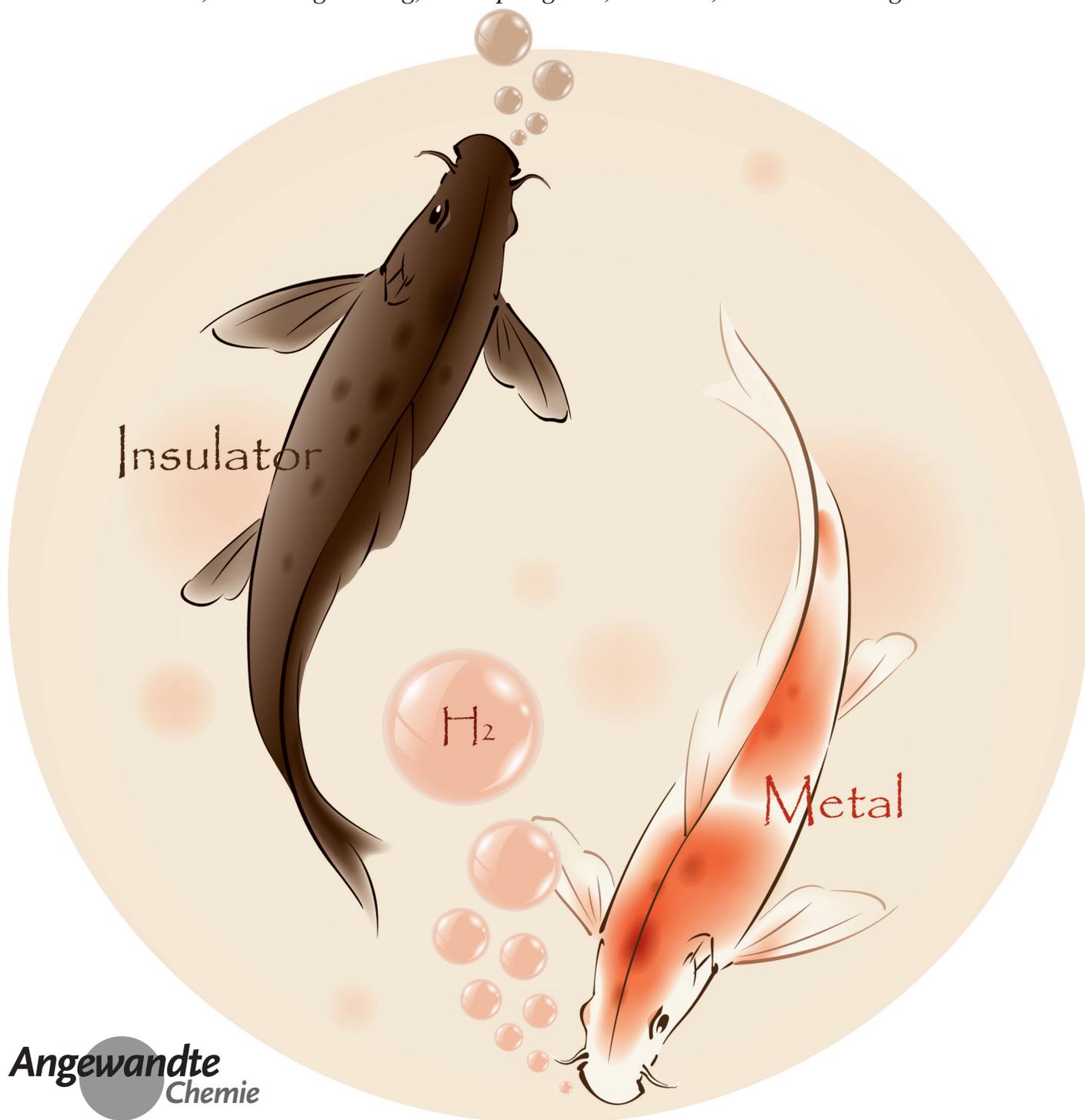


Supported Rhodium Catalysts for Ammonia–Borane Hydrolysis: Dependence of the Catalytic Activity on the Highest Occupied State of the Single Rhodium Atoms

