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In situ Raman monitoring and manipulating of interfacial hydrogen spillover via precise fabrication of Au/TiO$_2$/Pt sandwich structures

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Abstract: Understanding the activation and transfer of hydrogen species at interfacial sites is essential for catalytic hydrogenation, yet still remains a significant challenge. Herein, the spillover of hydrogen species and its role in tuning the activity and selectivity in catalytic hydrogenation have been investigated *in situ* using surface-enhanced Raman spectroscopy (SERS) with 10 nm spatial resolution through the precise fabrication of Au/TiO$_2$/Pt sandwich nanostructures. *In situ* SERS study reveals that hydrogen species can efficiently spillover at Pt-TiO$_2$-Au interfaces, and the ultimate spillover distance on TiO$_2$ is ~50 nm. Combining kinetic isotope experiment and density functional theory calculation, we find that the hydrogen spillover proceeds via the water-assisted cleavage and formation of surface hydrogen-oxygen bond. More importantly, the selectivity in the hydrogenation of the nitro or isocyanide group is manipulated by controlling the hydrogen spillover. This work provides molecular insights to deepen the understanding of hydrogen activation and boosts the design of active and selective catalysts for hydrogenation.

The development of efficient catalysts relies on the insightful understanding of the reaction mechanism and structure-activity relationship.[1] An outstanding catalyst usually consists of different catalytic sites that function individually, at the same time, interact synergistically or work cooperatively to achieve the catalytic cycle.[2] Therefore, revealing the fundamental interactions among different active sites and their influence on the catalytic behaviors is emerging as a central issue yet a major challenge in catalysis.[3] One typical example is the interfacial hydrogen spillover phenomenon in catalytic hydrogenation.[4]

Hydrogen spillover is a ubiquitous interfacial process in which active hydrogen species generated on one site via the dissociation of H$_2$ may migrate to other sites and participate in the hydrogenation of species adsorbed there.[5] It significantly affects the intrinsic catalytic behavior of catalysts thus changes their activity or selectivity.[6] Consequently, great efforts have been denoted to promoting the understanding on hydrogen spillover.[7] Temperature-programmed desorption and temperature-programmed reduction studies first evidence the existence of hydrogen spillover between metals and oxides.[8] Recently, hydrogen spillover at Pd-Cu and Pt-TiO$_2$-Fe$_2$O$_3$ interfaces was directly observed using scanning tunneling microscopy and single-particle X-ray absorption spectromicroscopy, respectively.[9] Density functional theory (DFT) calculations indicate hydrogen spillover might proceed via the migration of proton and electron pairs on the surface.[10]

Nevertheless, more insightful information, especially that is acquired *in situ*, is needed to understand hydrogen spillover at a molecular level. Surface-enhanced Raman spectroscopy (SERS) is an ultrasensitive vibrational technique that can provide fingerprint molecular information,[11] thus is promising for tracking catalytic reactions *in situ*.[12] Using *in situ* SERS, we have directly proved that hydrogen species can be transferred across the Pt-Au and Pt-TiO$_2$-Au interfaces, but would be blocked at the Pt-SiO$_2$-Au interfaces.[13] However, more fundamental aspects about hydrogen spillover, including the distance and molecular mechanism of hydrogen spillover and its influence on the catalytic performance, still remain unclear.

Herein, hydrogen spillover at Pt-TiO$_2$-Au interfaces and its influences on selective hydrogenation of the nitro group have been investigated with nanoscale spatial resolution. An exquisite Au/TiO$_2$/Pt sandwich nanostructure is fabricated, allowing the activation of hydrogen, hydrogen spillover, and hydrogenation reaction to proceed separately on Pt, TiO$_2$, and Au. Combining *in situ* SERS study, kinetic isotope experiment, and DFT calculation, we find that hydrogen species can efficiently spillover on the TiO$_2$ surface for 50 nm via the cleavage and formation of hydrogen-oxygen bond linked to titanium. Moreover, the selectivity of the hydrogenation of the nitro group in the presence of an isocyanide group can be significantly improved by precisely manipulating the hydrogen spillover distance.

