

Confinement-Induced Catalytic Dissociation of Hydrogen Molecules in a Scanning Tunneling Microscope

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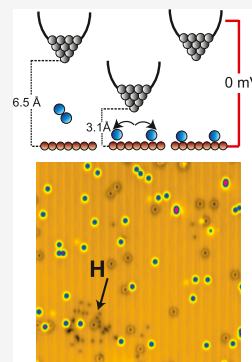


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ABSTRACT: The catalytic scission of single chemical bonds has been induced by the nanoscale confinement in a scanning tunneling microscope (STM) junction. Individual hydrogen molecules sandwiched between the STM tip and a copper substrate can be dissociated solely by the reciprocating movement of the tip. The reaction rate depends sensitively on the local molecular environment, as exemplified by the effects of a nearby carbon monoxide molecule or a gold adatom. Detailed mechanisms and the nature of the transition states are revealed by density functional theory (DFT) calculations. This work provides insights into chemical reactions at the atomic scale induced by localized confinement applied by the STM tip. Furthermore, a single diatomic molecule can act as a molecular catalyst to enhance the reaction rate on a surface.



INTRODUCTION

Mechanical motion and force may play an important role in chemical reactions. For example, in mechanochemical processes, the direct transfer of mechanical energies to reactants at room temperature can induce bond activations, which otherwise would require harsh reaction conditions. Besides, mechanical compression can confine a molecule in proximity to another reactant or catalyst, accounting for extraordinary catalytic effects in high-pressure chemistry.^{1,2} The potential applications for energy production and environmental protection are driving a growing interest in the mechanical activation of catalysts.^{3–5} Although significant progress has been made in both fundamental research and industrial application, the underlying mechanisms of many mechanical confinement-induced reactions are still somewhat elusive due to the technical difficulties involved with the control and visualization of reaction processes in most experimental measurements.⁶

The scanning tunneling microscope (STM), an apparatus originally designed for imaging surface structures with atomic-scale resolution but later adapted for spectroscopic and dynamic studies, offers an opportunity for understanding the roles of mechanical motion and force by controlling and observing chemical reactions in nanocavities formed by the STM tip and substrate.^{7,8} In general, the tip and substrate can apply a compressive force to squeeze molecules sandwiched in between.^{9–13} An unparalleled advantage of STM over traditional tools for studying the reaction induced by such a kind of compressive force is its spatial resolution at the single-molecular scale. It provides the means to separately probe the

effects of various factors on a mechanical confinement-induced reaction to establish clear physical insights into its mechanism.

Hydrogen dissociation is one of the simplest chemical reactions and is the precursor step for many hydrogenation reactions that are of great importance in chemical science, nanoscience, and life science.^{14–16} Here, we use hydrogen dissociation on a Cu(001) surface as a prototypical reaction to demonstrate the effects of mechanical motion of STM tip or hot tunneling electrons on the dissociation of the H–H bond. Since the occupation of the antibonding σ orbital of H_2 plays a key role in the bond breaking,¹⁷ we modify the local electron density of Cu(001) by adding carbon monoxide (CO) molecules and Au atoms onto the surface.^{18,19} Interestingly, both STM observation and density functional theory (DFT) simulations show that the presence of a CO molecule or a Au atom in the tip–substrate gap may alter the hydrogen dissociation rate. DFT calculations indicate that this alteration stems from the differences in the availability of electrons for the filling of the antibonding orbital of H_2 and the change of local symmetry. Our studies reveal that the compression of the STM tip continuously modifies the chemical environment of the trapped H_2 , which leads to charge redistribution, structural relaxation, and ultimately bond breaking. These results provide

