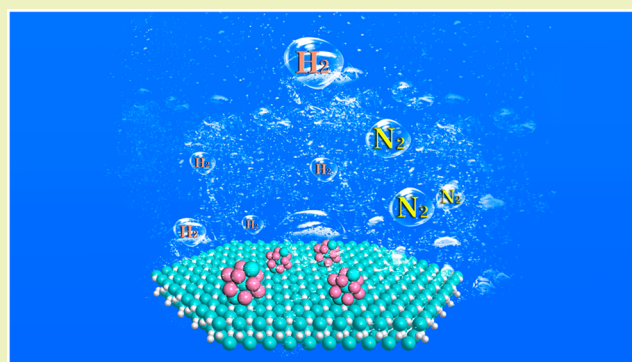
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Supporting Information

ABSTRACT: Development of active and earth-abundant catalysts is pivotal to render hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) viable as a hydrogen carrier. Herein, we report the synthesis of noble-metal-free Ni–W–O-derived catalysts using a hydrothermal method in combination with reductive annealing treatment. Interestingly, the thus-prepared Ni-based catalysts exhibit remarkably distinct catalytic properties toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition depending upon the annealing temperature. From a systematic phase/microstructure/chemical state characterization and the first-principles calculations, we found that the variation of the apparent catalytic properties of these Ni-based catalysts should stem from the formation of different Ni–W alloys with distinct intrinsic activity, selectivity, and distribution state. The thereby chosen Ni–W alloy nanocomposite catalyst prepared under an optimized condition showed high activity, nearly 100% selectivity, and excellent stability toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition for hydrogen production. Furthermore, this noble-metal-free catalyst enables rapid hydrogen production from commercially available $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ solution with an intriguingly high hydrogen capacity of 6.28 wt % and a satisfactory dynamic response property. These results are inspiring and momentous for promoting the use of the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -based H_2 source systems.

KEYWORDS: Hydrogen storage, Hydrazine monohydrate, Noble-metal-free catalyst, Ni–W alloy, Phase evolution



■ INTRODUCTION

Hydrogen is expected to play an essential role as an energy carrier in the future clean energy economy based on renewable energy resources. However, the widespread utilization of hydrogen is hampered by the technical difficulty involved in hydrogen storage and delivery.¹ The materials capable of reversible dehydrogenation have long been sought as possible candidates for high-capacity hydrogen storage.^{2–13} However, none of the existing materials met the requirements for hydrogen capacity (over 6 wt %), kinetics, and operation temperature. Recently, chemical hydrogen storage involving hydrolysis or thermolysis of hydrogen-rich materials and spent-fuel regeneration has emerged as a competitive alternative to a high-pressure hydrogen cylinder for vehicular and portable applications.^{14,15} Among the hydrogen-rich materials of interest, hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) is an appealing candidate thanks to its favorable combination of low cost, high hydrogen capacity (8.0 wt %), and good stability at ambient temperatures.^{16,17} In particular, the decomposition reactions of N_2H_4 yield only gaseous products, which is highly beneficial for the design and practical application of H_2 -source systems.

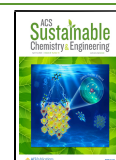
The development of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as a chemical hydrogen storage material requires highly active and selective catalysts

for promoting hydrogen production (HP), and meanwhile suppressing the formation of NH_3 . In the past decades, a number of transition metals/alloys have been investigated in terms of catalytic properties toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition.^{18–47} It was found that alloying is a highly effective approach for boosting the catalytic performance toward HP from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. The alloying aspect could be understood from two complementary effects: the geometric and electronic modifications of the catalyst surface.^{29,31} The bimetallic alloys composed of a combination of precious metals (like Pt and Ir) and nonprecious metals (like Ni, Co, and Fe) generally exhibited favorable performance in both activity and H_2 selectivity.^{20–24,28–33,39–42} In contrast, the catalytic activity of the noble-metal-free alloys is typically inferior. For instance, the reaction rates of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition over the representative Ni-based catalysts, such as NiCu/CeO₂, NiFe/

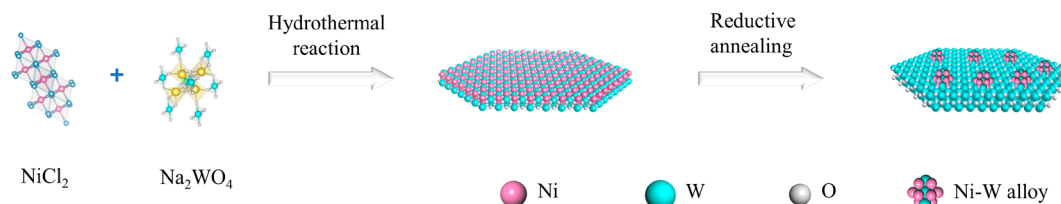
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Scheme 1. Schematic Diagram of the Fabrication Process of the Ni–W–O-Derived Nanocatalysts



