Coverage dependence of activation barriers: Nitrogen on Ru(0001)

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Exposing a Ru(0001) surface to an atomic beam of N produces a series of different states of atomic N adsorbed on the surface. For low atom doses, well-known low coverage states are produced, but for higher atom doses several previously unknown higher coverage states are sequentially filled up to a N coverage of almost 1 ML, N/Ru. These states show well-defined temperature programmed desorption (TPD) peaks. Recent density functional calculations demonstrate that the N–Ru bond strength decreases significantly with N coverage, and in fact that high coverage N adsorbate states are not thermodynamically stable relative to associative desorption. The observed high coverage states must, therefore, be only *metastable*, with lifetimes determined by the height of the barrier between gas phase N_2 and the adsorbed atomic state. Analysis of the TPD in combination with the theoretical adsorption energies allows us to estimate these coverage dependent barriers. Independent measurements of the coverage dependent barrier heights were also obtained via the technique of laser assisted associative desorption i.e., by measuring the translational energy distribution of desorbing N_2 via time of flight techniques induced by a short laser induced temperature jump. A barrier increases of ≥ 1 eV with N atom coverage was observed by both methods. © *2000 American Vacuum Society.* [S0734-2101(00)04004-5]

I. INTRODUCTION

The so called ''pressure gap'' in catalysis is an often quoted, but ill defined, rationale for the inability of ultrahigh vacuum (UHV) surface science studies to correctly simulate the conditions important in industrial catalysis. There are many aspects to this difference. In this article, we focus on one aspect that has not yet achieved much notoriety.

It is generally accepted that the barrier to dissociation of a gas phase molecule at a surface is often the rate-limiting step in many industrially important catalytic reactions. For example, the dissociative chemisorption of N_2 at the catalyst surface is the accepted rate-limiting step in NH_3 synthesis from N_2 and H_2. Most UHV surface science studies of dissociative chemisorption on metal surfaces, i.e., molecular beam studies, generally study the dissociative chemisorption on the bare metal surface in the limit of zero surface coverage. However, for industrially relevant conditions, the coverage of dissociated species is often quite high. While it is well recognized that a high coverage of the dissociated species can reduce the number of available dissociation sites, it is not well recognized that the presence of dissociated species on the surface can also strongly affect the height of the dissociation barrier at available sites. We will show here that barriers between gas phase molecules and the dissociated fragments can increase substantially with surface coverage due to what we believe are coverage dependent changes in the electron structure at the available sites. By way of example, we will discuss the coverage dependence of the barrier between gas phase N_2 and atomic N adsorbed on a Ru(0001) surface. It should be pointed out, however, that in

the use of supported Ru as a catalyst for NH_3 production, the high coverage of N studied here is not maintained.

There has been considerable interest in recent years in the interaction of N_2 with Ru(0001) since ruthenium makes a more active catalyst for NH_3 synthesis from N_2 and H_2 than the conventional reduced iron catalyst.[1] The dissociation of N_2 on Ru(0001) is strongly activated, with most barrier estimates in the range of $1–2$ eV.[2,3] In the process of dissociative chemisorption, the strong N_2 bond is broken and N becomes bound at the hexagonal-close-packed (hcp) three-fold sites.[4,5] While several lower coverage states for N adsorbed on Ru(0001) are now known ($\Theta_N = 0.25$, 0.33, and 0.36–0.44), there has been uncertainty as to the existence of higher coverage states and the maximum N coverage achievable. Many methods, including dissociative chemisorption of N_2, NH_3 (and N_2H_4), and electron or H-atom bombardment of NH_3, followed by an anneal to different surface temperatures, have been used to prepare the N-covered Ru(0001) surface.[6–10] However, the maximum coverage in each case is limited by the surface anneal temperature.

We have recently shown[11] that by dosing Ru(0001) with an atomic N beam, a series of different adsorbate N states can be prepared on the surface. For low atom beam doses, the known $p(2\times2)-N$, $(\sqrt{3}\times\sqrt{3})R-30°-N$ and heavy domain wall structures are produced. However, for higher atom doses we found sequential filling of several previously unknown and lower stability high coverage states, ultimately saturating at a maximum coverage of ≈ 1 ML N/Ru atom. The results showed a very large decrease in the thermal desorption peak temperatures with coverage, so that these high coverage states would not have been observable with surface temperatures used in previous experimental procedures to produce adsorbate coverages.