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Abstract: Supported metal nanocrystals have exhibited remarkable catalytic performance in hydrogen generation reactions, which is influenced and even determined by their supports. Accordingly, it is of fundamental importance to determine the direct relationship between catalytic performance and metal–support interactions. Herein, we provide a quantitative profile for exploring metal–support interactions by considering the highest occupied state in single-atom catalysts. The catalyst studied consisted of isolated Rh atoms dispersed on the surface of VO₂ nanorods. It was observed that the activation energy of ammonia–borane hydrolysis changed when the substrate underwent a phase transition. Mechanistic studies indicate that the catalytic performance depended directly on the highest occupied state of the single Rh atoms, which was determined by the band structure of the substrates. Other metal catalysts, even with non-noble metals, that exhibited significant catalytic activity towards NH₃BH₃ hydrolysis were rationally designed by adjusting their highest occupied states.

Hydrogen generation from chemical hydrogen storage materials in a catalytic process is a convenient, inexpensive, and effective approach to apply hydrogen energy in a practical fashion.^[1] Typical hydrogen storage chemicals include formic acid (HCOOH), hydrous hydrazine (N₂H₄·H₂O), methanol (CH₃OH), and ammonia–borane (NH₃BH₃), with hydrogen contents of 4.4, 8.0, 18.8, and 19.6 wt %, respectively.^[2–6] Finding efficient catalysts towards H₂ release from these materials under mild conditions is urgently required. Thanks to extensive efforts, supported metal nanocrystals have been reported to display remarkable catalytic performance, which was found to be significantly influenced and even determined by their supports.^[6–11] Accordingly, determining the relationship between catalytic performance and metal–support interactions is of fundamental importance. However, it remains challenging to quantitatively understand the nature of metal–support interactions owing to the lack of detailed knowledge of reaction processes in hydrolysis reactions and active sites at

the atomic level. Specifically, the well-established reaction paths of hydrolysis reactions under homogeneous catalysis cannot be directly applied to heterogeneous catalysis because of the existence of a phase interface and complex active sites in heterogeneous catalysis.^[3–5] The details of the reaction process of NH₃BH₃ hydrolysis over solid catalysts have not been determined experimentally. Density functional theory (DFT) calculations were conducted to gain insight into the reaction path but the theoretical energy barrier was much higher than the experimental activation energy.^[12] As for the exact active sites in this reaction, preliminary mechanistic studies suggested that the hydrolysis reaction occurred at the interface of metal and support, whereas some studies attributed the activity to the surface of the metal nanocrystals.^[7–10]

To solve the aforementioned problems, state-of-the-art single-atom catalysts have been proposed as an ideal platform to investigate metal–support interactions because interference from the size, shape, and orientation of the metal particles at the metal–support interface can be readily excluded.^[13,14] Moreover, phase-transition materials are regarded as suitable supports for single atoms to reveal the key role of metal–support interactions in the catalysis process, as the band structure of the substrate can be modulated while keeping the spatial distribution of the single atoms, and thus the active sites, unchanged. One of the most widely studied materials in this area is vanadium dioxide (VO₂), which undergoes a metal–insulator phase transition at approximately 341.0 K.^[15]

Herein, we provide a quantitative approach for exploring metal–support interactions by considering the highest occupied state in single-atom catalysts. The single-atom catalyst consisted of isolated Rh atoms uniformly dispersed on the surface of VO₂ nanorods (denoted as Rh₁/VO₂). During NH₃BH₃ hydrolysis, changes in the activation energy were induced by phase transitions of the substrate. Further experimental analysis and DFT calculations indicate that the catalytic performance directly correlates with the highest occupied state of the individual Rh atoms, which in turn depends on the band structure of the substrate. Based on the aforementioned reaction mechanism, other metal catalysts, even with non-noble metals, that exhibit significant catalytic activity towards NH₃BH₃ hydrolysis were rationally designed by adjusting their highest occupied states.

