Effect of Translational Energy on the Chemisorption of N_2 on Fe(111): Activated Dissociation via a Precursor State

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The initial dissociative chemisorption probability of N_2 on Fe(111) is found to increase by a factor of $\simeq 10^5$ with increasing kinetic energy, rising from $\simeq 1\times 10^{-6}$ at $\simeq 0.09$ eV to over 1×10^{-1} at 4.3 eV. This probability also increases with decreasing surface temperature, suggesting that reagent energy provides access to an intermediate state, such as α-N_2, whose population also increases with kinetic energy, consistent with the accepted mechanism at low energies.

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Dissociative chemisorption is one of the most elementary of all surface chemical reactions and is a key step in most complex surface chemistry. However, such bond-breaking processes are often associated with a sizable activation barrier, making dissociative chemisorption the rate-limiting step in many industrially important catalytic systems. A particularly good example is the Haber-Bosch synthesis of ammonia from N_2 and H_2 over iron-based catalysts, where reaction is limited in part by the dissociation of the N_2.[1,2] While creation of free sites for chemisorption may also be important in the kinetics of this system, it is clear that dissociation of N_2 is a key step in this process.[3] Model studies have focused on the N_2/Fe(111) system, which has a relatively high initial dissociative chemisorption probability,[2-5] and for which a microscopic understanding of the dissociation mechanism is now beginning to emerge. Recent studies reveal the presence of two weakly chemisorbed states on this surface,[6-10] γ-N_2 and α-N_2, the latter of which has been identified as the precursor to dissociation at close-to-ambient temperatures.[6-11] The binding energies of these states are known[9,10] and kinetic rate expressions have been deduced which can account for a wide variety of observations over the range $\simeq 70$ to 700 K.[10] However, the dissociative chemisorption probability is always found to be extremely small, $\simeq 10^{-6}$,[2,4,11] and the energetics of this system is somewhat puzzling. The dissociation probability is found to decrease with increasing temperature, consistent with the precursor picture, but indicating that the final barrier to dissociation lies *below* the energy level for the approaching molecule. This contrasts with the traditional view of dissociative chemisorption where low reaction rates are attributed to a barrier between precursor and atomic states.[12] The actual potential-energy diagram deduced for the reaction coordinate of this system shows no evidence of a potential barrier.[10]

Other recent studies of dissociative chemisorption [e.g., N_2[13,14] and CH_4[15] on W(110)] have shown that translation activation can be highly efficient at promoting such unreactive systems. However, for a system passing through a precursor, there are two opposing possibilities: Increasing translation energy might be expected to activate reaction if it is hindered by a potential barrier, yet trapping into a precursor would be expected to become less efficient with increasing energy.

We have now completed a series of molecular-beam experiments directed at probing the dynamics of the N_2/Fe(111) system and have observed behavior consistent with both sets of previous studies. We find that kinetic energy does indeed greatly enhance the dissociative chemisorption of N_2 on Fe(111), but with a persistent surface-temperature dependence that suggests that reaction occurs via a precursor state even at high energies. Thus we believe that reagent energy serves to provide access to this state rather than to promote direct dissociation.

Most aspects of the experimental apparatus and techniques employed are the same as those described previously.[13-16] Here we summarize our approach with emphasis on features peculiar to the present system. Supersonic N_2 beams are directed at an Fe(111) crystal mounted in a UHV chamber on a manipulator which permits accurate control of the incidence angle and provides for accurate temperature control permitting cooling to $\simeq 110$ K. The crystal was prepared and cleaned as described previously,[4] with use of sputter-anneal cycles to maintain a clean surface. Our crystal has a high bulk concentration of dissolved nitrogen which results from extensive previous dosing and which reduces diffusion of nitrogen atoms into the bulk. This allows Auger coverage measurements to be used to determine dissociation yields at temperatures where diffusion might otherwise cause problems.[4] The major surface contaminant in this work was oxygen, which deposited as water (introduced into the system during sputtering and from the Auger electron gun), present at levels of $\simeq 0.05$ monolayer during most measurements, as determined by Auger-electron spectroscopy (AES). Inspection of data obtained over a wide range of conditions indicated that the N_2 dissociation probability falls approximately linearly with O coverage, as observed previously,[17] so that such contamination introduces only small uncertainties into the results. All other contaminants were below AES detection limits and a sharp low-background (1 × 1) LEED pattern was obtained. Beam energies are varied by our changing the nozzle temperature from 300 up to 2000 K, and by our seeding in H_2 or He. These energies are determined from flight times from a high-speed chopper to a differentially pumped rotatable mass spectrometer.[16]

Initial sticking probabilities, S_0 (corresponding to dissociation on the clean surface), are determined from the initial slopes of coverage versus exposure curves. Here all coverages are estimated from Auger-electron spectroscopy, on the assumption that the N-atom coverage is proportional to the N(380 eV)/Fe(560 eV) peak-to-peak ratio.[4] Exposures are varied by control of the beam dose time where its flux is determined from the partial-pressure rise produced on the system.[16] This method permits accurate *relative* sticking probabilities to be obtained, but absolute values require calibration of the AES measurements,[4] as well as accurate knowledge of the beam profile, pressure calibration, and system pumping speed. While this has been done, we prefer to place the measurements on an absolute scale by comparison with sticking probabilities determined by an alternative direct method based on measurement of the fraction of the beam reflected by the surface.[16,18] This technique is only applicable for S_0 values $\gtrsim 5\times 10^{-2}$, which we found to be attainable only for $E_i \gtrsim 3$ eV. These energies are obtained with a tungsten nozzle resistively heated up to 2000 K and by the employment of H_2 as the seeding gas. The two methods (absolute AES and absolute S_0 determination) give good agreement within experimental uncertainties, but all results reported here are based on the latter approach.