Generally, the active sites for hydrogen activation and molecule hydrogenation in most traditional catalysts are the same or locate so close to each other that it is too challenging to investigate these processes separately. To overcome this bottleneck, we design an Au/TiO$_2$/Pt sandwich configuration that achieves the spatial isolation of the active sites for hydrogen activation (Pt), spillover (TiO$_2$), and hydrogenation (Au). As the Au nanoparticles used here have a very large size, they are inert towards hydrogen activation.[14] Thus, hydrogen can only be activated and dissociated to active hydrogen species at the underlying Pt surface (Figure 1a). These hydrogen species will

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spillover along the TiO_2 surface to the Au nanoparticles and trigger the hydrogenation of molecules adsorbed there. Meanwhile, the Au nanoparticles can generate strong electromagnetic fields to significantly enhance the Raman signals of species nearby,[15] allowing the *in situ* Raman monitoring of the hydrogenation reaction.[16] Therefore, interfacial hydrogen spillover can be *in situ* investigated using such a configuration, and the spillover distance can be precisely measured and manipulated by simply changing the thickness of the TiO_2 layer.

Guided by the above idea, a monolayer of TiO_2 nanoparticles with a diameter of ~10 nm was prepared via the Langmuir-Blodgett (LB) method (Figure 1b and S1) and deposited on a Pt film (Figure S2). The atomic force microscope (AFM) characterization illustrates that the height of the TiO_2 monolayer is ~10 nm (Figure 1c), well consistent with the TEM results. Furthermore, the height of the TiO_2, i.e., the hydrogen spillover distance, can be tuned from 10 to 50 nm by increasing the number of the TiO_2 layers (Figure 1d). Finally, a monolayer of 55 nm Au nanoparticles with para-nitrothiophenol (pNTP), the probe molecule for the hydrogenation reaction, adsorbed on their surface was prepared (Figure S3) and transferred on the TiO_2/Pt substrate, forming the Au/TiO_2/Pt multilayer nanostructure (denoted as Au/x-nm-TiO_2/Pt, where x-nm indicates the thickness of the TiO_2 layer). The multilayer structure of Au/TiO_2/Pt is clearly illustrated by the cross-sectional TEM image in Figure 1e. The TiO_2 layer is sandwiched between the Pt film and the Au nanoparticle monolayer. Such a sandwich structure is further confirmed by scanning transmission electron microscope (STEM), elemental mapping and scanning electron microscope (SEM) (Figures 1f and S4).

As mentioned above, Pt, TiO_2, and Au in the Au/TiO_2/Pt sandwich nanostructure work as the active sites for hydrogen dissociation, spillover, and hydrogenation, respectively. To test such an idea and confirm that the Au nanoparticles are unable to activate hydrogen, we first investigate the hydrogenation of pNTP on bare Au nanoparticles and Au/Pt nanocomposites. No reaction happens on bare Au nanoparticles, but pNTP is efficiently hydrogenated to para-aminothiophenol (pATP) on Au/Pt (Figures S5 and S6). These results corroborate that the hydrogen can only be activated on the Pt surface and the active hydrogen species generated on Pt will migrate across the Pt-Au interfaces and hydrogenate pNTP adsorbed on Au to pATP.

