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Maximizing the Synergistic Effect of CoNi Catalyst on α -MoC for Robust Hydrogen Production

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ABSTRACT: We report the syntheses of highly dispersed CoNi bimetallic catalysts on the surface of α -MoC based on the strong metal support interaction (SMSI) effect. The interaction between the nearly atomically dispersed Co and Ni atoms was observed for the first time by the real-space chemical mapping at the atomic level. Combined with the ability of α -MoC to split water at low temperatures, the as-synthesized CoNi/ α -MoC catalysts exhibited robust and synergistic performance for the hydrogen production from hydrolysis of ammonia borane. The metal-normalized activity of the bimetallic 1.5Co1.5Ni/ α -MoC catalyst reached 321.1 mol_{H2}·mol⁻¹_{CoNi}·min⁻¹ at 298 K, which surpasses all the noble metal-free catalysts ever reported and is four times higher than that of the commercial Pt/C catalyst.

• he recent developments in the atomically dispersed metal catalysts or single-atom catalysts (SACs) have attracted considerable interest because of their maximized noble metal utilization efficiency and unique electronic and/or geometric characteristics.¹⁻⁴ However, SACs also have their own limitations. For example, when the activation of reacting molecules requires more than one metallic center, SACs generally exhibit limited activities because of the lack of suitable multicenter active sites. Lu et al. showed that the Pt dimers possess much higher activity for the hydrolysis of ammonia-borane $(NH_3 \cdot BH_3, AB)$ than that of the Pt SACs.⁵ Therefore, for certain reactions such as the dehydrogenation of molecules that require diverse adsorption sites, the closely distributed under-coordinated metallic centers are more favorable for enhancing the catalytic performance.^{6,7} The heterometal combinations in the highly dispersed metal domains may also result in a special synergistic effect that the SACs generally lacks, although this synergy has rarely been reported.

In addition to the geometric factors, modulation of the electronic properties of active centers that is induced by their interaction with the support materials has also been proven essential in determining the catalytic performance, especially for the catalysts with high or even atomic metal dispersion.³, In our recent studies, we have demonstrated that both the geometric and electronic properties of Au and Pt can be tuned by the strong metal support interaction with α -MoC.⁹ After combining the unique nature of α -MoC that is capable of activating water and maintaining a high surface coverage of hydroxyl species at a temperature of 303 K,10,11 the assynthesized catalysts showed extraordinary activity for the lowtemperature water-gas shift and methanol reforming reactions. These unique properties of the α -MoC evoke us to explore the utility of its surface hydroxyl species in other catalytic reactions.

In this paper, we report the syntheses of highly dispersed CoNi bimetallic catalysts supported on α -MoC (CoNi/ α -MoC) for the efficient hydrogen production from the hydrolysis of ammonia borane.^{12–18} The metal-normalized activity of 1.5Co1.5Ni/ α -MoC (α -MoC loaded with 1.5 wt % Co and 1.5 wt % Ni) reached 128.5 mol_{H2}·mol⁻¹_{CoNi}·min⁻¹ at 25 °C which is 3.2 and 3.6 times higher than that of the monometallic 3Co/ α -MoC and 3Ni/ α -MoC catalysts, respectively. The improved catalytic performance of 1.5Co1.5Ni/ α -MoC is due to the synergistic effect between the nearly atomically dispersed Co and Ni atoms. Furthermore, by changing the reaction media from neutral to basic conditions, the optimum metal-normalized activity even reached 321.1 mol_{H2}·mol⁻¹_{CoNi}·min⁻¹, surpassing all the non-noble metal catalysts ever reported, ^{19–25} and achieving over four times higher activity than the commercial Pt/C catalyst.²⁶

The α -MoC support was synthesized by following the stepwise temperature ammonization/carburization of MoO₃ at 973 K.²⁷ Further, the α -MoC supported Co/Ni catalysts were synthesized by the impregnation method. The structure of the catalysts was first investigated using X-ray diffraction (XRD) (Figure 1a). No obvious crystal diffraction peaks of Co and Ni were observed in any of the samples, demonstrating the high dispersion of Co and Ni on the surface of α -MoC.

The electronic structures of the α -MoC supported Co/Ni catalysts were studied by *ex situ* X-ray photoelectron spectroscopy (Figure 1b and 1c). The binding energy of 283.3 eV for C 1s (Figure S1) and 228.4 eV for Mo $3d_{5/2}$

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Figure 1. (a) XRD patterns of CoNi/ α -MoC catalysts with different CoNi loadings. *Ex situ* XPS spectra of (b) Co 2p, (c) Ni 2p, and (d) Mo 3d of the CoNi/ α -MoC catalyst.

