Dynamic displacement of N₂ from Ru(0001) by incident D and H atoms

L. Diekhöner, H. Mortensen, C. Åkerlund, A. Baurichter, and A. C. Luntz
Fysik Institut, Syddansk Universitet: Odense Universitet, Campusvej 55, DK-5230 Odense M, Denmark

(Received 5 October 2000; accepted 8 December 2000)

Exposing a N₂ covered Ru(0001) surface to a D or H atom beam leads to desorption of the N₂ molecules. This displacement is kinetically prompt at all N₂ coverages and the process is identified as dynamic displacement. By showing that the cross section for displacement by D atoms is roughly twice that for H atoms, we suggest that the mechanism for this dynamic displacement is some phonon mediated process rather than an electronically nonadiabatic one suggested earlier. As a contrast, the displacement of Xe adsorbed on Pt(111) induced by CO adsorption has also been measured. In this case, the displacement is not prompt and there is a total coverage on the surface that is necessary to induce desorption of Xe. This seems well described by a thermodynamic displacement mechanism. © 2001 American Institute of Physics. DOI: 10.1063/1.1344924

I. INTRODUCTION

The dissociation of N₂ on Ru single crystal surfaces has received much attention in recent years because of the possible role of Ru as an end catalyst in the commercial production of NH₃ from N₂ and H₂. The rate-limiting step in the overall catalysis is generally believed to be the dissociative chemisorption of N₂.¹² There has been, however, a serious conflict between experiment and theory in the barriers for this dissociation. High-pressure kinetic studies show that the overall activation energy for the catalytic synthesis of ammonia is ~101 kJ/mole on a Ru(0001) surface.³ This sets an upper limit to the activation energy for N₂ dissociation since additional energy is needed under synthesis conditions to create free sites.³ On the other hand, the most recent density-functional theory (DFT) calculations give a barrier for N₂ dissociation on Ru(0001) of 190 kJ/mole (2 eV).⁴⁻⁶ This difference is much greater than expected uncertainties in the DFT calculations.

It has recently been suggested that this discrepancy can be explained by defects. It was shown experimentally that the (natural) presence of steps on a nominally well prepared single crystal surface strongly influences thermal rates of dissociation of N₂ on Ru(0001) by giving a much lower barrier for N₂ dissociation at steps.⁵ This strong lowering of the barrier at step sites was also confirmed in DFT calculations.⁵ The implication is that these steps or other defect sites are the active ones in real catalysis on catalyst particles as well as on single crystal surfaces.

Before the role of steps was clarified experimentally and theoretically, a completely alternative reaction pathway was also suggested for ammonia production as a means to resolve the discrepancy between theoretical and experimental barriers to NH₃ synthesis on single crystal surfaces.⁷ This mechanism had already been proposed as a catalytic mechanism for supported Ru particles on the basis of indirect kinetic evidence.⁸ In this mechanism it is assumed that molecularly adsorbed N₂ coexists with atomic H on the surface under working conditions of the catalysis (pressure and temperature). H atoms attach to N₂ initially forming adsorbed N₂H and are sequentially added to the fragment until N₂H₅ is formed which then readily breaks the N–N bond producing NH₃.

DFT calculations showed that this actually is a rather low-energy pathway with an overall activation energy of 90 kJ/mole.⁷ While this seems a very unusual process in terms of conventional heterogeneous catalysis, it should be pointed out that this is the mechanism of biological nitrogen fixation by some enzymes, where H is supplied by proton transfer. The active part of the enzyme where nitrogen bonds and reacts is believed to be a metal–sulfide cluster (MoFe6 S9) and DFT calculations show a low-temperature path for ammonia formation by sequential H atom addition.⁹

In an attempt to clarify the understanding of ammonia synthesis with respect to the above mentioned two models, we performed ultrahigh vacuum (UHV) experiments where we exposed N₂ molecules adsorbed on a Ru(0001) surface to an H-atom beam in the hopes of initiating addition of H to N₂ (i.e., hydrogenation) and hopefully ultimately forming ammonia at low surface temperature Tₛ. It has previously been observed that an H atom beam does hydrogenate iso-electronic CO adsorbed on Ru(0001) at low Tₛ via an Eley–Rideal mechanism to form formyl (HCO) and formaldehyde (HCHO).¹⁰

