Reduction of N₂ by supported tungsten clusters gives a model of the process by nitrogenase

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Metalloenzymes catalyze difficult chemical reactions under mild conditions. Mimicking their functions is a challenging task and it has been investigated using homogeneous systems containing metal complexes. The nitrogenase that converts N₂ to NH₃ under mild conditions is one of such enzymes. Efforts to realize the biological function have continued for more than four decades, which has resulted in several reports of reduction of N₂, ligated to metal complexes in solutions, to NH₃ by protonation under mild conditions. Here, we show that seemingly distinct supported small tungsten clusters in a dry environment reduce N₂ under mild conditions like the nitrogenase. N₂ is reduced to NH₃ via N₂H₄ by addition of neutral H atoms, which agrees with the mechanism recently proposed for the N₂ reduction on the active site of nitrogenase. The process on the supported clusters gives a model of the biological N₂ reduction.

In nature, one finds various metalloenzymes that catalyze difficult and essential chemical reactions under mild conditions¹, which, on the other hand, require high temperature and gas pressure in industry. The enzymes often harness small clusters involving transition metal atoms at their active centers, which are the key materials that enable the difficult chemical reactions. Since metalloenzymes are homogeneous systems working in environments with water, structures and functions of the enzymes have been studied by using metal complexes in solutions.

The well-known and intensively studied example of such enzymes is the nitrogenase. It reduces almost inert N₂ to NH₃ at 300 K and 0.8 atm², which is in stark contrast to the industrial Haber-Bosch process that requires harsh conditions like 800 K and 300 atm³. Among the nitrogenases, the Mo-dependent nitrogenase⁴ is best studied. It carries a complex metal cluster named FeMo cofactor (FeMo-co) with a multicenter core XFe₇MoS₉, where X has been identified as a carbon atom recently⁵,⁶. The core works as the site for N₂ activation and reduction⁴.

The fascinating biological N₂ reduction on nitrogenases has attracted much attention of chemists for more than four decades, which has led to continuing efforts to mimic the function of the enzyme to reduce N₂ to NH₃ under mild conditions. Up to now, N₂ formation under mild conditions has been reported for metal complexes in solutions³, including well-defined transition-metal complexes with a N₂ ligand⁸–¹⁰ and also a nitride¹¹,¹². These are homogeneous systems basically containing reductants and proton sources in solutions, in which N₂ is reduced by direct transfers of electrons and protons to N₂. The N₂ reduction mechanism is consistent in appearance with the generally accepted Lowe-Thorneley scheme for nitrogenase N₂ reduction which tells us that the biological N₂ reduction proceeds by coupled electron and proton transfers to FeMo-co¹³–¹⁵.

It has recently been suggested, however, the N₂ activated on FeMo-co is reduced not by the direct electronation/protonation but by addition of neutral H atoms that result from reduction of protons¹⁶–¹⁸: the protons, transferred to FeMo-co presumably through a water-filled channel connecting the surface of proteins surrounding FeMo-co and the cofactor¹⁹–²¹ are likely to be bound to its sulfur sites¹⁶–¹⁸,²²,²³ and reduced to the H atoms²⁶–²⁸. This mechanism is needed because the amino acid residue located near the active Fe site of FeMo-co (valine), which works as a “gate keeper” to control access of substrates to the active site²⁴–²⁶, is hydrophobic and anhydrous and thus it is unlikely that protons gain direct access to N₂²⁷,²⁸. This then suggests the N₂ reduction on FeMo-co proceeds in a “dry” environment isolated from H₂O while the whole nitrogenase system functions in an environment with water. This is supported by the X-ray crystallography analysis that the surroundings of the active site of FeMo-co are free from water²⁷,²⁸,²⁹,³⁰.
Accordingly, following the novel mechanism, the N₂ reduction by FeMo-co comes down to addition of neutral H atoms to N₂ on the metal cluster in a dry environment. This suggests we may be able to mimic the function of nitrogenase if metal clusters are available that enable hydrogenation of N₂ with the H atoms, without recourse to the traditional method using direct protonation in solutions. However, there have been no studies to explore such a possibility.