First, VO₂ nanorods in the monoclinic phase were synthesized with an average diameter of 240 nm (see the Supporting Information, Figure S1). Owing to the fully reversible phase transition between monoclinic VO₂(M) and rutile VO₂(R), these VO₂ nanorods underwent a typical metal–insulator transition at approximately 341.0 K as revealed by the changes in the resistance as a function of temperature (Figure S2 A), with a transition region of 337.2–344.2 K. We prepared single-atom Rh₁/VO₂ catalysts by simply injecting Na₃RhCl₆ solution into an aqueous solution containing VO₂ nanorods, followed by stirring at 300 rpm at room temperature for 1 h. In this process, the Rh³⁺ ions in the Na₃RhCl₆ solution are reduced to Rh⁺ by V⁴⁺ in the VO₂ nanorods as the average molar ratio of leached V species to supported Rh single atoms was determined to be 2.1 (see the

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Experimental Section in the Supporting Information). The Rh mass loading was determined to be 0.5% by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The electric properties of Rh₁/VO₂ are similar to those of VO₂ (Figure S2B). Figure 1A shows a high-angle annular dark-field scanning transmission electron microscopy (HAADF-

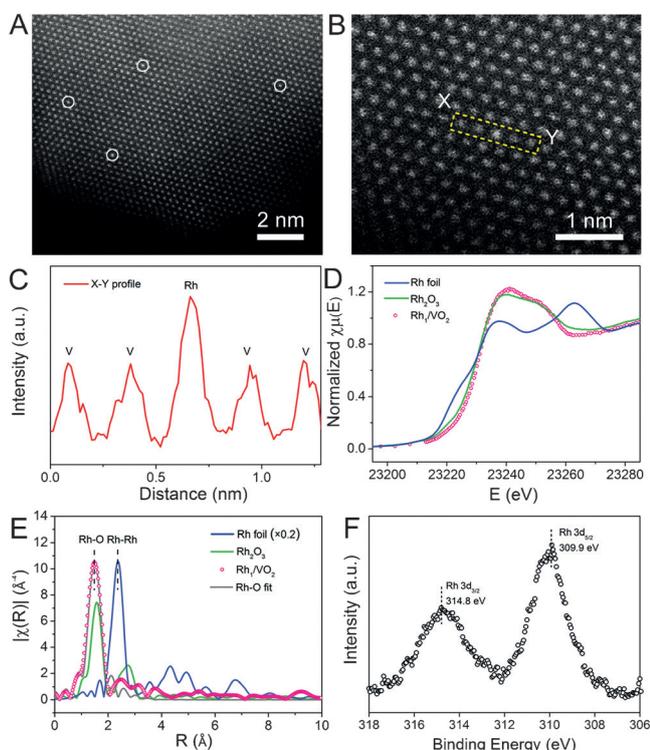


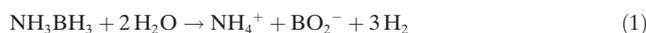
Figure 1. A) HAADF-STEM and B) magnified HAADF-STEM images of Rh₁/VO₂. C) Intensity profile along the X–Y line in (B). D) Rh K-edge XANES spectra for Rh₁/VO₂, Rh₂O₃, and Rh foil. E) Rh K-edge EXAFS spectra in R space for Rh₁/VO₂ with the corresponding fitted curve, Rh₂O₃, and Rh foil. F) XPS spectrum of Rh 3d for Rh₁/VO₂.