Unfortunately, when N₂ adsorbed on Ru(0001) was exposed to a H atom beam, a very efficient displacement of the adsorbed N₂ was observed so that it was impossible to observe any hydrogenation. We cannot, therefore, evaluate whether a hydrogenation process H(gas) + N₂/Ru(0001) can occur, only that its cross section must be much smaller than for the displacement process. For H(gas) + CO/Ru(0001), the displacement is endothermic and does not occur so that a small cross section Eley–Rideal hydrogenation can be observed.

Because adsorption driven desorption is an interesting dynamic phenomenon in its own right, we have investigated desorption of adsorbed N₂ by H in some detail in...
order to understand the mechanism. We find that desorption occurs by so-called dynamic displacement, a mechanism suggested to account for some other cases of H or O atom driven desorption, e.g., H(gas) + O(1D)/Pt(111), H(gas) + CO/Cu(111) and CO + O2/Pt(111). The kinetic behavior of dynamic displacement is contrasted with that observed for thermodynamically driven displacement of Xe/Pt(111) induced by CO adsorption. It has previously been suggested that dynamic displacement is due to electronic excitation of the metal substrate during the adsorption of the reactive atom. In an attempt to clarify whether this nonadiabatic mechanism dominates desorption, or whether a more conventional phonon mediated process dominates, we have looked at the relative cross sections for desorption of H(gas) + N2/Ru(0001) vs D(gas) + N2/Ru(0001). If a nonadiabatic electronic excitation mechanism dominates, we anticipate that the cross section for desorption by H will be larger than that for D. On the other hand, if a phonon excitation mechanism dominates, then we anticipate that the cross section for desorption by D will be larger than that for H. We find that the D atom cross section is nearly a factor of 2 larger than that for H and this indicates that the phonon mechanism must dominate desorption. Our picture is that the H (D) adsorption process creates a hot H (D) atom. Either this “hot precursor” collides with a nearby N2 before thermalizing with the lattice and causes desorption or the H (D) adsorption causes a strong local phonon excitation in the lattice which causes desorption of a nearby adsorbed N2.

II. EXPERIMENT

The overall experimental apparatus consists of a UHV chamber with sample manipulator, sputter ion gun, Auger electron spectroscopy (AES), low-energy electron diffraction, a quadrupole mass spectrometer (QMS) monitoring the background gas in the chamber, a QMS in a differentially pumped chamber for low-background temperature programmed desorption (TPD), a rotatable differentially pumped QMS that can observe all beams including a triply differentially pumped atomic beam and a quadrupole mass spectrometer monitoring the direct beam. During these experiments the partial pressures of Xe and CO in the chamber were recorded using the QMS in the main chamber. The clean Pt(111) surface at T s = 90 K was exposed to a thermal beam of Xe essentially hitting the entire surface. For these experiments T s was measured with a type K thermocouple. The geometry of the Xe beam source was the same as described above for the H (D) atom source. The sticking coefficient S of Xe was constant up to a certain coverage Θ Xe, above which the sticking suddenly began to decrease. We did not accurately determine the absolute value of Θ Xe, but it was previously suggested that this occurs at saturation of the Xe adlayer at Θ Xe = 0.41 ML. All Xe doses presented here were terminated before reaching Θ Xe, and the resulting lower coverages were determined relative to Θ Xe* by integrating the sticking probability S(t) over the duration of the dose. After the Xe dose, a supersonic nozzle beam of ~1% CO seeded in He, with an average translational energy of 0.42 eV was allowed to hit the surface at normal incidence.