The effect of translation energy on the initial sticking probability of N_2 on Fe(111) for normal incidence and at a surface temperature, T_s, of 520 K is displayed in Fig. 1. The data points correspond to the measured S_0 values and are placed at the mean beam kinetic energy. As such, these results represent averages of S_0 over the beam kinetic energy spread. The solid curve is the result of a nonlinear least-squares fit to the data points which takes into account this spread and which therefore corresponds to the function $S_0(E)$ for monoenergetic incidence energy. This function is given by

$$\log_{10}(S_0) = a + b[1-\exp(-cE)] + [1-\exp(-dE)], \quad (1)$$

where $a=-6.6397$, $b=4.8608$, $c=2.2125$, and $d=0.35674$. In this representation 10^a is the sticking probability in the limit of low energy, the second term governs the initial dramatic rise in S_0, while d controls the gentler increase at high energy. No allowance has been made in this analysis for possible contributions due to differing concentrations of vibrationally excited molecules in the beam; however, comparison of data obtained at the same kinetic energy but with different source temperatures indicate that such contributions will be small.

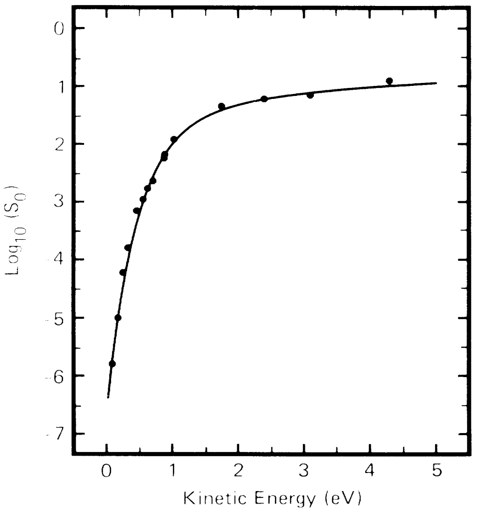

FIG. 1. Effect of incident energy on the dissociative chemisorption probability of N_2 on Fe(111) at normal incidence and at a surface temperature of 520 K.

The sticking probability for any arbitrary incidence energy, E_i, and angle, θ_i, dependence can be obtained from Eq. (1) by evaluation of the mean over this function. For a Maxwellian gas at 300 K we obtain S_0(300-K gas) $=1.2\times 10^{-6}$ if we assume total energy scaling, and S_0(300-K gas) $=5.7\times 10^{-7}$ if we assume scaling with the so-called "normal energy," $E_n = E_i \cos^2\theta_i$. Selected measurements for $\theta \neq 0°$ are found to be inconsistent with both limiting scaling laws.[19] Notwithstanding this uncertainty, it is clear that the present results are in good agreement with previous measurements on this system, which place S_0 at 10^{-7}–10^{-6},[3] and $\simeq 5\times 10^{-6}$,[10] for ambient N_2 gas.

While the data in Fig. 1 were obtained at 520 K, we have also investigated the surface-temperature dependence of the initial sticking probability at various energies. To minimize the possibility of our having different levels of contamination or surface diffusion, the surface temperature is kept at the same value ($\simeq$600 K) until just prior to beam exposure, after which the temperature is returned to this temperature for AES measurement of the coverage. In every case we find a small but definite increase in S_0 with *decreasing* temperature. Typically, S_0 increases by about 50% on going from 600 to 300 K. Figure 2 shows results obtained for an incidence energy of 1.05 eV at normal incidence. Qualitatively similar behavior has been reported previously[11] for dissociative chemisorption of ambient N_2 gas. In this gas S_0 was observed to roughly double on going from $T_s = 423$ to 214 K.

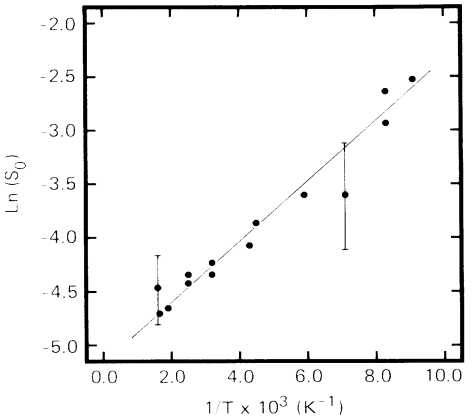

FIG. 2. Effect of surface temperature on the dissociative chemisorption probability of N_2 on Fe(111) at normal incidence and at a kinetic energy of 1.05 eV. Here the sample was kept cold for an additional 200 s following exposure at $T_s > 150$ K, in order to ensure that reaction had gone to completion before warming. The solid line is intended to serve as a guide to the eye and has a slope equivalent to -270 K. Selected error bars indicate approximate 95% confidence level in relative values.