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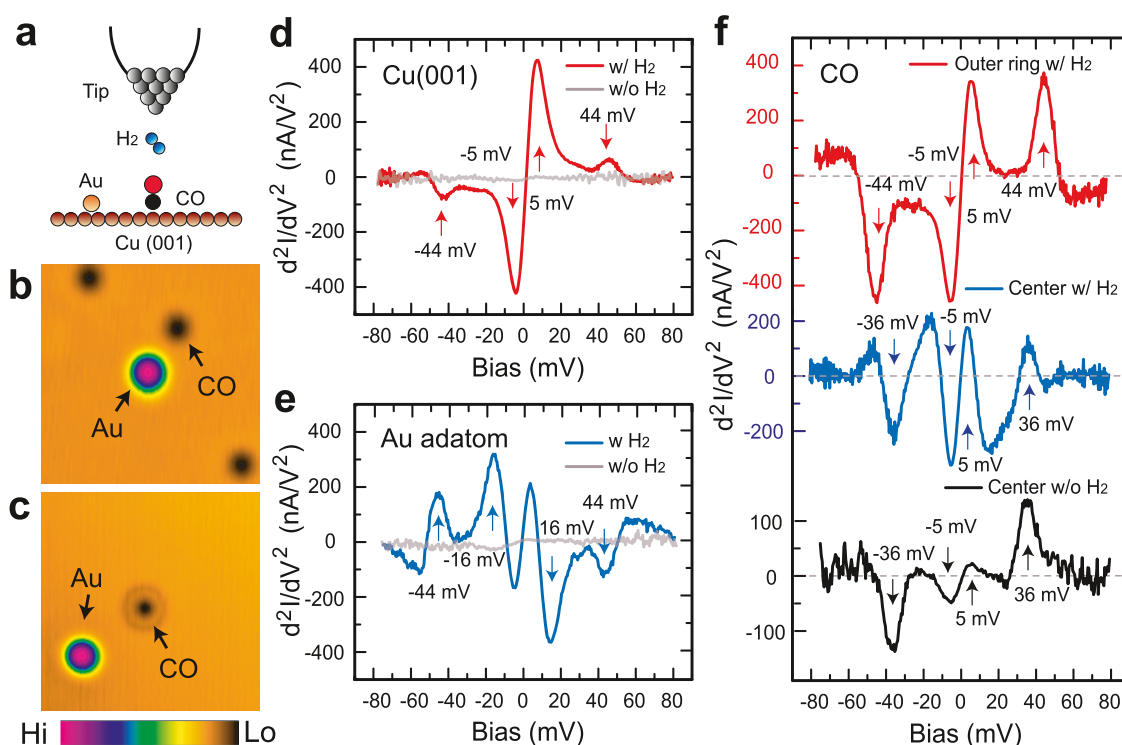


Figure 1. Molecular hydrogen in the STM junction. (a) Schematic diagram of a hydrogen molecule trapped in the STM junction. (b, c) Topographic images taken before (b) and after (c) dosing hydrogen, acquired with 50 mV, 1 nA set point. (d–f) d^2I/dV^2 taken over the bare Cu(001) surface (d), Au adatom (e), and CO molecule (f) before and after dosing hydrogen. The spectroscopic features observed at 44 mV after H_2 dosage are assigned to the rotational excitation of H_2 . The features at 5 mV for bare Cu and 18 mV for Au atom are assigned to the vibrational bouncing mode of H_2 . The spectra taken over the center of CO before dosing H_2 show the CO hindered translational mode at 5 mV and hindered rotational mode at 36 mV. The spectrum at the same position with H_2 dosed also shows CO hindered rotational features at 36 mV, but the features at 5 mV are different, which may arise from the mixture of H_2 vibrational and CO hindered translational features. The spectrum taken over the outer ring feature of CO shows H_2 rotational and vibrational signatures similar to that of the bare Cu surface but with a much stronger signal for the rotational mode.

useful guidelines for engineering nanocatalysts for reactions in a confined cavity.

RESULTS AND DISCUSSION

Au adatoms and CO molecules coadsorbed on the Cu(001) surface can be easily distinguished from either STM topographic images or d^2I/dV^2 spectra, as shown in Figure 1. Au adatoms appear as protrusions sitting at the hollow sites of Cu(001), while CO molecules appear as depressions sitting at the atop sites (Figure 1b). Without H_2 , the d^2I/dV^2 spectra taken over the Cu(001) surface and a Au adatom are both featureless. Two fingerprinting vibrational features can be observed over a CO molecule, which correspond to the excitations of the hindered translational and hindered rotational modes, respectively (Figure 1f).²⁰ Once dosed, H_2 diffuses freely on the Cu surface and may temporarily be trapped in the STM junction. The CO molecule imaged with a H_2 trapped in the tip–substrate junction has an outer ring of 2.95 Å in radius (Figure 1c). The d^2I/dV^2 spectra taken over the Cu surface and Au adatoms are dominated by the H_2 rotational and vibrational excitations (Figure 1d,e).^{21,22} The spectrum taken above CO now shows a combination of CO and H_2 features, whereas the spectrum taken over the outer ring around CO is similar to that on the bare Cu surface aside from the much stronger signal for H_2 rotation (Figure 1f). No sign of spontaneous H_2 dissociation can be identified in STM images with 50 mV bias and a 0.1 nA tunneling current (tip–substrate gap distance is larger than 7 Å).²³