III. RESULTS

A. Hydrogenation of N2?

Absolutely no NH3 was observed to desorb into the gas phase with the background QMS when exposing a maximally N2 covered Ru(0001) surface at T s ~ 100 K (Θ N2 = 0.25 ML) to H atoms. Also no NH3 desorbed during a TPD experiment following the dosing. In addition, we looked for a product of eventual ammonia decomposition, i.e., atomic nitrogen. Desorption of molecular nitrogen is completed at 140 K, whereas associative desorption of N2 (at Θ N2 ~ 0.25) occurs at ~800 K. There was no hint of an associative desorption feature indicating that no atomic nitrogen was present on the surface after exposure to H. In short, there was absolutely no evidence that atomic H broke a N–N bond. In contrast, an efficient desorption of N2 was observed by exposure to H (D).

B. N2/Ru(0001) displacement induced by D adsorption

When a saturated N2/Ru(0001) surface is exposed to a D-atom beam with a flux of 0.013 ML/s, prompt desorption...
(within the time constant of the vacuum system) is observed by the QMS measuring the chamber background as shown in Fig. 1. Because we can not monitor the D atoms in the chamber because of their adsorption on the chamber walls, we monitor undissociated D$_2$ from the same incident beam as a marker of when the D atoms enter the chamber and strike the surface. Absolutely no delay is observed between the initiation of displacement and the incidence of D on the surface. If the microwave discharge is turned off no atoms in the beam no displacement of N$_2$ is observed.

A reasonable measure of the initial displacement rate is the initial N$_2$ pressure-jump (P-jump) when the D-beam strikes the surface. Using this measure, the initial rate of displacement increases linearly with the N$_2$ coverage $\Theta_0$ as shown in Fig. 2. For these experiments, the D atom flux was increased to 0.12 ML/s.

FIG. 1. Partial pressures of N$_2$ and D$_2$ in the chamber as a function of time, showing that N$_2$ is displaced promptly by incident D atoms. D-flux: $F = 0.013$ ML/s, $\Theta_0$ = 0.25.

FIG. 2. Initial N$_2$ pressure-jump as a function of initial N$_2$-coverage, $\Theta_0$.

Figures 1 and 2 pertain only to the initial rate of displacement. The displacement rate can also be followed when there is extended exposure to the D beam. Figure 3 shows the displaced N$_2$, over a long time period for three initial coverages of N$_2$ from 0.25–0.02 ML and for a D atom flux of 0.12 ML/s. It is seen that the displaced N$_2$ signal jumps to a maximum value almost immediately and then decays exponentially to zero. TPD experiments after the long exposure to D show that no N$_2$ remains on the surface. No delay between onset of D adsorption and N$_2$ displacement is observed for any of the initial $\Theta_0$ coverage. The decay of the N$_2$-desorption rate is fitted to a simple exponential function $\Theta(t) = \Theta_0 \exp(-t/\tau)$, where $\Theta_0$ is the initial N$_2$-coverage. The desorption rate is thus given by: $-d\Theta(t)/dt = \sigma F \cdot \Theta(t)$, where $\sigma$ is the cross section for an incident D-atom displacing a N$_2$ molecule, $F$ is the atom flux and $1/\tau = \sigma F$. The fit of the decay is shown in Fig. 3 as solid black lines.

Since the desorption rate is described by a simple exponential decay, the desorption rate is also independent of D coverage on the surface since this increases with exposure time. Otherwise we would have to add a term proportional to $\Theta_0$ to the rate. The same time-constant ($\tau = 7.1$ s) described the decay of all three curves. We can thus estimate the cross section for displacement from $1/\tau = \sigma F$ and find that $\sigma = 7.6 \times 10^{-16}$ cm$^2$ for displacing a N$_2$ by an incident D. There is some uncertainty due to the absolute calibration of $F$.

The absolute probability $p_D$ that a D atom which adsorbs onto the surface has induced desorption of N$_2$ (at maximum N$_2$ surface coverage) has also been measured by measuring the number of N$_2$ molecules desorbed and the number of D atoms adsorbed in a 5 s atom dose at low flux (0.013 ML/s). The number of N$_2$ molecules desorbed was obtained by subtracting the integrated TPD signal for N$_2$ remaining on the surface after D atom induced displacement from the integrated TPD for the initial N$_2$ coverage. The number of D atoms adsorbed was measured by the integrated TPD signal relative to the TPD area of a saturation coverage.
Using this method, we find that $p_D = 0.5$. 