CeO_2 , $\text{NiCo}/\text{NiO}-\text{CoO}_x$, and NiMo/NiMoO , were 1 or 2 orders of magnitude lower than those of the NiPt and CoPt catalysts.^{27,37,43–46} Currently, the less favorable modification effects of non-precious metals compared to noble metals are still poorly understood, but from the perspectives of the cost reduction and growth potential, non-precious-metal catalysts represent an important direction for future research of the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -based HP technology. In general, activity improvement of non-precious-metal catalysts can be pursued via composition/phase tuning and structure optimization. In this regard, in-depth study and better understanding of the phase–microstructure–activity correlation are clearly of significance for the design and synthesis of advanced catalysts. In addition, stability is a key issue in the study of the catalyst toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition. The existing $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition catalysts from the literature all suffered from serious activity loss in cyclic usage. Currently, the mechanistic reasons for the poor stability remain unclear. Possible factors influencing the stability of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition catalysts include particle agglomeration, subtle phase transformation, and strong binding of the products and/or intermediates on the catalyst surface.^{27,39,47}

We herein report the synthesis of a Ni–W–O-derived nanocatalyst toward HP from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ using a hydrothermal method in combination with reductive annealing. The catalyst prepared under optimal conditions showed excellent activity, nearly 100% selectivity, and exceptionally high stability in catalyzing $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition for HP. A combination of experimental and theoretical investigations was conducted to probe the temperature-dependent evolutions of the phase structures and microstructural features, and to reveal their correlation with the catalytic properties.

EXPERIMENTAL SECTION

Chemicals and Catalyst Synthesis. Nickel chloride hexahydrate ($\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, 98%), sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, 99.5%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%), sodium hydroxide (NaOH , 98%), and hydrazine monohydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, 98%) were obtained from commercial sources and used as-received. Deionized (DI) water and $\text{C}_2\text{H}_5\text{OH}$ were used for preparation of all aqueous solutions.

The target catalyst was synthesized by a two-step procedure involving hydrothermal reaction and subsequent annealing treatment under a reductive atmosphere. In a typical run, 2 mmol of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ was dissolved into 20 mL of DI water, followed by dropwise addition of an equal portion of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ aqueous solution. This process was operated under magnetic stirring, typically for 20 min. The obtained green milky suspension was transferred to a stainless steel autoclave (50 mL) and kept at 160 °C for 6 h. The sample was collected after cooling to ambient temperature and was sequentially washed with DI water and $\text{C}_2\text{H}_5\text{OH}$ and then vacuum-dried at 60 °C for 2 h. The thus-prepared sample was subsequently annealed at different temperatures (350, 400, and 600 °C) under a flowing H_2 atmosphere for 2 h.

Characterization of the Catalysts. The phase, composition, and structure of the as-prepared materials were characterized by X-ray

diffraction (XRD, Rigaku RINT 2000 using $\text{Cu K}\alpha$ monochromatized radiation), transmission electron microscopy (TEM, JEOL-2100F), Fourier transform infrared spectroscopy (FTIR, Nicolet IS10), Raman spectroscopy (Thermo Scientific DXR with an excitation wavelength of 532 nm), and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-ALPHA+ using an $\text{Al K}\alpha$ X-ray source). In the analysis of XPS results, the C 1s signal at 284.8 eV of adventitious carbon was used for calibration of the binding energy scale. The XPS PEAK 4.1 software was used for curve fitting. The N_2 adsorption/desorption isotherm measurements were conducted in a Micromeritics ASAP 2460 apparatus. The postused fuel solution was examined by ultraviolet–visible spectroscopy (UV–vis, Thermo Scientific Evolution 220) to determine whether or not hydrazine had completely decomposed.

Catalytic Performance Testing. The catalytic decomposition properties of dilute $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ solution was examined in a two-necked round-bottomed flask with an external heating apparatus. In a typical run, the flask containing the catalyst and an alkaline aqueous solution was preheated at the desired temperature under magnetic stirring. After injection of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ into the flask, the decomposition reaction immediately occurred. The generated gaseous products passed through a 1.0 M hydrochloric acid solution to absorb ammonia, if any, and then were measured by the water-displacement method using an electronic balance with a precision of ± 0.01 g.

In the test of the catalytic decomposition properties of concentrated $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ solution, an online mass flowmeter equipped with a silica drier (Seven-star Huachang CS 200, $\pm 1\%$ precision) was used to monitor the volume of the gaseous products. Each experiment was repeated at least twice to minimize the measurement error (no more than $\pm 2\%$).

The reaction rate was evaluated at a reactant conversion of 50%, assuming all the Ni atoms take part in the catalytic reaction.^{22,31} Here, because of the time dependence of the reactivity rate, the standard choice of the reaction time parameter is important for rationally comparing the activities of different catalysts. The selectivity toward HP (X) was determined by eq 1. The details about its derivation can be found in ref 31.

$$X = \frac{3Y - 1}{8} \left[Y = \frac{n(\text{N}_2 + \text{H}_2)}{n(\text{N}_2\text{H}_4)} \right] \quad (1)$$

Computational Methods. Density functional theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP 5.2).⁴⁸ The Perdew–Burke–Ernzerhof exchange–correlation functional of the generalized gradient approximation and the projector augmented-wave pseudopotential were used to describe the core electrons and the electron interactions, respectively.^{49,50} A plane-wave cutoff energy was taken to be 500 eV and the Brillouin zone was sampled with a $5 \times 5 \times 1$ mesh. The van der Waals interactions were taken into account using Grimme’s DFT-D2 method.^{51,52} The structure was fully optimized until all forces acting on atoms were less than 0.02 eV/Å.