To break apart H_2 molecules by electrons in the fixed tunneling gap, we applied voltage pulses to generate energetic tunneling electrons. During a voltage pulse, the tunneling gap was preset at 50 mV bias and a 0.1 nA tunneling current, and then the bias was suddenly increased for a short time with feedback off. Figure 2 shows the topographic images taken before and after applying a 540 mV and 500 ms voltage pulse over the bare Cu(001) surface. Twenty small depressions were generated by the pulse. d^2I/dV^2 measurements over these depressions revealed the same vibrational features as obtained from hydrogen atoms dissociated from acetylene,^{24,25} confirming their chemical identity as atomic hydrogen. These hydrogen atoms can spill over as far as 3 nm away from the pulse center, possibly due to their relatively high kinetic energy acquired from the hot electrons. The number of hydrogen atoms produced from a single voltage pulse was found to decrease as either the voltage amplitude or pulse duration was decreased. We found that no hydrogen atoms were produced under a threshold amplitude of around 510 meV, which can be assigned as the activation barrier (E_a) for hydrogen dissociation on Cu(001), in good agreement with our DFT calculations (see the Supporting Information) and the previous experimental report.²⁶

The same measurements were repeated over CO molecules and Au adatoms. Sixteen hydrogen atoms were generated by one 540 mV pulse on top of a Au atom, as shown in Figure 2e, whereas more than 130 hydrogen atoms were generated by an equivalent pulse over CO, as shown in Figure 2f. DFT

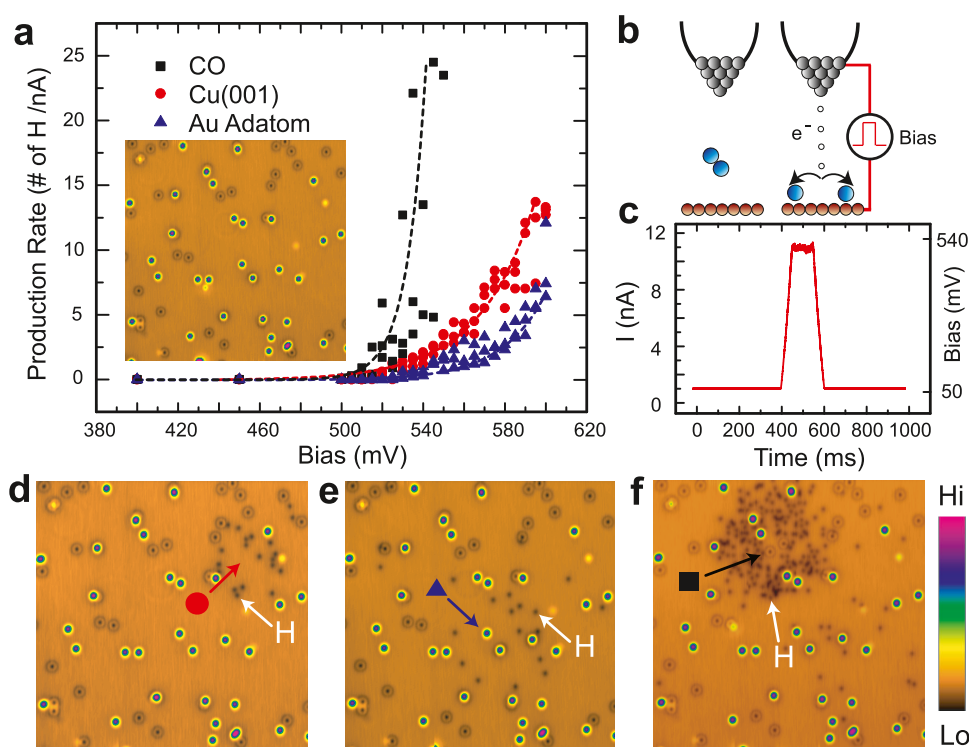


Figure 2. Hydrogen dissociation induced by voltage pulse. (a) The production rate over the bare Cu(001) (red), Au adatom (blue), and CO molecule (black) as a function of voltage pulse amplitude. The production rate is defined as the number of H atoms generated by one 500 ms duration voltage pulse divided by the current measured during the pulse. The inset is the topographic image taken before applying mechanical pulses. (b) Schematic diagram of the hot electron-induced hydrogen dissociation. (c) The current measured during a 540 mV and 500 ms voltage pulse. (d–f) Topographic images taken after applying one 540 mV and 500 ms voltage pulse over the bare Cu (d), Au adatom (e), and CO molecule (f). The H atoms can be desorbed from the scanning area by scanning at 1 V and a 1 nA tunneling set point, which allows us to repeat the measurement over the same area. The positions where the pulses are applied are marked by a red circle (Cu), a blue triangle (Au), and a black square (CO).