(Figure 1d) are identical to that of typical α -MoC.²⁸ The binding energies of Co $2p_{3/2}$ and Ni $2p_{3/2}$ in the tested samples were 778.7 and 853.2 eV, which are 0.4 and 0.5 eV higher than that of metallic Co⁰ $2p_{3/2}$ and Ni⁰ $2p_{3/2}$ standards, respectively.³⁴ The shift in the binding energies of Co and Ni without any profile change can be attributed to the electron transfer from Co and Ni to the α -MoC support, which is evidence of the strong metal support interaction between Co/Ni and the carbide substrate.^{10,29} However, no significant difference in the binding energies ($2p_{3/2}$) of Co and Ni species was observed between the mono- and bimetallic catalysts, indicating that the chemical environment and structure did not change significantly with the coexistence of the heterometal centers.^{7,30}

X-ray absorption fine structure (XAFS) spectra were obtained to investigate the local structure of the α -MoC supported Co/Ni catalysts. Figure 2a and b show the X-ray absorption near edge spectra (XANES) of the catalysts. The

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intensities of the "white-line" (8350.5 eV for the Ni K edge and 7726.4 eV for the Co K edge) are stronger than those of the metal foils but weaker than those of the metal oxide foils. This suggests that the d-band vacancies of the loaded metals in the catalysts are lower than that of their corresponding bulk metallic state but higher than those of their corresponding oxides, which proved the electron transfer from the supported metal centers to the substrate.

The Fourier transformed k²-weighted extended X-ray absorption fine structure (EXAFS) (Figure 2c and d) and wavelet transformation (WT) EXAFS oscillations (Figures 2e and f) of Co and Ni K edge exhibited obvious Co–C and Ni– C peaks at approximately 1.6 Å, indicating that both Co and Ni are in different coordination environments from their corresponding bulk metals. The results also suggest that both Co and Ni are mainly bonded with the C atoms of the α -MoC surface rather than the Mo atoms. Meanwhile, the small coordination numbers (Figure S2, Table S2) of Co–Co, Co– Ni, and Ni–Ni bonds solved from the least-squares EXAFS fitting (\leq 2.2 in all three samples) indicate that Co and Ni are highly dispersed on the surface of α -MoC without aggregation into large nanoparticles.

The EXAFS results also revealed that the mean bond length of Co–Co bond in $3Co/\alpha$ -MoC is 2.49 Å and that of the Ni– Ni bond in $3Ni/\alpha$ -MoC is 2.53 Å, which is consistent with the atomic radii of Co and Ni, respectively. Lying in between, the mean bond length of Co–Co(Ni) and Ni–Ni(Co) bonds in 1.5Co1.5Ni/ α -MoC is 2.50 Å, indicating the formation of hybrid Co–Ni bonds in the second nearest neighbor shells. The coordination numbers (Table S2) of Co–Co and Co–C in $3Co/\alpha$ -MoC determined from the fitting results of Co K edge spectra are 2.2 and 1.7, respectively, whereas those of Co–Co (Co–Ni) and Co–C in 1.5Co1.5Ni/ α -MoC are 0.4 and 3.3. These results confirmed a better dispersion of Co after the coimpregnation of Ni in the 1.5Co1.5Ni/ α -MoC, indicating the presence of a spatial correlation between the distribution of Co and Ni.

Figure 3 shows the scanning transmission electron microscopy (STEM) results of the 1.5Co1.5Ni/ α -MoC. The low magnification STEM images revealed that the α -MoC has



Figure 2. XANES profiles of (a) Co K edge and (b) Ni K edge of the CoNi/ α -MoC catalysts. EXAFS spectra in R space for (c) Co K edge and (d) Ni K edge of the CoNi/ α -MoC catalysts. WT analysis of (e) Co and (f) Ni in the 1.5Co1.5Ni/ α -MoC catalyst.

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Figure 3. (a) HAADF-STEM image of $1.5Co1.5Ni/\alpha$ -MoC. (b) High resolution HAADF-STEM image of the highlighted area in (a). (c) Overlay of Co and Ni EELS maps with the simultaneously recorded HAADF-STEM image. (d) Overlay of the projected spatial distribution of Co and Ni. (e) Enlarged image of the highlighted pixels in (d). The size of each pixel is 0.15 nm. (f) EELS spectra of the Co single atom and the Ni single atom in the corresponding regions in (e).

a porous structure consisting of irregular shaped particles with a grain size of \sim 5–10 nm (Figure S5 and Figure 3a). Because of the higher Z-contrast of Mo atoms compared to Co and Ni atoms, it is difficult to directly visualize the Co and Ni species on the surface of α -MoC (Figure 3b). To confirm the presence of atomically dispersed Co and Ni, we performed atomic-scale chemical imaging via STEM-EELS mapping. The results (Figure 3c and Figure S6) depict that most of the Co and Ni loadings are atomically dispersed at high density on the surface of α -MoC, with some additional small clusters consisting of only a few atoms. We observed that the spatial distribution of the Co and Ni species is highly correlated. Figure 3d-f show a pair of adjacent Co and Ni atoms that are less than 3 Å apart. The close proximity of the Ni and Co atoms suggests that they may be able to interact synergistically with the same reactant molecule during a catalytic reaction.