To examine the possibility, we investigated the N₂ reduction on monodispersed small tungsten clusters (W₅, n=2–6) fixed on graphite surfaces (see the Methods below and Supplementary Information 1). We have chosen the tungsten cluster because it activates N₂ in molecular form as FeMo-co does and H₂O dissociatively adsorbs on the cluster into H + OH. Consequently, if mixture gas of N₂ and H₂O is fed to the cluster, we have activated N₂ and H atoms coexisting on the cluster. Thus the supported tungsten cluster is an ideal system to check whether such a system can model the biological function of reducing N₂ to NH₃. In the following, we show the system indeed reduces N₂ to NH₃ under mild conditions as nitrogenases.

### Results

Figure 1a shows a typical N1s spectrum by X-ray photoelectron spectroscopy (XPS) for N₂ adsorbed by tungsten pentamers (W₅), fixed on a highly-oriented pyrolytic graphite (HOPG) surface at 296 K. It has a peak located at an N1s binding energy (BE) of ~399.2 eV, which is absent for bare W₅ or a N₂-fed bare HOPG surface. The single peak shows N₂ is adsorbed on the cluster with a W-N-N-W bridge or a η²- adsorption geometry. Our previous work has shown the total energy of the bridge adsorption geometry is lower than that of the η² geometry and hence suggests the adsorption with the bridge geometry is more likely. Another notable observation is that no peak is seen around 397.6 eV which is a fingerprint of N atoms resulting from N₂ dissociation. We have recently shown N₂ is highly activated in molecular form on the cluster27,30,31. The XPS observation in Fig. 1a therefore shows N₂ is bound in an activated molecular form on W₅ at room temperature.

The full width at half maximum of the peak is, however, more than 3 eV, which is larger than that of ~2.2 eV observed for a single nitrogen species such as N atoms on a bulk W surface. Moreover, the peak seems to have a hump at ~401 eV (the higher BE side of the peak). These observations suggest the peak is not due to N₂ alone but consists of those of a couple of nitrogen species. Since N₂ on the cluster is activated, the other species may be reaction products of N₂ with some adsorbates on the cluster. In the cluster deposition, it was found a few H₂O molecules from the ambient are adsorbed on the clusters and hence they could be the reaction counterpart. To check this, the N1s spectrum was measured for various amounts of adsorbed H₂O. The results given in Figs. 1b and 1c show the shape of the spectrum is very sensitive to the water adsorption: with an increase in the amount of H₂O, the intensity above ~400 eV becomes large, resulting in a broader spectrum (Fig. 1b) and when more than ~5 water molecules are adsorbed on the cluster, a single peak becomes distinct at ~400.8 eV (Fig. 1c). The number of N₂ molecules adsorbed per W₅ was ~0.1. Considering the experimental conditions (pressure of the N₂ gas, the gas exposure time, the number of clusters on the HOPG surface: see Methods below), the sticking probability of N₂ to the water-adsorbed cluster is ~10⁻¹ which is comparable to the initial sticking probability of the dissociative adsorption of N₂ to Fe(111) surface at 300 K27, which proceeds via a molecular adsorption state with a bridge geometry. The intensity of the peak was substantial only when both N₂ and H₂O are present on the cluster. All these observations suggest the nitrogen species other than N₂ originate from reactions between N₂ and H₂O.

As we have reported, the activated N₂ reacts with O from H₂O to form nitrous oxide (N₂O) at 140 K on the cluster22. In the present experiment at room temperature, however, double peaks at 402.6 eV and 406.6 eV, the fingerprint of N₂O, are absent in the N1s XPS spectrum (see Fig. 1c). This is presumably because N₂O, though it may form on the cluster at room temperature, would desorb from the cluster as soon as it forms, since the molecule desorbs from the cluster at ~ 145 K27. Then we have to consider the reaction of N₂ with H which results from dissociative adsorption of H₂O on W₅ (Supplementary Information 2). The calculation given in the supplementary information shows the electron population of the hydrogen for the most stable (H+OH) adsorption configuration on W₅ is 1.1 ~ 1.2 depending on the model for the population analysis. This indicates the hydrogen is a neutral H atom not a proton as expected. Therefore, the reaction of N₂ with H from H₂O is a process of addition of the neutral H atoms to N₂, which we call “hydrogenation with neutral H atoms” hereafter. Accordingly, the XPS spectral changes in Figs. 1a to 1c may show progress of the hydrogenation of N₂ at room temperature with an increase in the number of coadsorbed H atoms, leading to NH₃ formation.