calculations indicate that E_a for H_2 dissociation is 10 meV larger on Au/Cu(001) and 40 meV smaller on CO/Cu(001) compared to that on Cu(001), as shown in Figure S1. The change of E_a is related to the availability of free electrons that are required in the transition state (TS) of H_2 dissociation. On Cu(001) and CO/Cu(001), H_2 in TS draws 0.22 and 0.20 electrons from the Cu atoms underneath and expands the H–H bond from 0.75 Å to 1.19 and 1.14 Å. However, it is more difficult for H_2 to grasp electrons from Au adatoms due to their high electronegativity. More discussions on this aspect can be found in the Supporting Information.

To drive the hydrogen dissociation by mechanical confinement, we squeezed the trapped hydrogen molecule by quickly decreasing the tip–substrate separation. During one mechanical pulse, the tip–substrate gap was preset at 5 mV bias and a 0.1 nA tunneling current and then was suddenly decreased by around 3–4 Å for 500 ms (Figure 3). To rule out dissociation induced by tunneling electrons, the sample bias was decreased to nearly 0 meV during each mechanical pulse; the remaining tunneling current, in this case, was mainly produced by the minute work function difference between the silver tip (coated with Cu from repeated poking of the tip into the surface) and the copper substrate (Figure 3c).²⁷ Figure 3e shows the topographic image acquired after 1000 sequential mechanical pulses applied over the bare Cu(001) surface. Two hydrogen atoms were generated in the region close to the pulse center. The production rate over Au atoms was similar to that on the bare Cu surface (Figure 3d). Strikingly, when the mechanical pulse was applied above the outer ring of the CO molecule, as

shown in the inset of Figure 3a, 32 hydrogen atoms were generated (Figure 3f). In all three cases, the reaction rate increased as the tip–substrate gap was decreased (Figure 3a). When the pulses were applied over a Au adatom or a bare Cu surface, almost no dissociation events could be observed if the gap distance was larger than 3.8 Å during the mechanical pulses. However, dissociation events could be observed even with a 4 Å gap when the pulses were applied over the outer ring of CO, indicating the benefit of using CO to assist the compression-induced H_2 dissociation. As a side note, when the mechanical pulses are applied directly above a CO molecule, the molecule easily hops away from the STM junction. We therefore apply the mechanical pulses to the side ring of the CO for consistent experimental results.^{28,29}

To understand the unusual catalytic activity of CO on Cu(001) toward H_2 dissociation during mechanical pulses, we included the Cu STM tip in DFT simulations. Since the tip is conditioned by being repeatedly poked onto the substrate, the end apex of the Ag tip in the experiment is likely to be coated by Cu. This coating has been confirmed by previous measurements where a CO molecule on a Au(110) surface is transferred to a bulk Ag tip and the CO vibrational energies measured by inelastic electron tunneling spectroscopy are those for a CO attached to Au. As depicted in Figure 4a–c, a hydrogen molecule was placed within the nanocavity formed between the STM tip and the Cu surface, and we varied the tip–substrate distance to mimic the movement of the STM tip during a mechanical pulse.³⁰ The DFT calculations show that the H_2 bond can be spontaneously “cleaved” ($d_{H-H} > 1.3$ Å) as