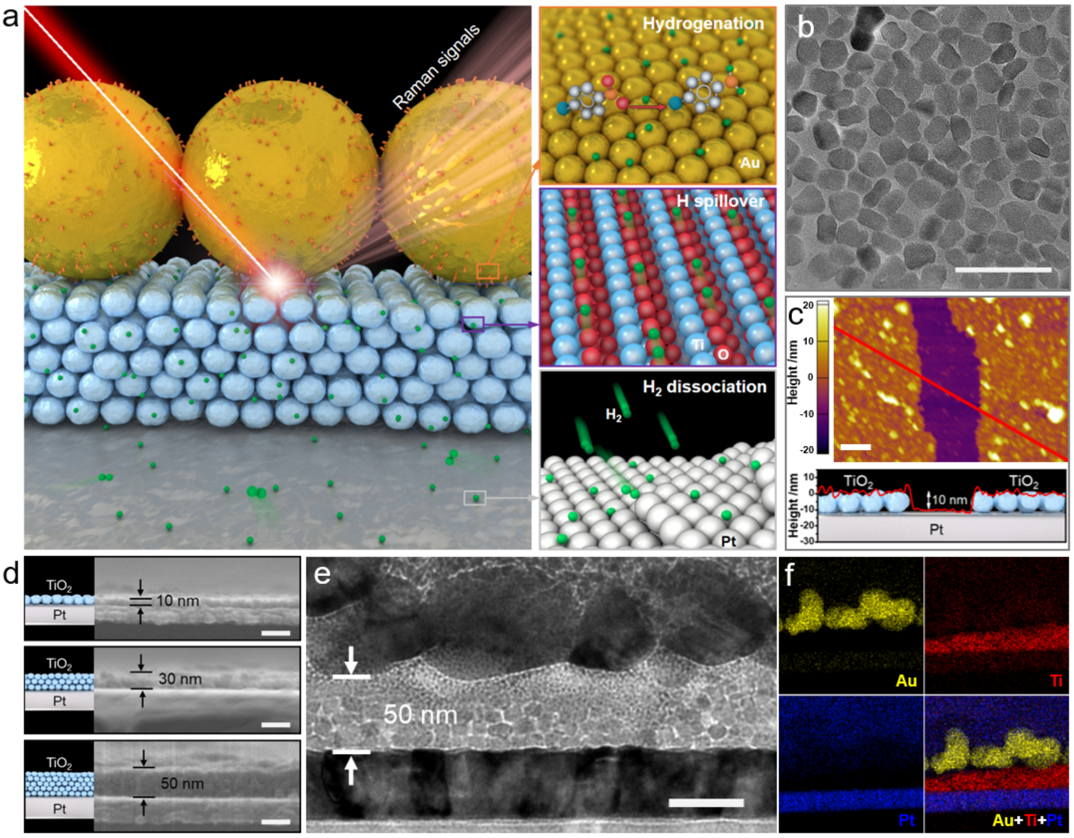

Figure 1. a) Schematic illustration of hydrogen spillover on Au/TiO_2/Pt sandwich nanostructures. b) TEM image of a TiO_2 nanoparticle monolayer. c) AFM image of the TiO_2 nanoparticle monolayer assembled on a smooth Pt film (TiO_2/Pt). d) Cross-sectional SEM images of TiO_2/Pt structure with 10, 30, and 50 nm TiO_2. e) Cross-sectional TEM image and f) elemental mapping of the Au/TiO_2/Pt sandwich nanostructure using a focused ion beam (FIB) system, respectively. Pt signals on the top region in f) result from the Pt nanoparticles introduced during the TEM sample preparation using FIB. The scale bar of all panels is 50 nm, except that of panel c) is 500 nm.

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The hydrogenation of pNTP was further investigated on the Au/TiO_2/Pt sandwich nanostructures using SERS. As for Au/10-nm-TiO_2/Pt, the Raman peaks at 1337 and 1570 cm^{-1}, assigned to the symmetric nitro stretching vibration and the phenyl ring modes of pNTP, respectively, decrease gradually with the increased reaction time (Figure 2a). Meanwhile, a new Raman band at 1586 cm^{-1} attributed to the benzene ring mode of pATP appears and rises. These results mean pNTP is efficiently converted into pATP on Au/10-nm-TiO_2/Pt, demonstrating that hydrogen can spillover from Pt to TiO_2 and finally reaches the surface of Au. This is well consistent with our previous results,[13] and is reasonable in terms of that TiO_2 is a well-known "active" support and has strong interactions with Pt or Au.[17] Additional control experiments show that the spillover of hydrogen proceeds at the TiO_2 surface rather than the TiO_2 bulk phase and it cannot occur at the Pt-SiO_2-Au interface (Figure S7).