Density functional theory (DFT) calculations show that

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the binding energy for N on Ru(0001) decrease rather strongly with adsorbate coverage,[2,4,12,13] indicating strong indirect adsorbate–adsorbate repulsive interactions. This large short range repulsive interaction has been confirmed in scanning tunneling microscopy experiments.[5] The DFT calculations also indicate that the higher coverage atomic adsorbate states are in fact not stable relative to associative desorption. Thus, the observed high coverage states must therefore be only *metastable*,[11] with a lifetime determined by the height of the barrier between gas phase N_2 and the adsorbed N states.

In this article, we focus on determination of these barrier heights as a function of N coverage, Θ_N, on Ru(0001). In principle, there are two equivalent means to determine barriers. One could measure the barrier to dissociative chemisorption directly, e.g., via N_2 energy dependent molecular beam studies.[3] Alternatively, one can measure the barrier via measurements of N_2 energies following associative desorption.[14] Since they are essentially time reversed experimental scenarios, the results of both seemingly different measurements should be related by detailed balance. While detailed balance may in fact be a good approximation for low Θ_N, we wish to argue here that at high Θ_N we anticipate that detailed balance will *not* be a good approximation. DFT calculations[12] indicate that the minimum energy path for dissociation connects the transition state to N atoms at two adjacent three-fold hcp sites. At high Θ_N, it is unlikely that there is an ensemble of two adjacent empty hcp sites. Thus, it is unlikely that the phase space available for the dissociated state allows a gas phase N_2 molecule to follow the minimum energy path, i.e., from the transition state to dissociated state. In essence, there is a steric constraint to the dissociative chemisorption and dissociation can then only occur through some higher energy path. On the other hand, there is no such steric constraint for associative desorption at high Θ_N since adjacent hcp sites are likely occupied and must merely deform somewhat to encounter the transition state or minimum barrier configuration. At low Θ_N, steric constraints in dissociative chemisorption are probably minimal and thus should see the same barrier as associative desorption (providing surface diffusion is sufficiently rapid that it is not rate limiting in the desorption).

In part because of the steric constraints at high Θ_N, we describe here coverage dependent measurements of the minimum energy barriers between gas phase $N_2+Ru(0001)$ and the adsorbed N atom states via associative desorption. This allows us to focus entirely on electronic aspects affecting the barriers rather than also on steric effects. We use two methods to determine barrier heights. The first method indirectly estimates barriers by combining associative desorption energies determined from temperature programmed desorption (TPD) peak positions with the DFT calculations of N atom binding energies. The second method is a new technique which we call laser assisted associative desorption (LAAD). This technique measures the translational energy distribution of N_2 following associative desorption from a laser induced temperature jump. A lower bound to the barrier height is the

highest translational energy observed for the desorbing N_2. Both methods demonstrate that the total energy of the barrier between gas phase $N_2+Ru(0001)$ and the adsorbed N atom states increases substantially with N coverage.

II. EXPERIMENT

Many of the details of producing and characterizing a variable coverage of N atoms on a Ru(0001) surface have been given elsewhere,[11] so we will merely summarize here a few of the important experimental aspects. The Ru(0001) crystal was of very high quality; with no observable chemical impurities at Auger sensitivity and with a surface defect density of $\leqslant 0.25\%$ as determined by CO titration. A N atom beam produced by microwave discharge in neat N_2 was used for N dosing of the sample. Because the N atom beam contained an oxygen atom impurity, initial experiments showed some build up of adsorbed oxygen as well as adsorbed N on the surface with extended beam exposures. We therefore developed a ''scrubbing'' procedure to remove the surface O without depleting significantly the surface N coverage. This scrubbing procedure was based on exposure of the surface with adsorbates to a H atom beam. The key fact that made the scrubbing feasible was that the removal rate by gas phase H atoms (presumably via Eley–Rideal reaction) of adsorbed O was $\sim$ four times greater than that for adsorbed N as measured by the disappearance of Auger peaks. By a combination of dosing with the N atom beam, scrubbing and anneals of the surface to various temperatures, it was possible to obtain a N atom coverage Θ_N between 0 and 0.86 with little O atom impurity. Θ_N was determined either from the N atom Auger intensity or from the integrated intensity of the N_2 TPD spectrum. Both methods were in good agreement with each other. TPD spectra formed by associative desorption of the various adlayers were obtained with a differentially pumped quadrupole mass spectrometer (QMS) with a conical orifice of 5 mm diameter placed 2 mm in front of the surface. This ensured that only molecules desorbing from the front surface were detected in the TPD.