STEM) image of Rh₁/VO₂. Individual Rh atoms, which were observed as bright spots and marked with white circles, were uniformly dispersed on the surface of the VO₂ nanorods. Further analysis of a magnified HAADF-STEM image of Rh₁/VO₂ shows that the Rh atoms exactly occupied the positions of V atoms (Figure 1B). The intensity profile (Figure 1C) along the X–Y line in Figure 1B corroborates the presence of isolated Rh atoms as the signal intensity is approximately proportional to the square of the atomic number.^[16]

The X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) profiles were recorded to determine the electronic structure and coordination of the Rh atoms in Rh₁/VO₂. The XANES profile of Rh₁/VO₂ is similar to that of Rh₂O₃ (Figure 1D), revealing that the Rh species in Rh₁/VO₂ were present in an oxidized state. As shown by the EXAFS spectrum in R space (Figure 1E), Rh₁/VO₂ exhibited a prominent peak at approximately 2.0 Å from the Rh–O shell with a coordination number of 6.4 (Table S1). No other typical peaks for Rh–Rh

contributions at longer distances (>2.0 Å) were observed, revealing the dispersion of isolated Rh atoms throughout the whole Rh₁/VO₂ structure, which is consistent with the HAADF-STEM data. To further characterize the electronic properties of Rh₁/VO₂, we conducted X-ray photoelectron spectroscopy (XPS) measurements. In general, the binding energy of Rh 3d_{5/2} for Rh⁺ ranges from 307.5 to 308.0 eV. In this case, the binding energy of Rh 3d_{5/2} of Rh₁/VO₂ was shifted to 309.9 eV (Figure 1F) owing to the strong metal–support interaction between single Rh atoms and the VO₂ nanorods.^[14d,17] Moreover, the V species in Rh₁/VO₂ were determined to be in the V⁴⁺ state (Figure S3). Cl signals were not detected in the XPS measurements (Figure S4), suggesting that the Rh single atoms are present in a bare state.

The hydrolysis of NH₃BH₃ was performed to study how the metal–support interactions in Rh₁/VO₂ change upon the metal–insulator transition. The volume of the evolved gas was measured with a gas burette (Figure 2). Without a catalyst or with VO₂ nanorods as the catalyst, no gas was detected. The use of Rh₁/VO₂ led to the generation of a large amount of gas according to Equation (1):



The volume of H₂ was continuously measured to monitor the kinetics of the reaction. We investigated the catalytic performance of Rh₁/VO₂ at temperatures from 323.2 to 358.2 K with 2.5 K increments. As shown in Figure 2, about 120 mL of H₂ were generated within 10 min over Rh₁/VO₂ at all of these temperatures. The volume of generated H₂ was consistent with the theoretical amount of H₂ according to Equation (1), indicating the complete consumption of NH₃BH₃ in this process. As expected, the rate of H₂ generation increased with an increase in temperature. To quantitatively evaluate the catalytic activity, the turnover

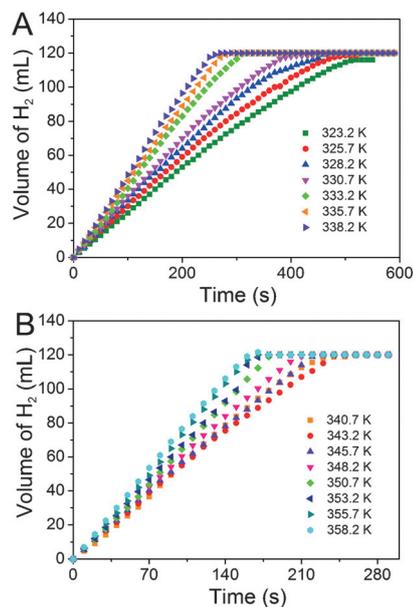


Figure 2. A, B) Time course of H₂ evolution from NH₃BH₃ using Rh₁/VO₂ single-atom catalysts at temperatures ranging from 323.2 to 338.2 K and from 340.7 to 358.2 K, respectively.

frequencies (TOFs) were calculated at different temperatures to construct an Arrhenius plot, showing the logarithmic TOF as a function of $1/T$ (Figure 3A). The TOF numbers were determined based on the slope of the reaction profile in the initial stage of the reaction (conversion < 20%). The TOFs of Rh_1/VO_2 were 1.2 and 0.8 s^{-1} at 353.2 and 333.2 K, respectively, which are comparable to those of state-of-the-art

variation in the apparent activation energy over Rh_1/VO_2 is related to the substrate.