The $\text{Ni}_{17}\text{W}_3(111)$ and $\text{Ni}_4\text{W}(211)$ surfaces were modeled by $(2\sqrt{3} \times 2\sqrt{3})$ and (1×1) five-layer slabs, respectively. Because both Ni_{17}W_3 and Ni belong to the same space group ($Fm\bar{3}m$, No. 255), the $\text{Ni}_{17}\text{W}_3(111)$ surface was simulated by a Ni(111) slab with 9 Ni atoms substituted by 9 W atoms in agreement with the ratio of Ni to

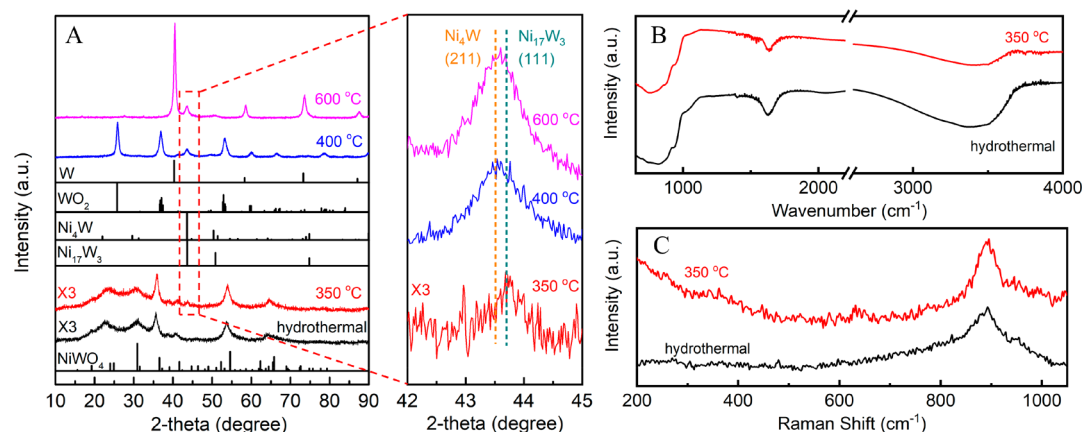


Figure 1. (A) XRD patterns of various samples. (B) FTIR and (C) Raman spectra of hydrothermal and 350 °C-reduced sample.

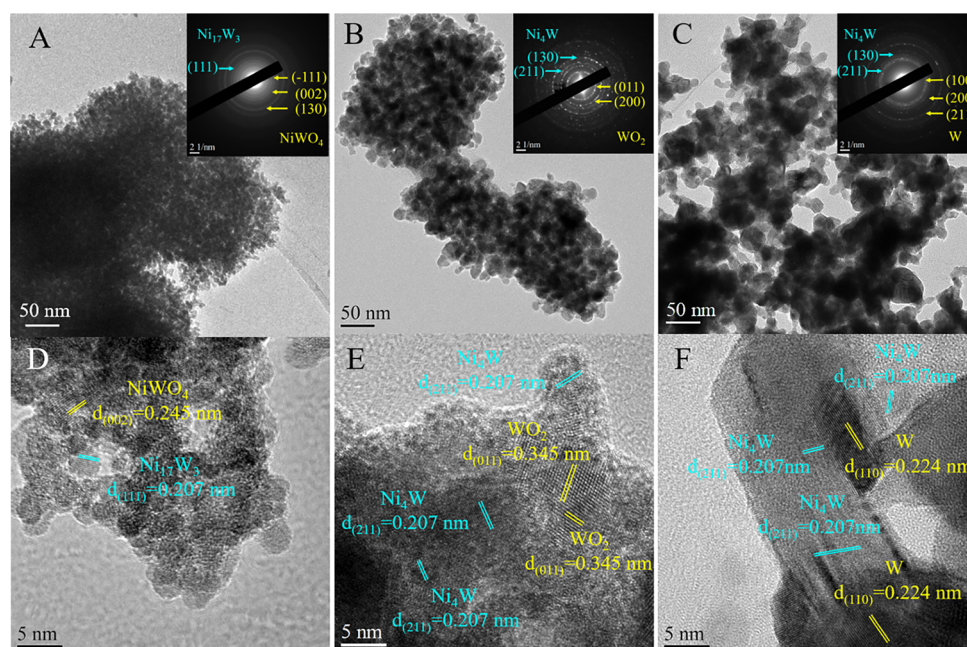


Figure 2. TEM and HRTEM images of the catalysts reduced at (A, D) 350 °C, (B, E) 400 °C, and (C, F) 600 °C. The insets showed the corresponding SAED patterns of the catalysts.

W atoms (17:3). Periodic images were separated by a vacuum region of 15 Å in the *z* direction (Figure S1, [Supporting Information](#)).

The adsorption energies of N_2H_4 (E_{ads}) were calculated as

$$E_{ads} = E_{X/surf} - E_{surf} - E_X \quad (2)$$

where E_X and E_{surf} represent the energies of N_2H_4 in the gas phase and the clear surfaces, respectively. $E_{X/surf}$ is the total energy of the surface with an adsorbed N_2H_4 molecule.