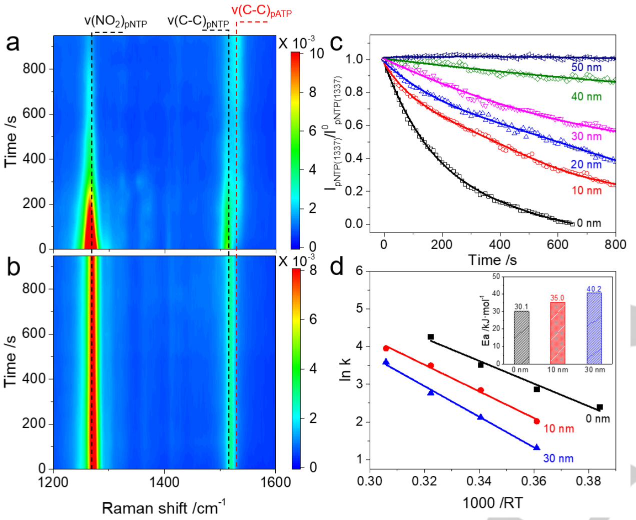

Figure 2. *In situ* SERS spectra of the hydrogenation of pNTP on a) Au/10-nm-TiO_2/Pt and b) Au/50-nm-TiO_2/Pt at 60 °C. c) Time-dependent intensity of the Raman band for pNTP (at ~1337 cm^{-1}) on Au/TiO_2/Pt with different thicknesses of TiO_2 layer. d) Arrhenius plot and the activation energy (inset) for the hydrogenation of pNTP over Au/TiO_2/Pt with different thicknesses of TiO_2 layer.

Different from Au/10-nm-TiO_2/Pt, the *in situ* SERS spectra of pNTP remains almost unchanged during the hydrogenation on Au/50-nm-TiO_2/Pt (Figure 2b). Quantitatively, with the increase in the thickness of the TiO_2 layer from 0 to 50 nm, the rate of pNTP hydrogenation on Au/TiO_2/Pt rapidly decreases, and the reaction is almost blocked when the TiO_2 thickness is 50 nm (Figure 2c). These results manifest that the thickness of the TiO_2 layer strongly influences hydrogen spillover and the hydrogen spillover distance on TiO_2 is less than 50 nm under the test conditions. The Arrhenius plots based on kinetic studies demonstrate that the activation energy slightly increases with the thickness of the TiO_2 layer (Figures 2d and S8), implying that the spillover of active hydrogen species is essential for the catalytic hydrogenation.

DFT calculations are performed to further reveal the fundamental mechanism of the hydrogen spillover over the TiO_2 surface. As shown in Figure 3a, electron and hydrogen transfer occur in a sequential mechanism. Hydrogen is transferred from one bridge oxygen (Obr) to the next Obr with a water molecule acting as a bridge for the hydrogen relay. The energy barrier is 0.34 eV, well consistent with the activation energy from the Arrhenius plots. Without water, electron and proton transfer occur in a concerted manner with a much higher activation energy of 3.09 eV (Figure S9). These theoretical results indicate that the spillover of hydrogen on TiO_2 involves the cleavage and generation of the surface Obr-H and trace water adsorbed on the TiO_2 surface plays an essential role on it.

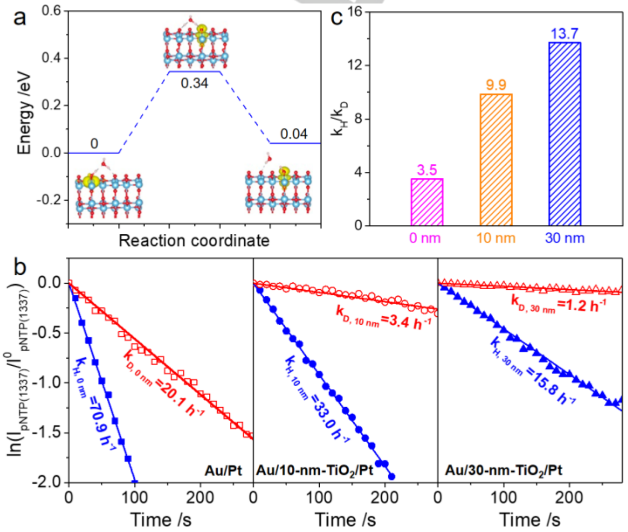

Figure 3. a) DFT simulation of the migration of hydrogen on TiO_2. Color coding: red, O; sliver, H; blue, Ti. b) Reaction kinetics and c) kinetic isotope effects of the reduction of pNTP over different TiO_2 distance using H_2 or D_2.