To investigate the effect of the Rh mass loading on the catalytic performance, Rh_1/VO_2 single-atom catalysts with Rh mass loadings of 0.2% and 0.8% were also synthesized. We conducted the NH_3BH_3 hydrolysis over 100 mg of the Rh_1/VO_2 catalysts with different Rh loadings at 353.2 and 333.2 K. As the Rh loading was increased, the reaction rate increased, but the TOF number remained almost unchanged (Figures S7 and S8). This result demonstrates that single Rh atoms served as the active sites in NH_3BH_3 hydrolysis.

To investigate the stability of Rh_1/VO_2 , we carried out a series of characterizations of the catalyst after NH_3BH_3 hydrolysis at 333.2 and 353.2 K. The HAADF-STEM images of Rh_1/VO_2 after the reactions showed that the Rh atoms were still atomically dispersed on the surface of the VO_2 nanorods (Figure S9A,B). In addition, the X-ray diffraction (XRD) patterns of Rh_1/VO_2 after the reactions could still be assigned to the monoclinic phase of VO_2 (Figure S9C). As shown in the XPS spectra, the binding energies of Rh and V in the used Rh_1/VO_2 system were identical to those in the as-prepared one, indicating the oxidized state of the single Rh atoms and the V^{4+} state for the V atoms (Figure S9D,E). Furthermore, we repeatedly reused the Rh_1/VO_2 catalyst to determine its catalytic stability. After five rounds of reaction at 333.2 and 353.2 K, more than 95% of the original reactivity was preserved (Figures S10 and S11). Collectively, Rh_1/VO_2 displays high structural and catalytic stability.

According to previous studies on the hydrolysis of NH_3BH_3 ,^[3,4,20] we propose two possible reaction pathways for this reaction (paths A and B; see the Experimental Section for a detailed discussion). In short, path A corresponds to the activation of a proton while path B describes the activation of both water and NH_3BH_3 molecules. To gain further insight into the reaction mechanism and determine the rate-limiting step, we conducted a set of experiments that involved changing the concentrations of NH_3BH_3 and H^+ . When the reaction was carried out at different concentrations of NH_3BH_3 over Rh_1/VO_2 at 333.2 K and 353.2 K, the curves of the H_2 evolution with time overlapped at the initial stage of the reaction even though the overall amount of generated H_2 differs (Figure S12A,B). As such, the reaction rate and the corresponding TOF numbers remained stable with varied concentrations of NH_3BH_3 at a certain temperature (333.2 K or 353.2 K; Figure S12C), which rules out path B. To investigate the influence of the H^+ concentration, the pH value was varied by using phosphate buffer instead of the aqueous solution (Table S3). In the absence of catalyst, the generation of H_2 was below 1.5 mL at pH 6 to 8 after 20 min (Figure S13), indicating that the influence of H^+ or OH^- ions on the reaction rate is negligible under these reaction conditions. When Rh_1/VO_2 was added, the reaction rate clearly changed upon varying the pH value (Figure S12D,E). As shown in Figure S12F, the TOF number decreased from 1.1 to 0.6 s^{-1} and from 1.6 to 1.0 s^{-1} when the pH value was increased from 6.0 to 8.0 at 333.2 and 353.2 K, respectively, indicating a positive correlation between the H^+ concentration and the reaction rate. Consequently, the above results show that the activation of a proton is the rate-limiting step and that path A