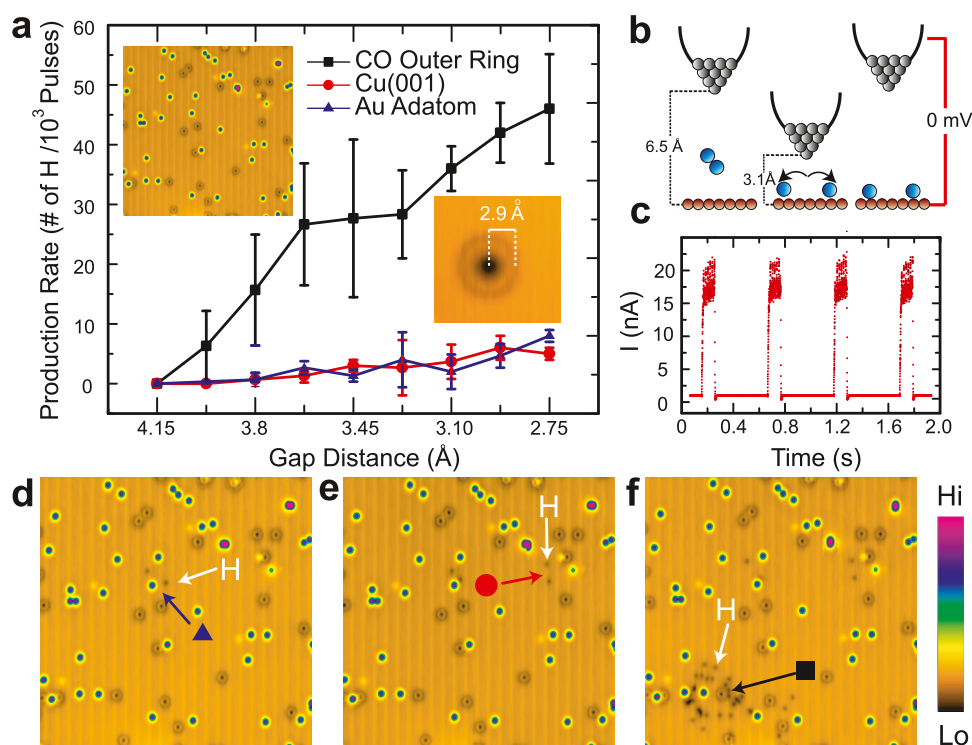


Figure 3. Hydrogen dissociation induced by mechanical pulses. (a) The production rate over the bare Cu(001) (red), Au atom (blue), and CO molecule (black) as a function of gap distance during the voltage pulse. The production rate is defined as the number of H atoms generated per 1000 mechanical pulses. The topographic image taken before applying mechanical pulses is shown in the inset. (b) Schematic diagram of the mechanical pulse-induced hydrogen dissociation. (c) The current measured during four mechanical pulses. (d–f) Topographic images taken after applying 1000 mechanical pulses over the Au adatom (d), bare Cu(001) (e), and CO molecule (f). The positions where the pulses are applied are marked by a red circle (Cu(001)), a blue triangle (Au adatom), and a black square (CO). The gap distance during the pulses is set at around 3.1 Å. The vertical stripes in the images arise from the creeping of the instrument piezo tube induced by the repeated mechanical movement.

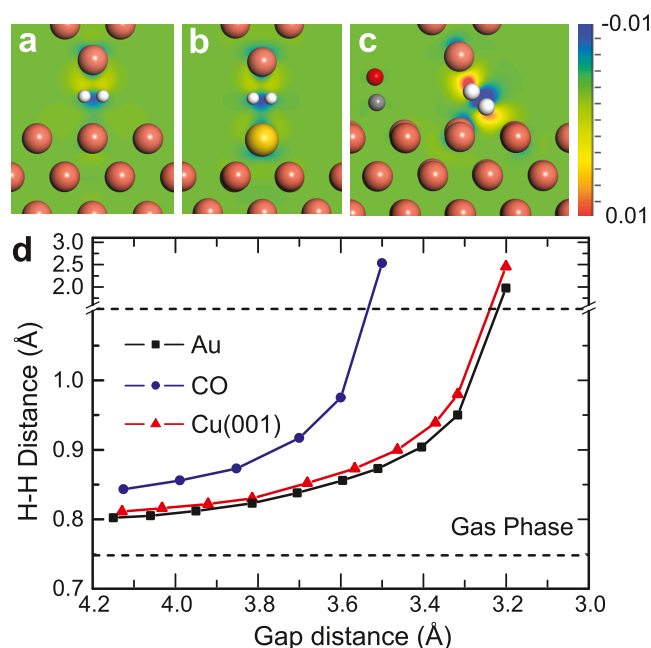


Figure 4. DFT calculations of hydrogen dissociation in the STM junction. (a–c) Geometries and charge density differences of H_2 over the bare Cu(001), Au adatom cavity, and next to CO, respectively. The gap distance is 3.6 Å. Red and blue represent the charge accumulation and depletion at $0.01 \text{ e}/\text{\AA}^3$, respectively. (d) The relationship of H_2 bond distance with the gap distance.

the tip–substrate gap is reduced to smaller than 3.2 Å on either the clean or the Au-adsorbed Cu(001) surface. With the presence of a CO in the nanocavity, the H–H bond breaking starts at 3.5 Å, indicating a better mechanocatalytic performance of the tip–CO/Cu(001) nanocavity compared to that of the tip–Au/Cu(001) and tip/Cu(001).