LAAD experiments where performed by irradiating the surface with a short laser pulse, after the Ru(0001) surface had been prepared with some specific Θ_N. For laser wavelengths in the near infrared, the laser is unlikely to induce any photochemical processes in the adsorbate adlayer or between it and the surface. Thus, for laser pulse lengths τ in the nanosecond regime, the resulting excitation of the surface is well described as a thermal temperature jump (T jump). Simple models give a good description of the surface thermal profile and show that the surface temperature profile basically follows the laser temporal profile (for τ in the 10–500 ns regime).[15–18] In our case, we use a laser pulse from a Light Age Alexandrite laser. This laser has a wavelength of $\sim$750 nm and $\tau=130$ ns. The light is incident on the surface at an angle of incidence of 57°, relative to the surface normal.

If the resulting T jump caused by the laser raises the surface temperature T_s above a temperature where associative desorption occurs, N_2 desorption is anticipated. However,

since the T jump is on the order of 130 ns, N_2 desorption is only occurring during this short time. Therefore, time of flight techniques (TOF) can be used to measure the translational energy distribution of the desorbing N_2. In our case TOF are measured via a differentially pumped QMS with the ionizer placed 97 mm in front of the surface. The ionizer viewed a small solid angle of 8×10^{-4} sr about the normal to the surface. In analyzing the TOF, careful attention was placed in calibrating all transit delays through the QMS and for the finite length of the ionizer. Because there is a lower background in the QMS signal at mass 30 than at mass 28, most LAAD experiments were performed with N^{15}.

Neglecting tunneling, we anticipate that the total energy of the desorbing N_2 is given roughly by the barrier height [relative to the $N_2 + Ru(0001)$ asymptote]. Because both internal excitation of the desorbing N_2 and translational excitation of N_2 are anticipated in associative desorption,[14] the highest translational energy observed in the TOF must represent a lower bound to the barrier height (after allowing for thermal broadening of the translational energy of $2k_BT_s$). If the lowest vibrational state ($v = 0$ N_2) is sufficiently populated to be observed in desorption, then this threshold measures the barrier height. Because laser irradiation is well known to cause surface damage under some circumstances,[19–21] we took special care to only irradiate with a few laser shots (typically 5–40) at a given spot on the surface while collecting TOF data. Then, the laser was moved to a new nonirradiated spot and the LAAD experiment was continued, etc. Typically, over 40 separate spots were studied on the surface for a given Θ_N. There was no observable difference in the TOF from spot to spot or with different number of laser shots at each spot. Nor were there any differences from day to day as the experiments were repeated under identical conditions. All indicate that laser damage is not a problem under our irradiation conditions. In addition, further investigations of the surface quality after LAAD showed no increase in surface defects as observed by CO titration or specular He atom scattering.

The T jump achieved for a given laser power was calibrated by measuring the TOF of CO laser desorbed from the Ru(0001) surface. In this case, TOF distributions were well described by Boltzmann distributions desorbing at $2k_BT_s$.

III. RESULTS AND DISCUSSION

N_2 TPD spectra (mass 14) at various Θ_N are given in Fig. 1. Detailed preparation procedures (N atom dosing, scrubbing, and surface anneals) and impurity content for the various adlayers are given elsewhere.[11] Measurements of Θ_N are appended next to the TPD spectra. At the lowest coverage, a single and broad desorption feature centered at ~800 K is observed. This TPD feature is well known from adsorption studies using filament assisted dissociation of molecular nitrogen[6] and thermal decomposition of ammonia[7] to result from the associative desorption of atomic nitrogen on the Ru(0001) surface. At higher Θ_N, we observe a series of desorption peaks at lower and lower surface temperatures that fill sequentially with increasing N atom coverage in the
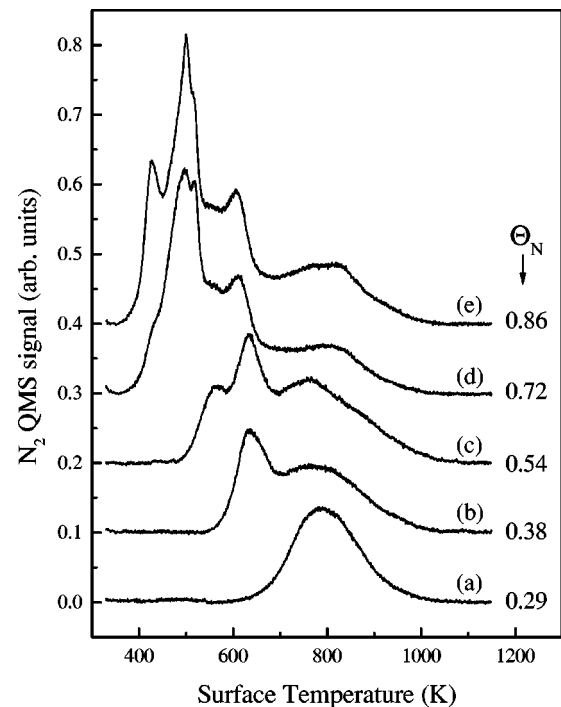