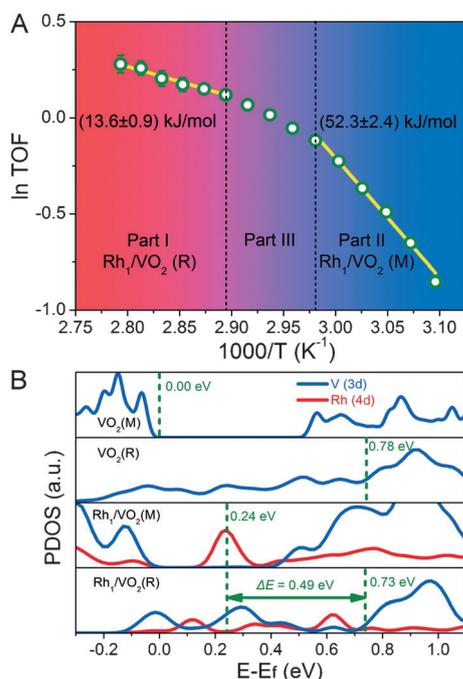


Figure 3. A) Arrhenius plot for NH_3BH_3 hydrolysis over Rh_1/VO_2 . B) Calculated PDOS of $\text{VO}_2(\text{M})$, $\text{VO}_2(\text{R})$, $\text{Rh}_1/\text{VO}_2(\text{M})$, and $\text{Rh}_1/\text{VO}_2(\text{R})$. E_f represents the Fermi level of $\text{VO}_2(\text{M})$.

catalysts (Table S2).^[10–12,18,19] Unlike the Arrhenius plots for hydrogen formation reactions over conventional catalysts, the current data points cannot be linearly fitted when the whole temperature region is considered. Interestingly, the data in part I (345.7–358.2 K) and part II (323.2–335.7 K) fit the linear plot well. Correspondingly, the activation energies for part I (E_{aI}) and part II (E_{aII}) were calculated as 13.6 ± 0.9 and $52.3 \pm 2.4 \text{ kJ mol}^{-1}$, respectively. The region in between was regarded as the transition region, part III (335.7–345.7 K); as this temperature range is in good agreement with the phase-transition temperature of the support (337.2–344.2 K; Figure S2), we believe that the change in activation energy might be caused by the phase transition of VO_2 . To support this hypothesis, Rh_1/C with individual Rh atoms dispersed on active carbon was synthesized as a reference compound; the dispersion of isolated Rh atoms was again confirmed by a HAADF-STEM image and EXAFS spectra (Figure S5 and Table S1). Rh_1/C was applied in NH_3BH_3 hydrolysis at temperatures from 323.2 to 358.2 K with 5.0 K increments (Figure S6A). According to the obvious linear Arrhenius behavior (Figure S6B), the apparent activation energy of Rh_1/C was $42.8 \pm 1.4 \text{ kJ mol}^{-1}$. The difference in the catalytic behavior of Rh_1/VO_2 and Rh_1/C demonstrates that the

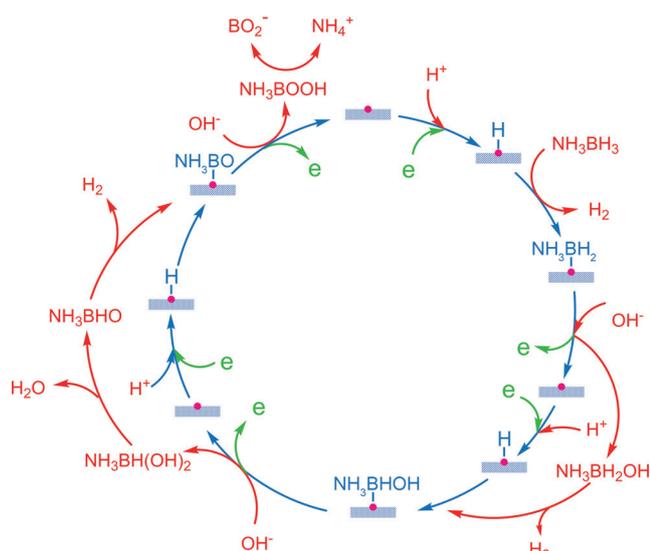


Figure 4. Proposed mechanism for NH_3BH_3 hydrolysis over Rh_1/VO_2 .

is operating. The whole reaction process (path A) is depicted in Figure 4.