The sensitivity of dissociative chemisorption to surface temperature is often interpreted in terms of competing rates for dissociation and desorption out of a molecular precursor.[11,20,21] Indeed, there is considerable evidence that dissociation proceeds via such a precursor in this system, at least a low energies.[6-11] The slope of Fig. 2 is then interpreted as an energy corresponding to the difference in activation barriers between these two paths; we obtain a phenomenological activation energy of $E^* = -0.023 \pm 0.006$ eV (-270 ± 70 K), which is in reasonably good agreement with the estimate of -0.034 eV in Ref. 11. However, this agreement may be somewhat coincidental, since the processes involved in these two cases may be rather different.[19] Note that this kinetic model assumes that all precursor molecules either desorb or dissociate at a given temperature. At low temperatures, this may not be true. If the temperature is raised too early, the results will apply to a higher and poorly characterized temperature. Clearly at low enough temperatures, an essentially infinite dwell time would be required. In practice, we find that results become sensitive to this dwell time only for surface temperatures below 150 K, requiring progressively longer times as the temperature is decreased. To minimize such errors, the data of Fig. 2 corresponding to $T_s < 150$ K were obtained with a delay of 200 s following exposure. As expected, shorter delays resulted in somewhat smaller inferred values for S_0. Since these data points are subject to this additional uncertainty, it is possible that they should be omitted in the estimation of the slope.

To reconcile the precursor model with the observed kinetic energy dependence, we propose that access to the intermediate state is blocked by a potential barrier. More precisely, we picture *a distribution of barriers*, the form of which can be obtained phenomenologically by differentiation of Eq. (1).[14,16,22] Note that at low energies its form may include contributions from molecules that overcome the barrier after first being trapped into the γ state.[9]

To test this picture, we have sought to correlate directly the increase in S_0 with population of the α-N_2 state. Thus we have ramped the surface temperature immediately ($\simeq 20$ s delay) following exposures at 120 K in efforts to detect the characteristic α-N_2 state desorption profile which is peaked at $\simeq 160$ K.[10,11] These have been observed and are found to closely resemble those reported previously,[10] except that the high-temperature tail was found to extend to about 250 rather than 230 K.[19] We find that population of this state does indeed increase with increasing kinetic energy, with an estimated trapping or sticking probability into this state of 0.05 ± 0.01 at 1 eV and $T_s = 120 \pm 10$ K, rising to 0.12 ± 0.002 at 3.9 eV. Long delays prior to ramping lead to smaller desorption features, but no systematic study has been made of this behavior. The observed sticking coefficients are to be compared to estimates of < 0.01 for adsorption of ambient gas (mean energy $\simeq 0.05$ eV) in this temperature range.[9,11] However, in this latter case, the α state is believed to be populated via the less strongly bound γ state,[9] for which the trapping probability is $\gtrsim 0.7$ at these low energies. Such a mechanism is unlikely to apply to the above results as velocity and angular distribution measurements reveal that trapping into the γ state falls rapidly with increasing collision energy.[19]

As further evidence in favor of a precursor mechanism, we observe that the saturation coverage of N atoms is found to be independent of incidence energy. Even at 4 eV, we are not able to increase the saturation coverage beyond that obtained with an ambient gas. This contrasts with previous findings for the dissociative chemisorption of O_2 (Ref. 16) and N_2 (Refs. 13 and 14) on W(110), which are believed to proceed by a direct mechanism and for which the saturation coverage is energy dependent. In the case of reaction via a precursor, insensitivity to incident energy can occur if all memory of the initial conditions is lost prior to dissociation.

We also note that the dramatic activation of chemisorption in this system appears to contradict earlier work by Böheim, Brenig, and Engel,[23] who failed to see enhanced dissociation with increasing kinetic energy in the N_2/Fe(110) system. Specifically, they concluded that $S_0 < 10^{-5}$ at 0.67 eV. It may be that higher energies are required for activation on this less reactive surface; only further work can resolve this apparent discrepancy.

In conclusion, we have shown that the dissociative chemisorption probability of N_2 on Fe(111) can be dramatically activated by initial kinetic energy. However, rather than promoting a direct dissociation process, we believe that this energy serves to overcome a potential barrier to an intermediate molecular species. The most likely candidate here is the α-N_2 state, which is found to be accessed with higher probability with increasing collision energy and which is known to be the precursor to chemisorption at thermal energies. However, it is possible that at high collision energies the intermediate may be significantly different, possibly being better described as a distribution of species which are chemically similar to and which include the α state. The most important difference here would be that the intermediate might have rather different kinetic properties from that populated at low energies.

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