RESULTS AND DISCUSSION

The Ni–W–O-derived nanocatalyst was prepared by a two-step procedure, as illustrated in [Scheme 1](#). First, a nickel tungsten oxide precursor was synthesized via a simple hydrothermal process. The thus-synthesized sample was then calcined at elevated temperature under an H_2 atmosphere to obtain the target catalyst. The XRD pattern of the as-synthesized hydrothermal sample ([Figure 1A](#)) resembles some features of that of $NiWO_4$ but with significant peak broadening and diffuse scattering, indicating the formation of a poorly crystallized product. Further annealing this sample at elevated

temperature (over 400 °C) in air could help remove possible solvent residue, improve its crystallinity, promote crystallite growth, and result in a well-defined XRD pattern consistent with that of $NiWO_4$ (JCPDS 15-0755) ([Figure S2, Supporting Information](#)). Because of the poor crystallinity nature of the as-synthesized hydrothermal sample, its phase assignment was further corroborated by the spectroscopic analyses. FTIR spectra of the hydrothermal sample ([Figure 1B](#)) exhibited an intense peak at 822 cm^{-1} corresponding to the stretching vibrations of O–W–O.^{53,54} And the IR bands at around 1650 and 3400 cm^{-1} in [Figure 1B](#) should be assigned to the OH bending and stretching vibrations of the adsorbed water molecules. The Raman spectrum ([Figure 1C](#)) clearly showed a strong band at 883 cm^{-1} , which should be ascribed to the stretching vibrational mode of terminal W=O bonds, consistent with the featured assembly of WO_6 octahedra in the $NiWO_4$ structure.^{53,54}

Reductive annealing the hydrothermal sample at various temperatures resulted in the formation of nanocomposite catalysts with varied phase compositions and structures. As

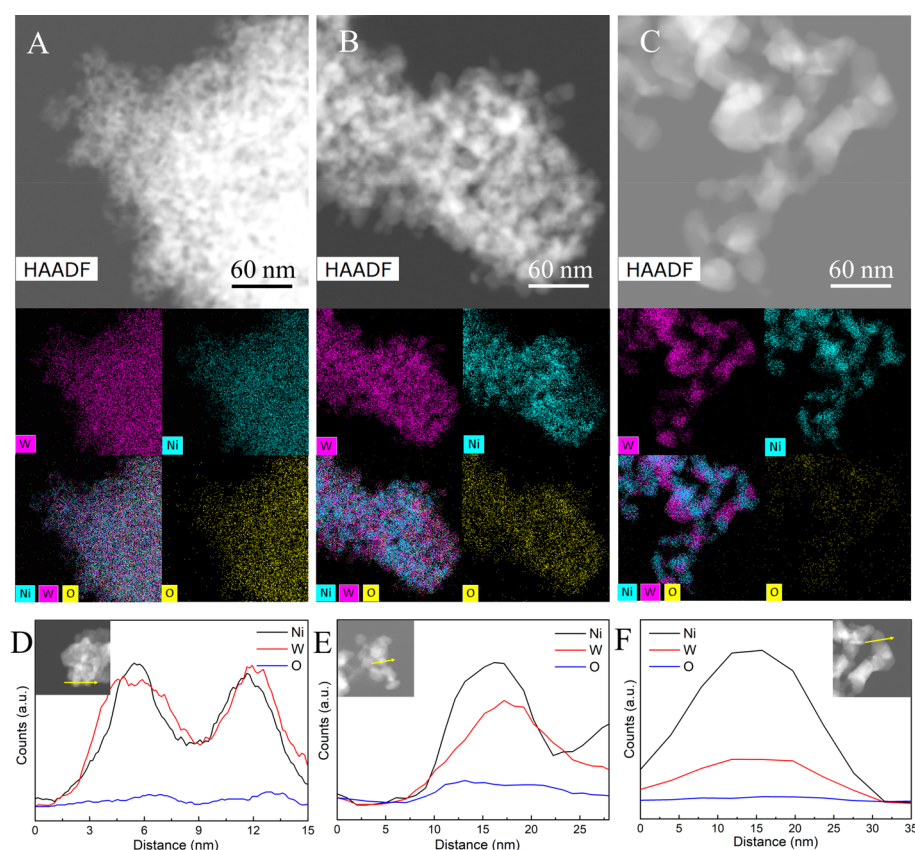


Figure 3. HAADF-STEM images and the corresponding EDS maps of the reduced catalysts at 350 °C (A), 400 °C (B), and 600 °C (C). The EDS line-scanning profiles of the reduced samples at 350 °C (D), 400 °C (E), and 600 °C (F).

shown in Figure 1A, the 350 °C-reduced sample showed a similar XRD pattern to that of the hydrothermal sample but with a new peak appearing at $2\theta = 43.68^\circ$, matching well with the (111) peak of the Ni_{17}W_3 phase (JCPDS 65-4828). Upon increasing the annealing temperature to 400 °C, this peak becomes intensified with a low-angle shift by 0.2° , which corresponds well to the (211) peak of the Ni_4W phase (JCPDS 65-2673). Meanwhile, the diffraction peaks from the hydrothermal sample completely disappeared and were replaced by the characteristic peaks from the WO_2 phase (JCPDS 32-1393). With further elevation of the annealing temperature to 600 °C, WO_2 was reduced to metal W (JCPDS 04-0806) but with the Ni_4W phase still preserved. The phase assignments of the 400- and 600 °C-reduced samples were further supported by the Raman spectra (Figure S3, Supporting Information).