Based on the aforementioned discussion, a possible mechanism was proposed to understand the different apparent activation energies for the two phases of VO_2 . The activation of a proton can be written as Equation (2):



In this case, $\mu(\text{H}^+)$, $\mu(e)$, and $\mu(\text{H}^*)$ would affect the apparent activation energy, where μ and $*$ represent the chemical potential and a surface site, respectively. An insulator–metal phase transition of the substrate will induce changes in both $\mu(e)$ and $\mu(\text{H}^*)$ whereas $\mu(\text{H}^+)$ is expected to remain almost unchanged. As a result, $\mu(e)$, which corresponds to the highest occupied state of Rh in Rh_1/VO_2 , plays a pivotal role in determining the difference between the apparent activation energies of the two phases of VO_2 . To investigate the metal–support interactions, we performed first-principle calculations for pure VO_2 and Rh_1/VO_2 . With the alignment of O 2s states, the projected densities of states (PDOS) of $\text{VO}_2(\text{M})$, $\text{VO}_2(\text{R})$, $\text{Rh}_1/\text{VO}_2(\text{M})$, and $\text{Rh}_1/\text{VO}_2(\text{R})$ are shown in Figure 3B. The Fermi level of $\text{VO}_2(\text{R})$ is located 0.78 eV above that of $\text{VO}_2(\text{M})$. When $\text{VO}_2(\text{M})$ is doped with Rh, new occupied states will arise in the band gap of $\text{VO}_2(\text{M})$ owing to the greater number of d electrons in Rh compared with V. For comparison, the highest occupied state of single Rh atoms supported on $\text{VO}_2(\text{R})$ is considered to be at an energy comparable to the Fermi level of $\text{VO}_2(\text{R})$ because of the low concentration of doped Rh as well as Rh and $\text{VO}_2(\text{R})$ both being in the metal phase. As expected, the highest occupied state of single Rh atoms supported on $\text{VO}_2(\text{M})$ was at 0.24 eV relative to the Fermi level of $\text{VO}_2(\text{M})$. Meanwhile, the highest occupied state of single Rh atoms supported on $\text{VO}_2(\text{R})$ was at 0.73 eV, similar to the Fermi level of $\text{VO}_2(\text{R})$. As H^+ ions need to take electrons from the catalyst to generate H^* according to Equation (2), a high $\mu(e)$ value is favorable to accelerate the reaction. Therefore, the difference between the

$\mu(e)$ values of $\text{Rh}_1/\text{VO}_2(\text{M})$ and $\text{Rh}_1/\text{VO}_2(\text{R})$ directly correlates with the difference in the apparent activation energies of these two systems. Taking the value of the in-gap state center as a reference, $\Delta\mu(e)$ was calculated to be 0.49 ± 0.10 eV (47.3 ± 9.6 kJ mol $^{-1}$) for $\text{Rh}_1/\text{VO}_2(\text{M})$ and $\text{Rh}_1/\text{VO}_2(\text{R})$, which is close to the difference of 38.7 ± 2.6 kJ mol $^{-1}$ in the apparent activation energy (ΔE_a). From the perspective of electronic modulation, a hypothesis was previously reported for to a support altered the charge state of the metal and therefore the catalytic performance.^[21,22] In this work, we directly associated the catalytic performance of Rh_1/VO_2 with the highest occupied state of the single Rh atoms, which was determined by the band structure of the substrate.