In an experiment to purposely feed NH₃ to W₅, the molecule was found to give an XPS spectrum with a single peak at 404.4 eV. Therefore, the nitrogen species that give the XPS spectrum in Fig. 1c may include NH₃. To examine this, we analyzed gases desorbing upon heating from W₅, to which N₂ and H₂O were simultaneously fed at 296 K (denoted as (N₂ + H₂O)/W₅ hereafter), by mass spectrometry. For the analysis, we first performed an experiment using ¹⁵N₂, hoping that we could detect ¹⁵NH₃. The experiment turned out to give a hint of ammonia formation but not in an unambiguous way. This is because the mass to charge ratio (m/e) of ¹⁵NH₃ is the same as that of H₂¹⁴O (m/e=18) and the major cracked species from these species. ¹⁵NH₂ and ¹⁴OH, also have the same m/e of 17. Thus the peaks due to desorption of ¹⁵NH₃ from the cluster totally overlap with those of H₂¹⁴O, which is a species always found in an ultrahigh vacuum ambient and also desorbs upon heating from W₅ concomitantly with the ammonia as shown below, in the mass spectrum. We therefore have chosen to use the combination of ¹⁴N₂ and H₂¹⁸O to have a conclusive result. With this combination one can keep the intensities of H₂¹⁴O and ¹⁸OH almost to the background level as seen in Fig.2a: comparison of the intensity for m/e=17 with that of the H₂¹⁸O⁺ peak should
make the desorption of $^{14}\text{NH}_3$ easily noticeable. Before heating the sample of ($^{15}\text{N}_2 + \text{H}_2^{18}\text{O}$)/$\text{W}_5$, XPS measurement was carried out to confirm that the spectrum was dominated by the peak at 400.8 eV. Figure 2a shows a mass spectrum measured before the sample is heated. It is a background mass spectrum owing to H$_2$O in the ultra-high vacuum ambient of the mass spectrometer chamber. The peak at m/e=18 is due to H$_2^{18}$O and the shoulder at m/e=17 with $\sim 1/3$ intensity of H$_2^{16}$O$^+$ is due to $^{16}$OH$^+$ that results from cracking of H$_2^{16}$O. When the sample is heated to $\sim 320$ K, we observed dramatic changes in the mass spectrum (Fig. 2b): three peaks with m/e of 16, 17 and 20, absent in the background spectrum, showed up. Since the intensity of the m/e=17 peak is comparable to that of the H$_2^{16}$O$^+$ peak (m/e=18), it is apparently not solely due to $^{16}$OH$^+$ but includes a substantial intensity of another species and it is $^{14}$NH$_3$:$^{14}$NH$_2^+$ is the only possible chemical species with m/e = 17 other than $^{16}$OH$^+$ for possible combinations of $^{14}$N, $^{16}$O, and H. We also notice substantial intensity increase for the peak with m/e=16, which we assign to $^{14}$NH$_2^+$ that results from cracking of $^{14}$NH$_3$. The assignment is consistent with the previous report that NH$_3^+$ and NH$_2^+$ are the major species (the intensity of NH$_3^+$ is $\sim 0.5$ of that of NH$_3^+$) when NH$_3$ is analyzed by a quadrupole mass spectrometer$^{35}$. The peak at m/e=20 is assigned to H$_2^{16}$O$^+$ that was fed to the cluster. After the gas desorption, the mass spectrum became similar to that prior to the heating (Fig. 2c). The desorption of NH$_3$ was observed in the same manner without the prior XPS measurement, indicating the formation of NH$_3$ is not induced by X-ray radiation. Thus the mass spectra give conclusive evidence that NH$_3$ forms from N$_2$ and H atoms originated from dissociative adsorption of H$_2$O on supported W$_5$.