A value for $p_D$ can also be estimated by noting that $p_D = N \sigma / A$, where $N$ is the number of $N_2$ molecules adsorbed and $A$ the area of the Ru(0001) surface. In terms of coverage $\Theta$, this can be written as $p_D = \Theta \cdot n_0$, where $n_0$ is the surface atom density ($n_0 = 5.8 \cdot 10^{15}$ cm$^{-2}$). In this way, we estimate that $p_D \approx 0.3$ at $\Theta = 0.25$ ML $N_2$. This is in reasonable agreement to the value of $p_D$ obtained via the absolute direct method, especially given the uncertainties in calibrating absolute atom fluxes and coverages required for the comparison.

C. Isotope effect for $N_2$/Ru(0001) displacement

In order to clarify the mechanism of $N_2$ displacement, we compared the relative displacement yield for incident H atoms to that for incident D atoms. In order to make accurate measurements of the relative yields of the two surfaces, in all cases the displacement from a saturated $N_2$/Ru(0001) surface was measured. When using the low flux atom beam ($F \sim 0.013$ ML/s), a well-defined $N_2$ pressure jump reaching an almost constant level is observed in the displacement before this decays due to a decrease in surface coverage of $N_2$. This initial $P$-jump normalized to the atom-flux is proportional to the cross section $\sigma$ for displacement. In this way, it is found that $\sigma_D / \sigma_H = 1.8$, i.e., there is a substantial isotope effect in which D atoms are twice as effective as H atoms in inducing displacement.

We have also measured the absolute probability $p_H$ for H atoms to displace $N_2$ at the saturation coverage of 0.25 ML by measuring the number of $N_2$ molecules desorbed and the number of H atoms adsorbed in a 5 s atom dose at low flux by TPD in a manner equivalent to that for D atoms. We find $p_H = 0.2$. Combining this with the previous measurement of $p_D = 0.5$ obtained by the identical method, we find $p_D / p_H = \sigma_D / \sigma_H = 2.5$. This is in good agreement with the relative measurement, where careful comparisons of the relative initial $N_2$ $P$-jumps were made, and thus confirms the strong isotope effect.

D. Displacement of Xe/Pt(111) induced by CO adsorption

Displacement kinetics that strongly contrast with that observed for $N_2$/Ru(0001) by H (D) atoms is the CO induced desorption of Xe/Pt(111). Figure 4 shows CO and Xe background partial pressures induced when a weak seeded supersonic molecular beam of CO is incident upon a partly covered Xe/Pt(111) surface at $\Theta_{Xe} = 0.34 \cdot \Theta_{CO}$ ML at $T_s = 90$ K. At time $t_0$, the CO beam is initially introduced into the chamber but strikes a nonreactive quartz flag prior to the surface. Removing the flag at $t_1$ exposes the Xe-covered Pt(111) surface to the CO beam. The initial sticking probability of CO is $S_0 = 0.43$, as seen from the decrease in CO partial pressure.\textsuperscript{23} The sticking of CO continuously decreases as CO builds up on the surface. CO dosing continues for 18 s before Xe desorption initiates abruptly at time $t_2$. All the Xe then seems to desorb rapidly with CO exposure, with Xe desorption ending before the CO beam is turned off at $t_3$. At the same time, as the Xe seems to be fully desorbed from the surface, the CO sticking probability seems to decrease to almost zero, presumably because the surface is now fully saturated with CO.

The above experiment has been repeated for different initial Xe coverages showing that the delay ($t_2 - t_1$) for which Xe desorption initiates depends upon the initial Xe coverage. Since this time delay $t_2 - t_1$ has no real physical significance, we instead calculate the amount of CO that is absorbed during this delay $\Theta_{CO} \sim \int_{t_1}^{t_2} S_{CO}(t) dt$. Figure 5 shows that $\Theta_{CO}$ depends linearly upon initial Xe surface coverage. In the limit of low Xe initial coverage, $\Theta_{CO}$ extrapolates within the experimental error (principally the imperfect overlap of CO beam with the full surface) to the CO saturation coverage. It is seen that the more Xe adsorbed, the less CO is needed to initiate Xe desorption. It is thus necessary to build up a sufficient total coverage of CO and Xe ($\Theta_{Xe} + a \cdot \Theta_{CO}$, where $a$ is a constant) before the weaker bound Xe is pushed off the surface.