To test the proposed mechanism, we conducted isotopic experiments by using D_2 in the hydrogenation of pNTP to quantify the kinetic isotope effect (KIE), which is a key factor to elucidate the reaction mechanism.[18] As shown in Figure 3b, all the reactions using H_2 or D_2 follow first-order kinetics. However, the reaction rate becomes significantly slower when changing H_2 to D_2, and this trend is more obvious with the increase of the thickness of the TiO_2 layer. The KIE, i.e., the ratio of reaction rate under H_2 relative to that under D_2 (k_H/k_D), for Au/Pt is about 3.5 (Figure 3c), which is a typical value for primary isotope effect. The KIE values increase to 9.9 and 13.7 for Au/10-nm-TiO_2/Pt and Au/30-nm-TiO_2/Pt, respectively (Figure 3c). Such a big increase of the KIE with the thickness of the TiO_2 layer directly evidences that the formation and cleavage of the O-H bond occur during the spillover of hydrogen species on TiO_2, well consistent with the DFT calculations.

More importantly, hydrogen spillover can be used to tune the selectivity in catalytic hydrogenation. As a reaction barrier exists during hydrogen spillover on TiO_2, the coverage of active hydrogen species at the Au sites decreases after a longer spillover distance (Figure 4a). The influence of the coverage of a surface species on its chemical potential can be expressed as:[19]

$$\mu_i(\theta) = \mu_i^0 + RT\ln\frac{\theta_i}{\theta_*}$$

Where θ_i and θ_* are coverages of adsorbed species i and available sites * on the surface, respectively, and μ_i^0 is the standard chemical potential of species i at temperature T. This means the chemical potential of the active hydrogen species after a longer spillover distance is lower. Hence, with decreased chemical potentials, the hydrogen species can only participate in the hydrogenation pathway needing lower energies, thus leading to a higher selectivity (Figure 4a).

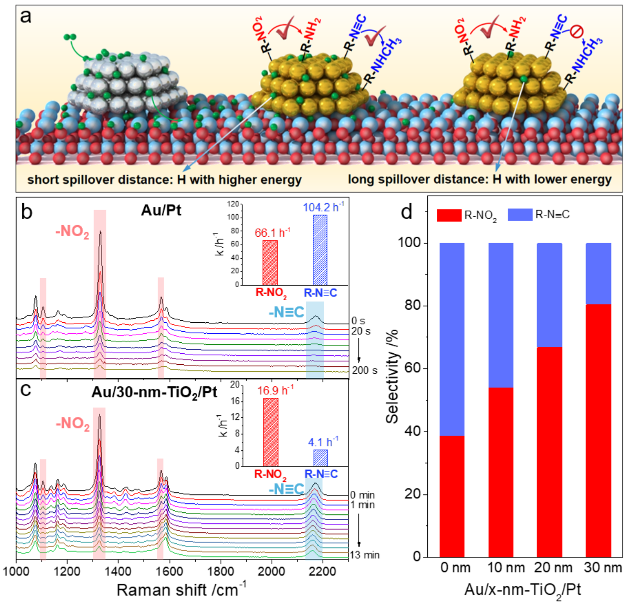

Figure 4. a) Schematic illustration of the selective hydrogenation of R-NO_2 in the presence of R-N≡C by controlling the hydrogen spillover distance. b), c) *In situ* SERS spectra of the selective hydrogenation of R-NO_2 in the presence of R-N≡C on Au/Pt and Au/30-nm-TiO_2/Pt, respectively. d) Selectivity of the hydrogenation of R-NO_2 in the presence of R-N≡C over Au/TiO_2/Pt with different thicknesses of TiO_2 layer.