FIG. 1. N_2 TPD spectra for various coverages of nitrogen Θ_N adsorbed on Ru(0001). The preparation procedures for the curves labeled (a)–(e) are given in Ref. 11.

adlayer. While desorption peak positions do shift slightly with changes in N atom coverage, there seems to be five well defined peaks in the TPD spectra; 790, 635, 565, 500, and 430 K. Each TPD peak appears to saturate with N coverage before a new peak at lower T_s emerges. The five TPD curves shown in Fig. 1 were chosen to approximately represent saturation of each successive peak without filling in the next lower T_s desorption peak.

We attribute these results to associative desorption from a series of well-defined states with different N coverage. Low-energy electron diffraction (LEED) studies of the adsorbate overlayers showed that preparation procedure (a) (Fig. 1) yielded a well defined $p(2 \times 2)$ pattern, procedure (b) gave a $(\sqrt{3} \times \sqrt{3})R - 30°$ pattern and a coverage between (b) and (c) gave the heavy domain wall LEED pattern. Only very diffuse LEED patterns [other than the (1×1)] were observed under preparation conditions (c)–(e). Our interpretation is that the peak at 790 K is desorption from low coverage up to $\Theta_N = 0.25$ and the peak at 635 K is desorption from the state with $\Theta_N = 0.33$. In approximate agreement with measured Θ_N values, we tentatively assign the peak at 565 K to an adlayer with $\Theta_N \approx 0.5$, the peak at 500 K to an adlayer with $\Theta_N \approx 0.75$, and the peak at 430 K to the adlayer with $\Theta_N \approx 1$. None of these higher coverage states ($\Theta_N \approx 0.5$, 0.75, and 1) have been observed previously and their structure is presently unknown. The assignment chosen facilitates comparison of the experimental results with theoretical calculations presented below of coverage dependent adlayer stability.