Based on the above assumption that the catalytic properties can be manipulated by tuning the highest occupied state of the single Rh atoms, we surmised that several other metals should be active catalysts in NH_3BH_3 hydrolysis upon changing their highest occupied states. To support this point, we conducted a set of extensive experiments following a similar procedure except for replacing Rh with other metals, including Fe, Co, Ni, Cu, Ag, and Au, to form metal-doped nanocrystals, denoted as M_1/VO_2 . All of the supported metals were shown to be present in oxidized states based on the XPS spectra (Figure S14). As expected, both noble and non-noble metal catalyst systems exhibited remarkable activity towards NH_3BH_3 hydrolysis (Table S2). According to the Arrhenius plots, there are obvious changes in the apparent activation energies of M_1/VO_2 that are induced by the phase transformation (Figure 5A), similar to the catalytic performance of Rh_1/VO_2 . Figure 5B shows a systematic comparison of the differences in the apparent activation energies for part I and part II for different catalyst systems. In

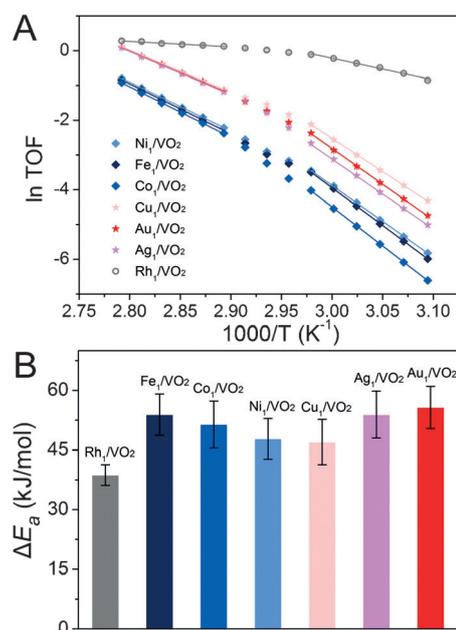


Figure 5. A) Arrhenius plots for NH_3BH_3 hydrolysis over Rh_1/VO_2 , Fe_1/VO_2 , Co_1/VO_2 , Ni_1/VO_2 , Cu_1/VO_2 , Ag_1/VO_2 , and Au_1/VO_2 and B) the corresponding ΔE_a values. ΔE_a represents the difference in the apparent activation energies of $\text{M}_1/\text{VO}_2(\text{M})$ and $\text{M}_1/\text{VO}_2(\text{R})$.

spite of the large discrepancies in catalytic activity and E_a between different catalysts, the ΔE_a values for all of these systems were roughly identical, ranging from 38.7 to 55.7 kJ mol⁻¹ (Table S4). This result is reasonable based on our aforementioned mechanism, which associates the activation energy with the highest occupied state. The energy differences of the highest occupied states of single metal atoms supported on VO₂(M) and VO₂(R) range from 0.23 eV to 0.78 eV (22.2–75.2 kJ mol⁻¹); these values were estimated based on the gaps from the Fermi level of VO₂(R) to the valence-band maximum and the conduction-band minimum of VO₂(M), respectively. It is worth noting that the TOF numbers of VO₂ nanorods doped with non-noble metals are comparable to that of Rh₁/VO₂ at high temperatures (>353.2 K), revealing significant activity for M₁/VO₂. Among these single-atom catalysts, Rh₁/VO₂ showed the lowest activation energy and the highest activity. The NH₃BH₃ hydrolysis could be approximately regarded as the zero-voltage equivalent of the hydrogen evolution reaction. Accordingly, the volcano curve for the activity and hydrogen adsorption energies could be adopted.^[23] As indicated by the volcano curve, Rh is endowed with the optimal hydrogen adsorption energy and thus has the highest activity among the metals studied in this work.

In conclusion, a quantitative relationship between the catalytic performance and metal–support interactions was established in terms of the highest occupied state by using Rh₁/VO₂ single-atom catalysts in NH₃BH₃ hydrolysis. Based on the proposed influence of the metal–support interaction, remarkably high catalytic activities towards the hydrolysis of NH₃BH₃ were achieved with other metals, even non-noble metals, by changing the highest occupied states of the catalysts. This work provides a guideline for the rational design of efficient and inexpensive catalysts towards hydrogen generation by controlling the band structures of the catalysts.

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Conflict of interest

The authors declare no conflict of interest.

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