Phase structure evolution of the hydrothermal samples upon reductive annealing was further investigated by operating TEM in high-resolution and selected-area electron diffraction (SAED) modes. As shown in Figure 2A–C, the SAED patterns discern the evolutionary reduction of the small NiWO_4 crystallites in the hydrothermal sample during the reductive annealing process, from the initial precipitation of Ni_{17}W_3 to the concurrent formation of Ni_4W and WO_2 , and further to the metallic Ni_4W and W phases. The high-resolution TEM images reveal the microstructure and phase constitution of the reduced samples. In the 350 °C-reduced sample, the lattice fringes with interplanar distances of 0.207 and 0.245 nm could be assigned to the (111) plane of Ni_{17}W_3 and the (002) plane of NiWO_4 , respectively (Figure 2D). Similarly, the characteristic d -spacings from the crystalline Ni_4W and WO_2 nanoparticles were identified in the 400 °C-

reduced sample (Figure 2E). Compared to the Ni_{17}W_3 phase in the 350 °C-reduced sample, Ni_4W nanoparticles showed both increased amount and particle size, consistent with the XRD results. In the 600 °C-reduced sample (Figure 2F), the lattice fringes with an interplanar distance of 0.224 nm can be safely assigned to the (110) plane of the W phase, and the dispersion of Ni_4W nanoparticles on the W substrate was clearly evidenced. In addition, some disordered domains were also observed, indicating the presence of amorphous phase in these reduced samples at different temperatures. In an effort to determine how the Ni–W alloy phases distribute on the W-containing substrates, we examined the reduced samples by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in combination with energy X-ray dispersive spectroscopy (EDS) analysis. As shown in Figure 3A–C, the Ni and W elemental distributions gradually change from the atomic dispersion to the segregated nanoclusters with increasing annealing temperature. For the 400 °C-reduced sample, the segregation of Ni and W elements became detectable because of the formation of the distinct Ni_4W and WO_2 phases. Further increasing the annealing temperature to 600 °C resulted in aggravated segregation Ni and W, owing to the formation of W and the particle growth and aggregation of Ni_4W . A close examination of the samples by EDS line-scanning profile analysis (Figure 3D–F) suggested that the size of the Ni_4W nanoparticles increased from around 15 to 30 nm upon elevation of the annealing temperature from 400 to 600 °C.

The chemical states of the constituent elements in the hydrothermal and reduced samples were also examined using the surface-sensitive XPS. As presented in Figure 4, the

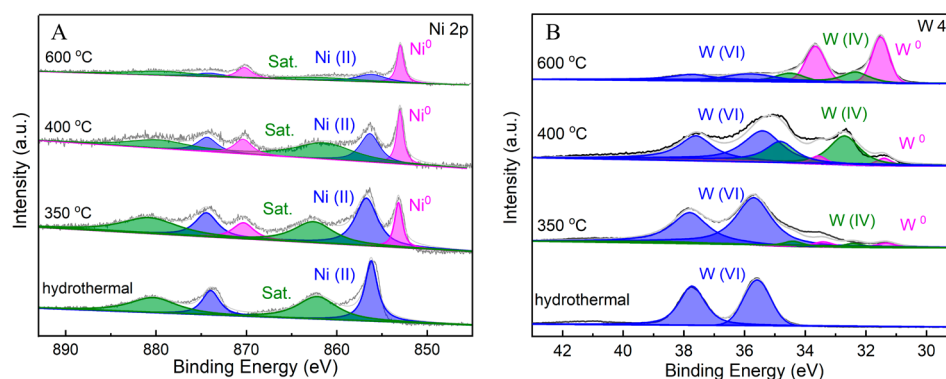


Figure 4. XPS results of the hydrothermal and reduced samples: (A) Ni 2p spectra and (B) W 4f spectra.

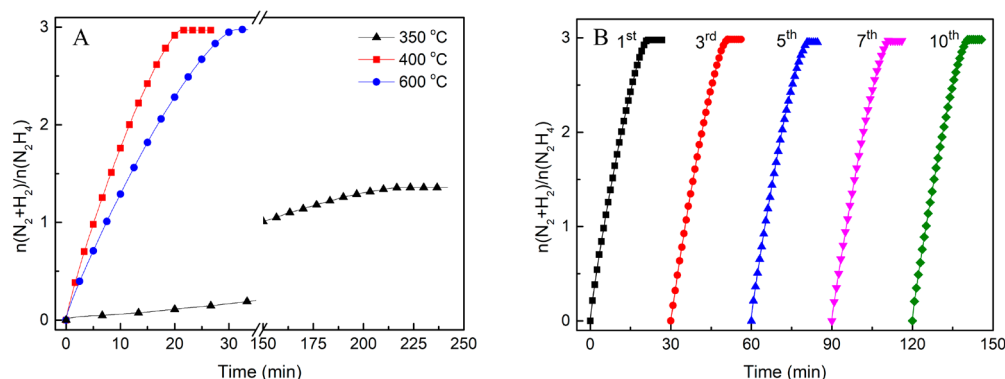


Figure 5. Kinetic curves of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition over the reduced catalysts at different temperatures. (B) Cyclic performance of the 400 °C-reduced catalyst. (reaction conditions: 2 mL solution composed of 0.5 M $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and 2.0 M NaOH at 50 °C, catalyst/ $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ = 1:20).