As mentioned above, N$_2$ is activated in molecular form on W$_5$. Hence the N$_2$ hydrogenation may proceed by addition of H atoms to N$_2$, yielding intermediate hydrazine-like species N$_2$H$_x$ (x = 1~4). To examine the possibility of such a process and the existence of hydrogenated species, we measured the N1s XPS spectrum of hydrazine monohydrate (N$_2$H$_4$·H$_2$O) purposely fed to W$_5$ (N$_2$H$_4$/$\text{W}_5$, Fig. 3a) and compared it with the spectrum for (N$_2$ + H$_2$O)/$\text{W}_5$ at 296 K (Fig. 3b). We also compared XPS spectra for the two systems after they were heated to 380 K (Fig. 3c for N$_2$H$_4$/$\text{W}_5$ and Fig. 3d for (N$_2$ + H$_2$O)/$\text{W}_5$). As is readily noticed, the XPS spectra for (N$_2$ + H$_2$O)/W$_5$ bear striking resemblance to those for N$_2$H$_4$/$\text{W}_5$. Although the signal to noise ratio for the former is much smaller than that for the latter owing to the small number of N$_2$ adsorbed on W$_5$, it is evident for the Goth systems that (1) the main peak is located at $\sim 400.8$eV and a shoulder at $\sim 398.4$ eV before the heat treatment; (2) after being heated to 380 K, the intensity above 400 eV decreases whereas the intensity below 400 eV increases; (3) the total nitrogen intensity decreases by the heat treatment, indicating a fraction of the species responsible for the main peak desorbed. This observation that the XPS spectra of the two systems have common features in many respects strongly indicates similar hydrogenated nitrogen species exist in N$_2$H$/\text{W}_5$ and (N$_2$+H$_2$O)/$\text{W}_5$ and this means N$_2$ in (N$_2$+H$_2$O)/$\text{W}_5$ is hydrogenated, i.e., reduced at room temperature. As noted above NH$_3$ gives the XPS spectrum with the peak energy of 400.4 eV. Thus the observation (1) indicates the presence of a species with the binding energy larger than that of NH$_3$ for the both systems.
To identify the hidden hydrogenated species, we carried out factor analysis first for the spectra of N₂H₄/W₅ (Fig. 3a and Fig. 3c) because they have large signal to noise ratios tolerable for the analysis. We then used the result of the analysis for examining the spectra for (N₂ + H₂O)/W₅. The result of the factor analysis is given by solid lines in the inset of Fig. 3a. As seen in the inset, the experiment (red dots) is well reproduced by the analysis (the black solid line) if four species with the BEs of 398.1 eV, 399.2 eV, 400.4 eV and 401.2 eV are assumed. The factor analysis including the four species also well explains the spectrum after the heat treatment (the inset of Fig. 3c). Previous studies dealing with N₂H₄ adsorption on metal surfaces and supported metal clusters have shown the molecule is adsorbed intact at low temperatures but easily dissociates at elevated temperatures to yield N₂H₄(x=1~3), NH₃, N₂ and H₂. The literature suggests the species with the BE of 398.1 eV is NH₃ and there is no sign of nitrides (the BE = 397.6 eV). The species with the BE of 399.2 eV is probably N₂ as suggested from Fig. 3a. The peak at 400.4 eV is assigned to NH₃ because the BE matches the N1s peak energy of the NH₃ XPS spectrum. The peak intensities of NH₃ and the species at 401.2eV decrease by heating, which concomitantly occurs with the intensity increase of NH3 (compare the insets of Fig. 3a and Fig. 3c) and the decrease of the total nitrogen intensity. Similar intensity changes of the species were observed even at room temperature as will be described below. These observations can be understood as a result of decomposition of the species at 401.2eV to NH and desorbing NH₃ and hence suggests it is N₂H₄(x=1~4). It is notable that the peaks due to NH and NH₃ already have substantial intensities before the heating (Fig. 3a inset). This can be explained by immediate decomposition upon adsorption of the N₂H₄ molecule that arrives first to W₅, which is a reaction with large exothermicity. Since the decomposition pattern of N₂H₄ upon heating mentioned above is similar to that of N₂H₄, it is strongly suggested the N₂H₄ is due mainly to N₂H₄, N₂H₃ observed in the spectrum in Fig. 3a is probably the molecule that arrived later at the cluster and was stabilized by preadsorbed N₂H₄. The peak assignments are supported by thermal desorption spectroscopy (TDS) for N₂H₄/W₅ which shows desorptions of NH₃ and N₂H₄ upon heating the system (Supplementary Information 3): this is consistent with the finding by the XPS spectra that the intensities of the N₂H₄ and NH₃ peaks greatly decrease upon heating.