The catalytic performance of the CoNi/ α -MoC and reference catalysts was evaluated in the low-temperature hydrolysis of ammonia borane (NH₃·BH₃, AB) for hydrogen production. In contrast to the negligible hydrogen production rate with pure α -MoC (Figure 4a), both 3Ni/ α -MoC and 3Co/ α -MoC catalysts showed drastic improvement in their activity with the full release of hydrogen realized in around 4 min. However, when a small amount of Ni was added to the Co/ α -MoC catalyst (Co/Ni mole ratio = 9:1), a steep increase in the reactivity was observed as the duration of full release of hydrogen was reduced to 2.5 min. Further increase in the fraction of Ni led to a continuous increase in the reactivity,



Figure 4. (a) Catalytic hydrolysis of AB by CoNi/ α -MoC with different molar ratios of n(Co):n(Ni). (b) Metal-normalized activity of different catalysts in (a). (c) Long-term stability test of the 1.5Co1.5Ni/ α -MoC catalyst in 0.5 M NaOH aqueous solution.

which attained the maximum at a Co/Ni ratio of 1:1. To clarify this tendency, the metal-normalized activity was plotted as a function of the Co/Ni ratio (Figure 4b) that demonstrated a volcano-type relationship. For monometallic $3Co/\alpha$ -MoC and $3Ni/\alpha$ -MoC catalysts, the metal-normalized activity was 40.2 and 35.7 mol_{H2}·mol⁻¹_{CoNi}·min⁻¹, respectively. In contrast the bimetallic 1.5Co1.5Ni/ α -MoC catalyst attained an optimum activity of 128.5 mol_{H2}·mol⁻¹_{CoNi}·min⁻¹, which is more than three times higher than those of the monometallic catalysts, confirming the presence of a strong synergistic effect between the highly dispersed Co and Ni species.

For the AB hydrolysis reaction, the O-H bond cleavage of water combined with the surface OH* attack on the adsorbed AB molecule via the S_N2 mechanism was proposed to be the rate-limiting step.^{22,23,31} The presence of extra OH⁻ could drastically shorten the induction period of the S_N2 process and, therefore, improve the catalytic performance. To confirm the role of H₂O in the rate-determining step of this reaction, we performed an isotopic experiment by replacing H_2O with D_2O . The result (Figure S9) demonstrated a large kinetic isotope effect of 4.23, indicating that the cleavage of the O-H bond of water is indeed the rate-determining step. The absorption and reaction of water on the surface of α -MoC and 1.5Co1.5Ni/ α -MoC (Figure S10) were further investigated. The stoichiometric hydrogen was immediately generated and detected by the mass spectrometer, which demonstrates the cleavage of the O-H bond of water at room temperature forming hydroxyl species (or possibly a very small amount of O* species) that remain on the surface of the catalysts.¹¹ Based on the aforementioned results, the outstanding performance of $CoNi/\alpha$ -MoC can be attributed mainly to the combined influence of two factors: (i) the synergistic effect of the highly dispersed and closely associated Co-Ni species known for their anisotropic nature to effectively activate the B-N bond in AB and (ii) the ability of α -MoC to activate the water and form OH* groups on the surface of the catalyst at a low temperature.

Further, the activity of the 1.5Co1.5Ni/ α -MoC catalyst was tested in the aqueous NaOH solutions (Figure S12). The metal-normalized activity drastically increased from 128.5 mol_{H2}·mol⁻¹_{CoNi}·min⁻¹ in neutral water to 240.9 mol_{H2}·mol⁻¹_{CoNi}·min⁻¹ in 0.1 M NaOH aqueous solution because of the presence of extra OH⁻ groups. When the concentration of NaOH was increased from 0.1 to 1.0 M, the turnover frequency value increased to a maximum value as 321.1 mol_{H2}·mol⁻¹_{CoNi}·min⁻¹ and then decreased slightly, surpassing all the noble metal-free catalysts ever reported (Table S3).^{32,33} In a 10-time recycling experiment, the catalyst exhibited stable performance throughout all 10 consecutive runs (Figure 4c). After the subsequent recovering and washing, the catalyst was able to fully release hydrogen even in the 11th run with almost the same activity as the original one (1st run).

In summary, we designed and synthesized a CoNi/ α -MoC catalyst for the robust hydrogen production from the hydrolysis of ammonia-borane. Our findings provide new insights into the design and application of the catalysts, having highly dispersed heterogeneous active centers as well as the synergistic effect, for the low-temperature hydrolysis and hydrogen production reactions.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c11285.

Materials, ICP results, general methods for catalysts preparation and evaluation, supplementary TEM, XPS and XAFS informations, the kinetics results (PDF)

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Notes

The authors declare no competing financial interest.

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