hydrothermal sample exhibited only Ni(II) and W(VI) signals. After the reductive annealing treatment, additional signals of metallic Ni^0 were detected, and their intensities increase with increasing annealing temperature. Similarly, the W 4f spectra of the reduced samples clearly manifested the formation of W(IV) and W^0 species upon reduction. These results were in accord with XRD, SAED, and HRTEM observations, supporting the evolutionary formation of Ni–W alloys and W-containing substrate phases during the reduction process. A close examination of the XPS spectra further found subtle but significant binding energy (BE) shifts of Ni^0 and W^0 . Specifically, the BEs of Ni^0 in the reduced samples were observed to negatively shift in comparison with the BE of pristine metal Ni at 853.3 eV. Meanwhile, the W^0 in the reduced samples showed positive BE shifts relative to pure W (31.0 eV). These results clearly indicated the electron transfer from W to Ni as a consequence of Ni–W alloys formation.^{22–24,37,55} In addition, XPS analysis clearly detected Ni(II) and W(VI) signals throughout the reduced samples but with decreased intensities upon high-temperature annealing. These results, together with the XRD, Raman, and HRTEM characterizations (Figure 1A, Figure 2F, and Figure S3), suggested the presence of NiWO_4 and WO_{3-x} amorphous phases in the reduced samples. On the basis of the combination of phase, microstructure, and chemical state analyses, the resulting nanocatalysts from reductive annealing of the NiWO_4 precursor at different temperatures were denoted as $\text{Ni}_{17}\text{W}_3/\text{NiWO}_4$ (350 °C), $\text{Ni}_4\text{W}/\text{WO}_2/\text{NiWO}_4$ (400 °C), and $\text{Ni}_4\text{W}/\text{W}/\text{WO}_{3-x}$ (600 °C), respectively.

Catalytic properties toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition were then studied on these Ni–W–O-derived nanocomposite

catalysts. According to control experiments, changing the molar ratio of Ni/W precursors caused a variation of catalytic properties toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition, and the optimal Ni/W precursors molar ratio was determined to be 1/1 (Figure S4, Supporting Information). Additionally, it was found that the reductive annealing temperature exerted significant influence on the catalytic properties of the resulting catalyst. As presented in Figure 5A, the 350 °C-reduced catalyst showed a very low reaction rate of 2 h^{-1} and a poor H_2 selectivity of only 25%. In sharp contrast, the 400 °C-reduced catalyst exhibited a higher rate of 33 h^{-1} and a H_2 selectivity of 99%, which enabled a complete decomposition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 50 °C within 18 min. Further increasing the annealing temperature, however, seems to deteriorate the reaction rate, from 33 to 28 h^{-1} . We then investigated the drastic changes of the apparent catalytic properties of these nanocomposite catalysts from the aspects of investigating the intrinsic catalytic properties, comparing the number of active sites and understanding the metal–support interactions. For the different catalytic properties of the 350- and 400 °C-reduced samples, we first examined and compared their specific surface areas (SSA) using N_2 adsorption/desorption method. It was found that increasing the annealing temperature from 350 to 400 °C resulted in a decrease of SSA from 76.2 to 30.9 $\text{m}^2 \text{g}^{-1}$ (Figure S5, Supporting Information), which was contrary to their catalytic property improvements. We then conducted control experiments to evaluate the possible effect of support materials on the catalytic properties via metal–support interactions. Specifically, we fixed the annealing temperature at 350 °C and examined the annealing time dependence of phase structure and catalytic properties. It was found that

prolongation of annealing time from 2 to 5 h caused no appreciable change of NiWO_4 substrate phase but resulted in the formation of Ni_4W instead of Ni_{17}W_3 phase (Figure S6, Supporting Information). A property test found that the 5-h-reduced sample (350 °C) showed an over 9 times increase of activity and an increase of H_2 selectivity from 25% to 87% compared to the 2-h-reduced sample (350 °C). The catalytic activity and H_2 selectivity of the 5-h-reduced sample (350 °C) were even comparable to those of the 400 °C-reduced catalyst, which was composed of Ni_4W , WO_2 , and NiWO_4 amorphous phases (Figure S7, Supporting Information). These results suggested that the substrate phase did not play an important role in the present system, and the observed catalytic property differences between the 350- and 400 °C-reduced samples should be attributed to the variation of the active phases. The different catalytic behaviors of the Ni_4W and Ni_{17}W_3 phase were further evaluated and supported by our first-principle calculations as stated below. For the catalytic property differences of the 400- and 600 °C-reduced samples, we noticed that the two catalysts shared a common Ni_4W active phase, and metallic W was experimentally demonstrated to be inactive toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition. Therefore, the activity degradation of the 600 °C-reduced sample might stem from the particle growth and aggregation of the Ni_4W species at elevated temperatures, as evidenced by the increased Ni–W alloy particle size observed in EDS line-scanning profile analysis (Figure 3E,F). In addition, the N_2 adsorption/desorption isotherm measurements revealed that the SSAs of the catalyst samples decreased from 30.9 to 12.6 $\text{m}^2 \text{g}^{-1}$ upon increasing the annealing temperature from 400 to 600 °C (Figure S5, Supporting Information).