Then we examined the spectrum for (N₂ + H₂O)/W₅ at 296 K (Fig. 3b) and that after heating to 380 K (Fig. 3d). As mentioned above, the XPS spectra for (N₂ + H₂O)/W₅ bear striking resemblance to those for N₂H₄/W₅. In accordance with this, the factor analysis with the above four species, i.e., NH, N₂H, NH₃ and N₂H₄ can explain the observed spectrum at 296 K rather well (Fig. 3b inset). As seen in the inset, the intensity of the N₂ peak is much smaller than those of the NH, NH₃ and N₂H₄ peaks as in N₂H₄/W₅. Since NH and NH₃ result from decomposition of N₂H₄ on W₅ as mentioned above, the finding suggests that N₂, once activated by W₅, is readily hydrogenated to N₂H₄, which then decomposes to NH₃ and NH: it is seen from Fig. 3b inset that most of the N₂ molecule coadsorbed with H₂O on W₅ are hydrogenated to N₂H₄ and nearly half of N₂H₄ are converted to NH and NH₃ at room temperature. The facile formation of N₂H₄ from N₂ is consistent with the theoretical calculation that it is an exothermic process after the first addition of H₂. The observed changes in the spectral shape and intensity upon heating (the observations (2) and (3) above, compare Fig. 3b with Fig. 3d) can be explained by the decomposition of N₂H₄ to NH and NH₃ and the desorption of the latter. This is consistent with the observation of NH₃ by TDS shown in Fig. 2b. However, the desorption of N₂H₄ observed for N₂H₄/W₅ by TDS, was not found for (N₂ + H₂O)/W₅. A possible explanation for this is that N₂H₄ on the clusters are all subjected to reaction upon heating with the surface H atoms that are more abundant for (N₂ + H₂O)/W₅ than in N₂H₄/W₅. It is notable that N₂H₄ cracks to yield NH₃ by electron bombardment in a mass spectrometer with the intensity of ≈ 0.5 of that of N₂H₄. We checked the cracking of N₂H₄ by monitoring a mass spectrum while admitting N₂H₄/H₂O into the vacuum chamber and found that the most prominent species was N₂H₄. The finding that N₂H₄ desorption was not observed for (N₂ + H₂O)/W₅ therefore suggests that the observation of NH₃ shown in Fig. 2b is not due to cracking of desorbed N₂H₄ and thus the NH₃ molecule had formed on the cluster before it desorbed.

In the experiments described above, we have focused on W₅ but it is not the only tungsten cluster to adsorb and activate N₂ in a bridge geometry. The 1st principles calculations for isolated tungsten clusters show W₄ and W₆ are also capable of similar N₂ activation. In accordance with this, these clusters gave the N₁s peak at 400.8 eV in XPS spectra, indicating the formation of the hydrogenated nitrogen species. Surprisingly, the formation of the hydrogenated species was also found for W₇ and W₉, which do not support such stable bridge adsorptions of N₂. It was found by calculation, however, that water adsorption stabilizes N₂ bridge adsorption on the clusters (Supplementary Information 4 online), which may have enabled the clusters to mediate the formation of the hydrogenated nitrogen species.

Discussion

The results described above are summarized as follows: supported small tungsten clusters activate N₂ in molecular form and convert the molecule to NH₃ via N₂H₄ at room temperature. The N₂ reduction is done by hydrogenation with neutral H atoms on the cluster, which is distinct from the mechanism of the traditional N₂ reduction using electronation and protonation in solutions. The hydrogenation mechanism is similar to those proposed for FeMo-co7,18,23 of the nitrogenase and thus gives support to them.