The adsorption energies E_N for a series of known and (previously) unknown higher coverage N adsorbate states on
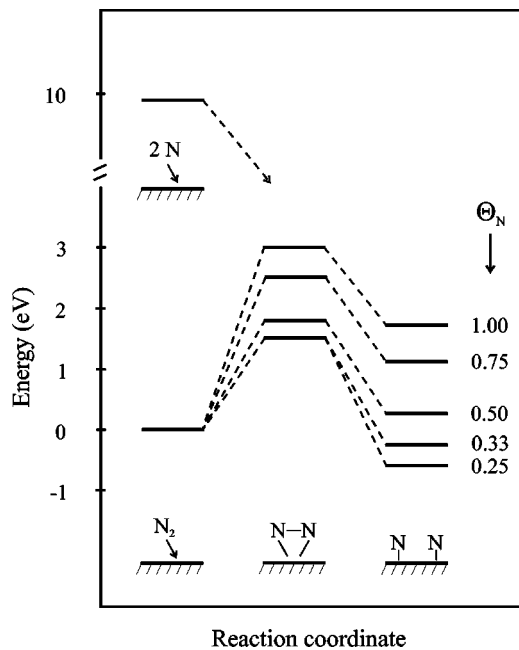
FIG. 2. Schematic energy diagram for the interaction of N_2 and 2N with the Ru(0001) surface. The origin of energy is taken as the N_2+Ru(0001) asymptote. The left side is the entrance channel for dissociative chemisorption or the exit channel for associative desorption. The right-hand side is the atomic adsorbed state and is based on the DFT RPBE adsorption energies. The center is the estimate of $V^*(\Theta_N)$ by combining the theoretical adsorption energies with the desorption energies obtained from the TPD. Note that dissociating N_2 in the gas phase provides enough energy to readily overcome all barriers and form all adsorbate states.
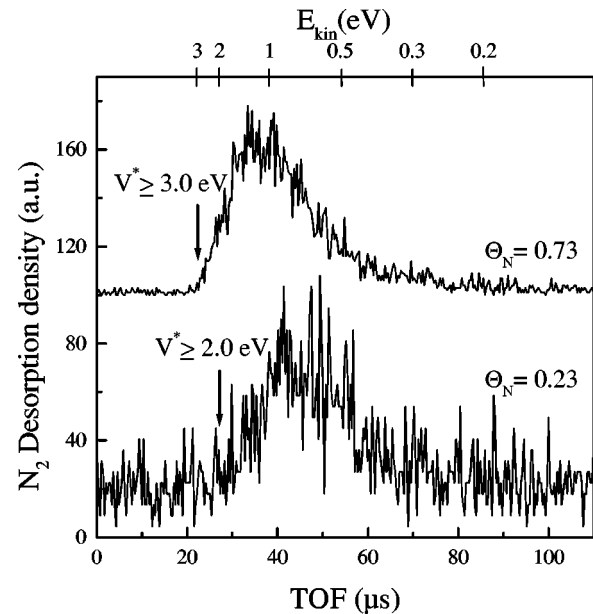

FIG. 3. TOF curves for $N_2{}^{15}$ associative desorption induced by a laser T jump of 130 ns duration (LAAD). Results are presented for two N coverages: $\Theta_N = 0.23$ (enlarged by a factor of 6) and $\Theta_N = 0.73$. The $N_2{}^{15}$ kinetic energy is indicated on the top axis. The arrows mark lower limits to the overall energy of the barrier (relative to N_2 in the gas phase).

the Ru(0001) have recently been calculated using DFT.[2,4,12] Initial calculations were based on using the so-called PW91 exchange-correlation functional.[4,12] It has recently been suggested that a slightly different functional, the so-called RPBE functional, gives improved adsorption energetics.[22] Calculations with both functionals predict the same important trend, i.e., that the N atom binding energy decreases drastically with N coverage. A summary of the calculations is given as the right-hand side of Fig. 2. This shows that the stability of the adsorbate states decreases with N coverage, from -0.29 eV/N atom for $\Theta_N = 0.25$ to $+0.86$ eV/N atom for $\Theta_N = 1$, relative to the gas phase molecule. In fact states with $\Theta_N \geq 0.5$ are not predicted to be thermodynamically stable on the surface. Since these high coverages were observed here, they must represent *metastable* states on the surface.

Assuming all desorption peaks are due to second order associative desorption, conventional Redhead analysis allows us to estimate desorption energies (E_{des}) for each "state" from the desorption temperature peaks. Using a pre-exponential for desorption for all states from Tsai and Weinberg,[23] we obtain $E_{des} = 2.0, 1.6, 1.4, 1.3$, and 1.1 eV, respectively, for desorption at the 790, 635, 565, 500, and 430 K peaks, i.e., a large decrease in E_{des} as the coverage is increased. The value of $E_{des} = 2.0$ eV obtained here for the lowest coverage state ($\Theta_N = 0.29$) is in good agreement with earlier experimental work; 1.91^{23} and 1.97 eV.[6]

$E_{des}(\Theta_N)$ estimated from the thermal desorption experiments represents the energy difference between the barrier

$V^*(\Theta_N)$ and the adsorbate state. It should be noted that although $V^*(\Theta_N)$ is the barrier for associative desorption, it is measured relative to the N_2+Ru(0001) asymptote, i.e., $E_{des}(\Theta_N) = V^*(\Theta_N) - 2E_N(\Theta_N)$. The notation emphasizes that all three terms are functions of the N coverage. Combining $E_{des}(\Theta_N)$ obtained here from the TPD measurements with $E_N(\Theta_N)$ from the DFT calculations allows predictions of $V^*(\Theta_N)$. A summary of this is shown in Fig. 2. It is immediately apparent in Fig. 2 that V^* increases substantially with Θ_N.