To gain more insight into the catalytic properties of the Ni–W–O-derived catalysts, we conducted DFT calculations to investigate the activities and selectivities of Ni_4W and Ni_{17}W_3 alloys. On the basis of the bond-order conservation principle, we adopted the adsorption strengths of N_2H_4 on the metallic surfaces as an indicator of the activity toward N_2H_4 decomposition.^{56,57} As seen in Figure 6, the most stable adsorption conformation of N_2H_4 was one-N-atom conformation on the Ni atom of both surfaces (for details, see Figure S8, Supporting Information). The adsorption strength of N_2H_4 was enhanced on the Ni_4W surface as compared to that on the

Ni_{17}W_3 surface, suggesting a higher activity of Ni_4W toward N_2H_4 dissociation than Ni_{17}W_3 . This may well account for the experimentally observed activity change of the 350- and 400 °C-annealed samples. With respect to the selectivity, a fundamental understanding of adsorption and decomposition behaviors of N_2H_4 over metal surfaces is required to identify a suitable indicator for the complex multiparametric system. Previous studies illustrated that different initial adsorption conformations of N_2H_4 over metal surfaces can lead to distinct reaction pathways.^{58–60} In the case of only one N atom of N_2H_4 bonded to the metal surfaces, N–H bond cleavage of N_2H_4 molecules is energetically more favorable than N–N bond cleavage, which preferably results in H_2 production. In contrast, the adsorption conformation with both N atoms of N_2H_4 bonding to the surfaces dominantly leads to NH_3 formation. Hence, the adsorption energy difference between one-N-atom and two-N-atom conformations can serve as an indicator to evaluate the reaction selectivity of N_2H_4 decomposition. According to the DFT calculation results, the adsorption energy difference on the Ni_4W surface is larger than that on the Ni_{17}W_3 surface by nearly a factor of 2, implying a significantly higher H_2 selectivity for Ni_4W . This is in good accordance with the experimental results. Therefore, it can be concluded that the improved catalytic performance of the Ni–W–O-derived catalysts upon increasing the annealing temperature from 350 to 400 °C should stem from the resultant Ni_4W with higher intrinsic activity and H_2 selectivity than Ni_{17}W_3 .

Next, we focused on the best-performing 400 °C-reduced catalyst sample for a detailed property test. We first inspected its stability as the poor stability is a common and critical problem for the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition catalysts. In the present study, the newly developed $\text{Ni}_4\text{W}/\text{WO}_2/\text{NiWO}_4$ nanocomposite catalyst was found to exhibit surprisingly high stability. For instance, the catalyst showed no appreciable decay of activity and H_2 selectivity after 10 cycles of use (Figure 5B), which were unprecedentedly better than the performance of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition catalysts hitherto reported (Table S1, Supporting Information). XRD and TEM analyses of the 400 °C-reduced catalyst after 10 cycles of use show no significant change in morphology, microstructure, and phase structure (Figures S9 and S10, Supporting Information), suggesting high stability of the Ni–W–O-derived catalyst. The mechanism of the excellent stability of the present $\text{Ni}_4\text{W}/\text{WO}_2/\text{NiWO}_4$ nanocomposite catalyst is still under investigation. A high-capacity HP system consisting of the commercial 98 wt % $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (17.5 M) solution and NaOH (2.0 M) promoter was employed by using this catalyst. As shown in Figure 7A, the decomposition reaction of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was immediately triggered with no appreciable lag time when the $\text{Ni}_4\text{W}/\text{WO}_2/\text{NiWO}_4$ catalyst contacted the fuel solution. The reaction rate of the system rapidly reached its maximum (90 mL ($\text{N}_2 + \text{H}_2$) min^{-1}) within ~ 1 min and maintained at a level of ~ 80 mL ($\text{N}_2 + \text{H}_2$) min^{-1} for over 100 min. After completion of the reaction, we examined the postused fuel solution by UV–vis spectroscopy (Figure S11, Supporting Information). The invisibility of the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ signal in UV–vis spectroscopy analysis clearly indicated a 100% fuel conversion. In particular, the thus-constituted system yielded a hydrogen capacity as high as 6.28 wt %.

The dynamic response property to the varied hydrogen demands is also a key parameter for practical H_2 source systems. In the present work, we tested the dynamic response performance of the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -based HP system by periodi-

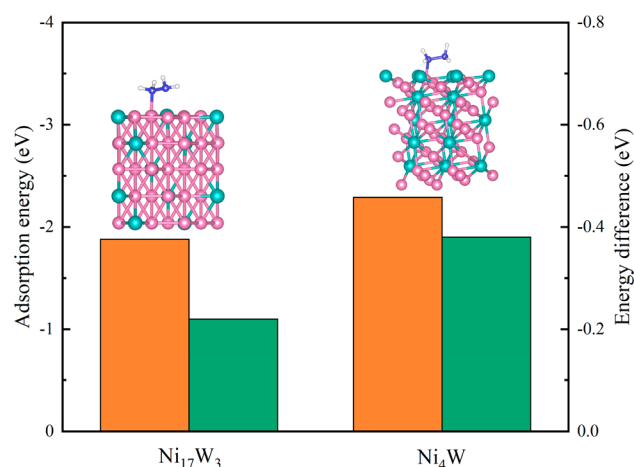


Figure 6. Adsorption energy (orange) of N_2H_4 and the adsorption energy difference (olive) between one-N-atom and two-N-atom adsorption configurations on Ni_{17}W_3 (111) and Ni_4W (211) surfaces.