FIG. 4. CO and Xe chamber partial pressures of a partially Xe covered Pt(111) surface as a function of exposure time $t$ to a CO molecular beam. At time $t_0$ the CO beam hits an inert quartz flag, at $t_1$ the flag is removed and the CO beam strikes the surface, at $t_2$ Xe desorption sets in and at $t_3$ the CO beam is shut off.

FIG. 5. CO coverage when Xe desorption sets in as a function of the initial Xe coverage before CO exposure starts.
Several mechanisms have previously been suggested to account for adsorbate desorption induced by incident molecules in various experiments and are summarized in Fig. 6. For example, collision-induced desorption (CID) can occur for incoming species at high-incident energies where enough energy is transferred to an adsorbate in a direct collision to overcome the adsorbate binding to the surface. In this case, the incoming species usually does not bind to the surface. There are many examples of CID for relatively weakly bound adsorbates, including the CID of $N_2$ from Ru(0001) by incident high-energy Ar or Kr. Another mechanism is so-called dynamic displacement in which an incoming species chemisorbs, releasing the adsorption energy to the adsorbate/lattice. This causes a direct desorption of the more weakly bound adsorbate in some poorly specified, but nonthermal manner. Several examples now exist for this process; e.g., O, N or $H_2/O_2/\text{Pt}(111)$, $H+CO/\text{Cu}(111)$, and $CO+O_2/\text{Pt}(111)$. Hallmarks of this process kinetically are that a prompt displacement is induced of the weakly bound species. The rate is first order in the incoming strongly bound gas species but is independent of the initial coverage of weakly bound species and also of adsorbed strongly bound species. Dynamics experiments have also shown that the desorbed or displaced species leaves the surface with both translational energy and internal states far from thermal equilibrium. For use later, we note that there could be significant isotope effects for this mechanism that depend on its dynamic origin. A third mechanism for displacement is what we call thermodynamic displacement. It is evident that if the surface is only initially partly covered, then no desorption of the weakly bound species will occur upon exposure to the strongly bound one until some critical total surface coverage is obtained, i.e., there can be a delay in displacement with initial exposure. We also note that there should be little isotope effect for this mechanism since energetics are roughly the same for all isotopes.

It is evident from the discussion just presented that the CO driven displacement from Xe/Pt(111) is well described by thermodynamic displacement. Both the delay of initial displacement until a critical coverage is reached and its dependence on initial Xe coverage are consistent with this picture. On the other hand, the prompt first order (in gas-phase H or D) displacement of $N_2$ from Ru(0001) by H (D) and independence in the rate to initial adsorbed $N_2$ coverage or adsorbed H (D) coverage and the existence of an isotope effect are very strong evidence for a dynamic displacement mechanism.

The physical basis for dynamic displacement is quite unclear. All we know with certainty is that in some indirect way the adsorption energy released when a species from the gas phase forms a strong bond to the surface can cause prompt nonthermal desorption of a weakly bound species. It has been suggested that atomic adsorption from the gas phase excites in some unspecified manner an electronic excitation of the adsorbate which induces desorption. Electron and photon induced nonthermal desorption of molecules from metals is well known, so that this is a reasonable suggestion. In these cases, the mechanism is generally discussed in terms of ‘‘hot’’ electrons, i.e., the creation of electron–hole pairs by the excitation and their transient scattering by the adsorbate. Whatever the details of any electronic mechanism for dynamic displacement, it must represent an electronically nonadiabatic process in which some electron–hole pairs are created by the act of atomic adsorption. It is generally accepted that electron–hole pair excitation at metal surfaces via interaction with a gas-phase species is only large when charge transfer is involved, e.g., when an atomic affinity level $\varepsilon_A$ crosses the Fermi level $\varepsilon_F$ of the metal. The extent of nonadiabatic excitation depends upon the time scale for this charge transfer, i.e., the rate in which $\varepsilon_A$ passes through $\varepsilon_F$. In the limit of very slow passage, no electronic excitation is anticipated and conversely rapid passage implies strong excitation of electron–hole pairs. Since the energy of $\varepsilon_A$ depends upon the distance of the atom from the surface, this rate (and hence the extent of electron–hole pair excitation) is proportional to the velocity of the atom normal to the surface. This is the origin of the much discussed isotope effect in sticking of H or D atoms on metal surfaces due to electron–hole pairs. Since H atoms have a higher velocity, they excite more electron–hole pairs and induce more sticking than D atoms. We anticipate exactly the same isotopic behavior if displacement of $N_2$ induced by H or D adsorption is due to excitation of electron–hole pairs, i.e., $\sigma_H/\sigma_D<1$. Since this is not observed, we conclude that the dynamic displacement does not have its origin in electronic nonadiabaticity.