It is interesting to note that in biochemical experiments dealing with nitrogenases N₂H₄ is suggested as a N₂ reduction intermediate. Thus, the present cluster system and nitrogenase convert N₂ to NH₃ via the common intermediate. The formation of N₂H₄ means both N atoms of N₂ are hydrogenated before the cleavage of the N-N bond. This is consistent with the observation in the present experiment by the XPS spectra in Fig. 3b and 3d that show no sign of N atom formation and is called the “alternative mechanism” for the N₂ reduction by nitrogenase that is theoretically19,42 and experimentally33 thought likely to be the case.

Since the N₂ reduction by W₅ proceeds in a manner similar to those proposed for the FeMo-co of nitrogenase, findings on the reduction process on the cluster may shed light on the long-standing mysteries in the mechanism of the biological N₂ reduction how the robust N-N triple bond of N₂ cleaves46 and why the N₂ reduction to NH₃ easily occurs at room temperature. As discussed above, N₂H₄ is the N₂ reduction intermediate for the present cluster system and also suggested as an intermediate for the biological systems. N₂H₄ is an intrinsically unstable molecule with the free energy of formation of 38.07 Kcal/mol and the N-N bond easily cleaves on metal surfaces as mentioned above. The instability of N₂H₄ at room temperature on W₅ is evidenced by the time evolution of the XPS spectra for N₂H₄/W₅ at 296 K shown in Figs. 4a to 4c. As seen in the figures, the shoulder at ~398.0 eV gradually grows bigger compared to the peak at ~400.8 eV. This is due to gradual intensity decreases of N₂H₄ and NH₃ with concomitant intensity increase of NH as seen in the insets of Fig. 4, which is summarized in Fig. 4d. The intensity decrease of N₂H₄ with time indicates the N-N bond of the species is unstable on the cluster at room temperature and cleaves to yield NH and NH₃ as mentioned above. The resultant NH₃ gradually desorbs from the cluster, which explains the decreases in the total N₁s and NH₃ intensities shown in Fig. 4d. It is likely N₂H₄ is also unstable and reactive on the CFe₇MoS₉ cluster of FeMo-co at ambient temperature as on W₅ and therefore, once it forms, its N-N bond easily cleaves, leading to the formation and the subsequent
desorption of NH$_3$. The formation of the intermediate species, N$_2$H$_4$, is a consequence of the N$_2$ activation in molecular form and thus this mode of N$_2$ activation by FeMo-co is the key to the biological NH$_3$ formation from N$_2$ under mild conditions.

We have shown supported small tungsten clusters reduce N$_2$ to NH$_3$ under mild conditions as nitrogenases do. N$_2$ is reduced to NH$_3$ via N$_2$H$_4$ by hydrogenation with neutral H atoms in a dry environment. The N$_2$ hydrogenation mechanism is consistent with and thus gives support to the recently-proposed model that N$_2$ is reduced by hydrogenation on the active site of nitrogenase, FeMo-co, with H atoms resulting from reduction of protons. The overall mechanism of the N$_2$ reduction to NH$_3$ by the tungsten cluster is similar to those proposed for the N$_2$ reduction of nitrogenase and thus the process on the supported clusters gives a model of the biological N$_2$ reduction. The key material common to the enzyme in nature and in the present study is the small metal cluster that can activate N$_2$ in molecular form, which leads to the NH$_3$ formation at room temperature. In nature, small metal clusters in various metalloenzymes are known to work being isolated from water as FeMo-co and thus, if appropriate metal clusters are available, they may be used in dry environments to mimic the functions of the enzymes.