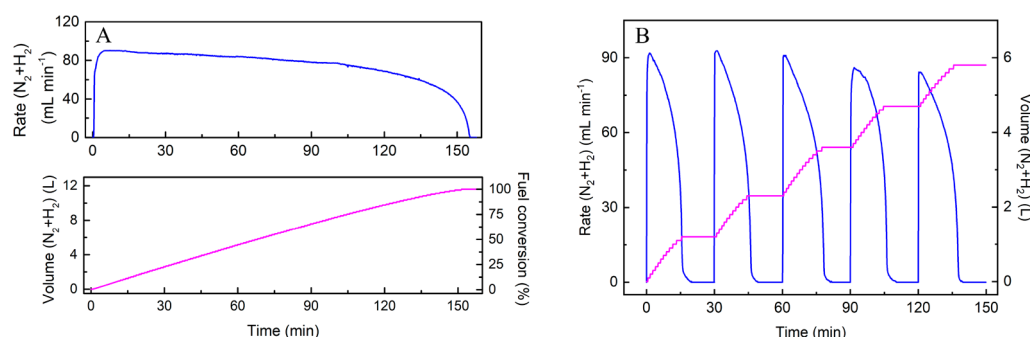


Figure 7. Kinetic curves of concentrated $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition over the 400°C -reduced catalyst at 50°C . (A) Time course profiles of 10 mL concentrated $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition reaction rate (top) and fuel conversion (bottom) (B) Start/stop hydrogen production dynamics profile of 1 mL concentrated $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition. (System composition: 17.5 M $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ + 2 M NaOH + 400 mg of catalyst.)

cally feeding the fuel solution into the reactor with preloaded $\text{Ni}_4\text{W}/\text{WO}_2/\text{NiWO}_4$ catalyst. As shown in Figure 7B, the catalytic decomposition reaction of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ immediately occurred upon contacting the fuel solution with the catalyst, and importantly, the system rapidly reached the maximum rate within ~ 1 min and completed the HP process within approximately 20 min for each start/stop cycle test. Examination of the kinetics profiles found that the maximum reaction rates decreased slightly with increasing the cycle number, which might be attributed to the dilution of the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ fuel solution by the water byproduct from the previous cycle. Evidently, a favorable combination of high hydrogen capacity, rapid dynamic response, and stable HP performance of the present $\text{Ni}_4\text{W}/\text{WO}_2/\text{NiWO}_4$ composite catalyst may lay foundation for the practical applications of the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -based H_2 source system.

CONCLUSIONS

The Ni–W–O-derived nanocomposite catalysts can be readily synthesized by a hydrothermal process in combination with reductive annealing treatment. Depending upon the annealing temperature, the thus-prepared catalysts exhibited remarkably distinct catalytic performances toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition regarding both activity and H_2 selectivity. On the basis of a combination of phase/microstructure/chemical state analyses and DFT theoretical calculations, the observed catalytic property changes can be correlated with the temperature-dependent evolutions of phase structure and microstructural features of the catalyst in the reductive annealing process. Our study revealed that the phase constitution and distribution state of Ni–W alloys played important roles in the catalytic performance toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition. Specifically, a $\text{Ni}_4\text{W}/\text{WO}_2/\text{NiWO}_4$ nanocomposite catalyst showed high activity, nearly 100% selectivity, and exceptionally high stability toward $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition for hydrogen production. Using this noble-metal-free catalyst, we have developed a $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -based hydrogen production system with a material-based hydrogen capacity as high as 6.28 wt % and rapid dynamic response property. Our study could enlighten and encourage future exploration of catalytic decomposition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as a practical on-demand hydrogen production technology for mobile and portable applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.9b07782>.

Computational models of Ni–W alloys and N_2H_4 adsorption conformations on the catalyst surfaces, XRD patterns and Raman spectra of the reduced samples, kinetic curves of the catalysts with different Ni/W molar ratios, N_2 adsorption/desorption isotherms and pore size distribution curves, performance dependence of the catalyst on annealing temperature or annealing time, XRD patterns and TEM images of the catalyst before and after stability test, UV–vis spectra of the postused hydrous hydrazine solution, and table showing a comparison of catalytic performances of noble-metal-free catalysts (PDF)

AUTHOR INFORMATION

Corresponding Author

Ping Wang – School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, P.R. China; orcid.org/0000-0002-7704-2538; Phone: +86 20 3938 0583; Email: mspwang@scut.edu.cn

Authors

Qing Shi – School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, P.R. China

Deng-Xue Zhang – School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, P.R. China

Hui Yin – School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, P.R. China

Yu-Ping Qiu – School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, P.R. China

Liang-Liang Zhou – School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, P.R. China

Chen Chen – School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, P.R. China

Hui Wu – NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, United States; orcid.org/0000-0003-0296-5204

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acssuschemeng.9b07782>

Notes

The authors declare no competing financial interest.

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