The experimental trend of the confinement-induced dissociation of all three nanocavities can be satisfactorily reproduced through DFT calculations, as shown in Figure 4d. Fundamentally, the probability of having H_2 dissociated in a nanocavity depends on two main factors. First, the nanocavity needs to be able to attract and confine H_2 in its vicinity. Comparing the adsorption energy of H_2 on the clean Cu(001) surface without the presence of STM tip, we found that the energy gains for H_2 in the tip/Cu(001), tip–Au/Cu(001), and tip–CO/Cu(001) nanocavities compared to those for a free molecule are 20, 10, and 60 meV, respectively. Obviously, the presence of CO makes the tip–substrate nanocavity more attractive toward H_2 . The second factor is the ability to activate H_2 dissociation by occupying its antibonding orbitals. To demonstrate the variations in electron density caused by CO and Au adsorption, we present the charge density difference for H_2 in each configuration ($\Delta\rho = \rho_{\text{H}_2+\text{cavity}} - \rho_{\text{H}_2} - \rho_{\text{cavity}}$) in Figure 4a–c. With the same gap distance of 3.6 Å, the H–H bond is reasonably activated ($d_{\text{H-H}} = 0.97 \text{ \AA}$) in the tip–CO/Cu(001) nanocavity but not in the other two nanocavities ($d_{\text{H-H}} = 0.86 \text{ \AA}$). While H_2 loses electrons from its bonding orbital in all three cavities, the filling of its antibonding orbital only occurs in the tip–CO/Cu(001) nanocavity. Bader charge

analysis indicates that H₂ receives 0.19 electrons through hybridization with both the tip and substrate in a tilted geometry, where the antibonding state of H₂ overlaps spatially with Cu orbitals. In contrast, H₂ prefers the horizontal adsorption geometry in the tip–Cu(001) and tip–Au/Cu(001) cavities and no hybridization occurs between the antibonding states of H₂ and states of Cu/Au atoms. Obviously, the availability of donor electrons in the environment near CO molecules and the tilted geometry of H₂ are both important for cleaving the hydrogen bond.

The combined experimental and theoretical results provide insights into the microscopic mechanism of this confinement-induced reaction. While the mechanical motion of the STM may noticeably enhance the reaction rate of H₂ dissociation, this is not done through the direct transferring of mechanical (kinetic) energy to the reactants. We found that the speed of the tip motion has no measurable effect on the reaction rate. In fact, the mechanical motion of the STM tip occurs on a much longer time scale (ms to μ s) than that of bond breaking (ps to ns), and the energy transfer through electron–phonon coupling is inadequate for meaningful chemical reactions. Instead, the proximity of the tip modifies the interaction energy of the trapped H₂ with its environment and continuously drives the trapped molecule toward the state where the H–H bond tends to be easily cleaved.²⁶ Based on our results, the essence of confinement-induced chemical processes in this system is derived from the continuous evolution of the catalytic environment from inert to active as the hydrogen molecule is guided toward the surface. This offers new opportunities for tuning the performance of nanocatalysts by selecting the pace of motion and special dopants.

CONCLUSIONS

In conclusion, we demonstrate that the mechanical motion of the STM tip induces one of the simplest chemical reactions: hydrogen dissociation. This brings the study of the effects of mechanical confinement in chemical processes to the single-molecular level, with unmatched controllability and visibility. The electronic and vibrational properties of both reactants and products can be characterized and quantified quickly by real-space spectroscopy and microscopy, allowing side-by-side comparisons with theoretical simulations. Our results indicate that the mechanical confinement can alter the reaction coordinates and lead to catalytic activation of inert chemical bonds. Such kinds of confinement-induced chemical processes rely on the generation of active chemical environments by the mechanical confinement. This scheme is potentially impactful but largely overlooked in mechanochemical studies, where, for instance, the collision of mill balls may form different cavities and turn their inert surfaces active. We anticipate that our study demonstrates a general approach to studying the catalytic effect of mechanical confinement and compression at the single-molecular level and provides guidance for the design of efficient nanocatalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c00005>.

Details of experimental and computational methods, DFT calculations of hydrogen dissociation, and properties of the adsorbed hydrogen molecule (PDF)

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Notes

The authors declare no competing financial interest.

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