A direct method of estimating the barrier height to associative desorption is the technique of laser assisted associative desorption outlined earlier. TOF results for LAAD for a N coverage of 0.23 and 0.73 ML are given in Fig. 3. Flight times are corrected for all transit delays and the corresponding translational energy of $N_2{}^{15}$ is indicated on the top axis. We note immediately that the associatively desorbing molecules are indeed hyperthermal due to their passage over the barrier. There is no thermalized component at $2k_B T_s \sim 0.2$ eV. It is also apparent that the signal to noise ratio for $\Theta_N = 0.23$ is significantly lower than that for $\Theta_N = 0.73$. This is because the desorption yield drops strongly with N coverage.

Because both strong vibrational and translational excitation of the desorbing N_2 are anticipated in this associative desorption,[14] the measured TOF curve represents a sum of TOF curves for each individual vibrational state weighted by the population with which it is produced in the associative desorption. If $v = 0 N_2$ is sufficiently populated to be detectable, then the highest translational energy observed corresponds to the barrier height (after allowing for thermal broadening of the translational energy of $2k_B T_s$). If only

higher vibrational states are populated sufficiently to be observed, then this high translational energy threshold forms a lower bound to the barrier. Details of the theoretical analysis will be presented elsewhere.[24] Here we simply mark in Fig. 3 with arrows the bounds to the barrier heights determined by the analysis.

The results in Fig. 3 are in qualitative disagreement with Murphy *et al.*[14] who used a somewhat different technique to measure the state resolved TOF distribution of N_2 associatively desorbing from Ru(0001). They observed that desorption was predominate at low translational energies, but that the desorption distribution tailed to high energies. It has been suggested that their results are strongly influenced by desorption from steps or defects since these are known to strongly reduce the barrier to dissociation of N_2 on Ru(0001).[2]

The key result in Fig. 3 is that the barrier must increase with Θ_N; from 2 to 3 eV as Θ_N increases from 0.23 to 0.73. The increase of the barrier by ≥ 1 eV is nearly identical to that obtained by combining the TPD measurements with the theoretical atomic adsorption energies (see Fig. 2). We also note that there is reasonable, but not perfect, agreement in absolute determinations of barrier heights from LAAD and the indirect method. There are, however, limitations for both methods in determining absolute barriers and these will be discussed elsewhere.[24]

IV. CONCLUSIONS

There has been considerable confusion as to the maximum coverage obtainable for N adsorbed on Ru(0001) and whether high coverage adsorbate states exist on this surface. We report here a way to produce high coverage states of nitrogen atoms on Ru(0001) using a N atom beam. The results show that in fact a coverage of $\Theta_N \approx 1$ can be formed by atom dosing. A whole series of states of different coverage are observed on the surface as separate TPD peaks by varying the atom dose. The lowest coverage states agree with previous observations, but the higher ones are entirely new.

DFT calculations for N adsorbed on Ru(0001)[2,4,12] indicate that the higher coverage states are in fact not stable relative to associative desorption. They must therefore be *metastable*, with a lifetime determined by the height of the barrier between gas phase N_2 and the adsorbed N states.

Combination of the experimental TPD results with the DFT calculations allows us to estimate these coverage dependent barriers. We find that the overall barrier height (relative to gas phase N_2) increases significantly with N coverage and this is in fact a necessary aspect of the metastability of the highest coverage states.

Independent confirmation of this increase in overall barrier height was obtained via the technique of laser assisted associative desorption, i.e., by measuring the translational energy distribution of desorbing N_2 via TOF techniques induced by a short laser T jump. Barrier increases of ≥ 1 eV with Θ_N were observed by both methods.

Since barriers have been measured in all cases via associative desorption, the change in overall barrier height with Θ_N must represent a purely electronic effect, with no influence of steric constraints. We believe that the decrease in desorption energy and increase in overall barrier height (relative to gas phase N_2) with Θ_N observed here are very likely quite general phenomena since the origin is in general changes in electronic structure induced by surface adsorption. Consequently, we anticipate that these coverage dependent energy changes may be an important aspect of the so-called pressure gap in catalysis in some cases. For example, in NH_3 synthesis over reduced Fe catalysts, the coverage of adsorbed N is quite high and does play a significant role in rate limiting this process. On the other hand, for NH_3 synthesis over supported Ru, the coverage of adsorbed N is much lower and in fact this is one reason for its higher activity.

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