To testify such a hypothesis, the selective hydrogenation of the nitro group (pNTP, R-NO_2) in the presence of the isocyanide group (phenyl isocyanide (PIC), R-N≡C), which is a key reaction for the industrial production of fine chemicals,[2c] was studied. PIC is vertically adsorbed on the Au surface with the C-terminus of the N≡C group,[20] and it can be hydrogenated then desorbed from the surface.[21] This is demonstrated by the *in situ* SERS study, which shows that the Raman peaks of PIC are gradually weakened in H_2 but remained unchanged under Ar (Figure S11).

Hydrogenation of pNTP and PIC was carried out over Au/TiO_2/Pt with different thicknesses of TiO_2 layer. Figure 4b shows the *in situ* SERS spectra of the selective hydrogen of R-NO_2 and R-N≡C over Au/Pt. The Raman bands for the N≡C and N-O stretch mode locate at 2171 and 1337 cm^{-1}, respectively. With prolonged reaction time, both R-N≡C and R-NO_2 are efficiently hydrogenated on Au/Pt, leading to the simultaneous decline of their Raman intensities. However, when using Au/30-nm-TiO_2/Pt as the catalyst, the decrease of the Raman band of N≡C is much slower than that of NO_2 (Figure 4c). These results mean the hydrogenation of NO_2 is dominant on Au/30-nm-TiO_2/Pt.

This can be further quantitatively revealed by the rate constants of Au/Pt and Au/30-nm-TiO_2/Pt. The rate constant of the hydrogenation of R-N≡C ($k_{N≡C}$) is slightly bigger than that of R-NO_2 (k_{NO_2}) ($k_{N≡C} > k_{NO_2}$) for Au/Pt (inset of Figure 4b). On the contrary, as for Au/30-nm-TiO_2/Pt, $k_{N≡C}$ becomes much smaller than k_{NO_2} ($k_{N≡C} << k_{NO_2}$). Thus, the selectivity towards the NO_2 hydrogenation is remarkably improved with the increase of the thickness of the TiO_2 layer (Figure 4d). Such results directly verify the hypothesis proposed in Figure 4a and demonstrate that manipulation of the hydrogen spillover is an efficient strategy to tune the selectivity in catalytic hydrogenation.

In summary, the spillover of hydrogen at Pt-TiO_2-Au interfaces and its role on the activity as well as selectivity in catalytic hydrogenation have been investigated using *in situ* SERS through the fabrication of Au/TiO_2/Pt sandwich nanostructures. *In situ* SERS results directly show that active hydrogen species generated on Pt can be transferred to Au via the TiO_2 surface and the spillover distance of such hydrogen species on TiO_2 is measured to be ~50 nm. Kinetic isotope experiment and DFT calculation reveal the molecular mechanism of hydrogen spillover on the surface of TiO_2, which involves the water-assisted cleavage and formation of surface hydrogen-oxygen bond. Furthermore, the selectivity in catalytic hydrogenation can be tuned by controlling the hydrogen spillover distance. With increased hydrogen spillover distance, the selectivity towards the hydrogenation of the NO_2 group in the presence of the N≡C group is significantly improved. This work provides fundamental insights to boost the understanding of hydrogen spillover at metal-oxide interfaces.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: surface-enhanced Raman spectroscopy • *in situ* • hydrogen spillover • catalytic hydrogenation

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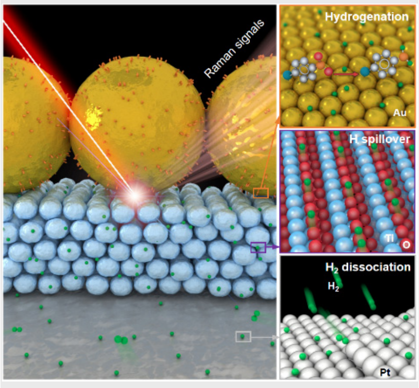
COMMUNICATION

Spillover of hydrogen species at Pt-TiO_2-Au interfaces has been investigated *in situ* using SERS with nanoscale spatial resolution through the precise fabrication of Au/TiO_2/Pt sandwich nanostructures, and the fundamental mechanism of hydrogen spillover and its influence on selective hydrogenation are revealed.



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