Another possible scenario is that even though the H (D) atom is incident at thermal energies (~0.03 eV), the adsorp-
tion well accelerates the particle so that it impacts the surface at a high translational energy. Because, the atom-surface potential is highly corrugated, there can also be considerable conversion of normal to parallel translational energy before impact with the surface. This is the essence of a so-called hot precursor. The adsorption energy of H (D) must be eventually dissipated by the lattice—N$_2$ system. One scenario is that thermalization with the lattice is relatively slow and the hot H (D) collides with (and transfers energy) to a N$_2$ causing desorption. Because D will transfer more mechanical energy in a collision with N$_2$ than H, we anticipate an isotope effect $\sigma_D/\sigma_H$ $>$ 1. This hot precursor mechanism is rather different than traditional CID because the conversion of normal energy to parallel energy increases the probability of collision with N$_2$. In fact, the cross sections observed for desorption of N$_2$ by D (H) are even larger than those of CID of N$_2$ by Ar and Kr at modest incident energies. Another possible scenario for dissipating the H (D) adsorption energy could occur if the thermalization of the hot H atom with the lattice occurs in a time comparable to lattice relaxation times. If this case, a local lattice “hot spot” on the surface can be created where the H atom looses much of its energy and this hot spot can cause desorption of N$_2$. The efficiency or rate for transfer of initial kinetic energy of H (D) in adsorption well into mechanical energy in the lattice will be larger for D relative to H due to the smaller mass mismatch between gas atom and surface atom, and hence D will create a larger and more localized phonon excitation upon adsorption. Thus, we also anticipate an isotope effect $\sigma_D/\sigma_H$ $>$ 1. Both scenarios described are simply limiting behaviors for phonon-mediated-dynamic desorption. We anticipate that any more complicated phonon-mediated process will also have an isotope dependence $\sigma_D/\sigma_H$ $>$ 1.

V. SUMMARY AND CONCLUSION

In an unsuccessful attempt to observe hydrogenation of molecular N$_2$ adsorbed on Ru(0001) by incident H (D) at low T$_s$ [as a test of a proposed low-temperature mechanism for NH$_3$ production on Ru(0001)], we observed facile displacement of the N$_2$ by the incoming H (D). This displacement was kinetically important at all N$_2$ coverage and the displacement rate was independent of both adsorbed N$_2$ and H (D) coverage. We identify this process as due to dynamic displacement. By showing that the cross section for displacement by D atoms is roughly twice that for H atoms, we suggest that the physical basis for this dynamic displacement is phonon mediated, i.e., the creation of a hot H atom precursor or a lattice hot spot. We have also measured the displacement of Xe adsorbed on Pt(111) induced by CO adsorption. In this case, there is a threshold total coverage on the surface ($\Theta_{Xe} + \Theta_{CO}$) that is necessary to induce desorption of Xe so that the displacement is not prompt. This seems well described as a thermodynamic displacement mechanism.

ACKNOWLEDGMENTS

The authors wish to thank the Danish Research Council for supporting this work under Grant No. 9601724. L.D. and H.M. wish to acknowledge support from the Danish Research Academy, and C.A. the Swedish Foundation for International Cooperation in Research and Higher Education.