**Methods**

Generation, deposition and fixation of size-selected tungsten clusters on a highly-oriented pyrolytic graphite (HOPG) surface. Tungsten cluster ions (W$_n^+$, $n=2$–6), sputtered from W plates by high-energy (~23 kV) Xe$^+$ ion beams, were cooled by collision with helium gas and size-selected by a quadrupole mass-filter and then deposited on an HOPG surface at 296 K. The cluster beam has a mean kinetic energy of ~2.5 eV to the surface and is decelerated by applying a positive voltage with the same magnitude to the substrate. By doing this, kinetic energies of the cluster ions incident to the surface is reduced to less than ~0.3 eV/cluster, making them “soft land” on the surface. The number of the incident clusters was typically 2.3x10$^{13}$,32. Since W-W bond energy (e.g., ~5 eV for W$_2$) is much larger than the incident energy, it is ensured that the clusters are non-destructively deposited. Prior to the cluster deposition, the HOPG surface was bombarded by an Ar$^+$ ion beam with a collision energy of 50 eV. This creates defects on its outermost surface that work for anchoring the clusters separately.

**Figure 4 | Evolution of the N1s XPS spectra for (N$_2$+H$_2$)W$_n$ at 296 K with time.** The spectra were measured at (a) 7 min, (b) 40 min and (c) 80 min after feeding N$_2$H$_4$+H$_2$O to W$_2$. The notations for the insets are the same as those in Fig. 3. The XPS spectral changes depend on the time elapsed after feeding N$_2$H$_4$+H$_2$O to the cluster but not on the time spent for the XPS measurement, indicating they are spontaneous changes and not induced by the X-ray radiation. (d) N1s intensity changes of each species with time. The intensity of each species is the area for each peak deduced from the factor analysis of the XPS spectrum. The lines in the graph are the results of curve fitting of the data points.

Measurement and analysis of chemical reactions on the clusters. Size-selected W$_n^+$ ($n=2$–6), supported on an HOPG substrate at 296 K, were exposed to excessive amount of N$_2$ (99.9999 % purity) or a mixture of the N$_2$ plus degassed H$_2$O (distilled water or ultrapure water for ultratrace analysis) or water-$^{18}$O ($^{18}$O content 95–98 %) from a pulsed valve or an all-metal leak valve. The exposure to N$_2$ was performed with an ion gauge off to prevent adsorption of excited N$_2$ on the clusters. Typically the N$_2$ pressure was ~10$^{-5}$ Torr and the exposure time was 90 sec. N$_2$H$_4$+H$_2$O (98 % purity) was fed to the clusters also with an ion gauge off through a needle valve with a doser made of glass to prevent cracking of the molecule. XPS was done using MgX$_2$ (1253.6 eV) X-rays and a hemispherical electron energy analyzer. The factor analysis of XPS spectra was performed using the program XPSPEAK ver. 4.1 (http://www.kwoksys.com/). To obtain mass spectra of desorbing gases with a substantial signal to noise ratio, the gases were fed through the all-metal leak valve heated to ~400 K; this procedure gave XPS spectra identical to that in Fig. 1c but with enhanced intensity. The effect of heating the gas is possibly to increase the fraction of the N$_2$ molecules that overcome the barrier for the bridge adsorption state$^{42,43}$. In measuring mass spectra of thermally desorbing gases, the substrate was heated with a constant temperature rise of ~8 K/sec by electron bombardment using a tungsten filament located at the back of the substrate. The substrate temperature was monitored with an alumel-chromel thermocouple. Desorbed species were analyzed by a quadrupole mass spectrometer and the resulting mass spectra were monitored by an oscilloscope. A movie was taken by a digital camera to record the changes of the resulting mass spectra with the rise of the substrate temperature. The mass spectra in Fig. 2 are the snap shots from a movie recording mass spectrum changes by heating the sample from 300 K to 400 K. All the experiments were done in a stainless-steel vacuum chamber with a base pressure of low 10$^{-10}$ Torr.
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Acknowledgements

We are grateful to S.L. Anderson and Y. Norikane for their advice on handling hydrazine. We also thank M. Yokoi for his help in solving the operation problems of the quadrupole mass systems of the cluster machine.

Author contributions

J.M. designed and performed the experiments and analyzed the data. W.Y. constructed data acquisition systems for thermal desorption spectroscopy and also performed the DFT calculations. Both contributed to writing the paper.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/.

Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Murakami, J. & Yamaguchi, W. Reduction of N2 by supported tungsten clusters gives a model of the process by nitrogenase. Sci. Rep. 2, 407; DOI:10.1038/ srep00407 (2012).