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Role of Steps in N₂ Activation on Ru(0001)

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Using adsorption experiments and density functional calculations we show that N₂ dissociation on the Ru(0001) surface is totally dominated by steps. The measured adsorption rate at the steps is at least 9 orders of magnitude higher than on the terraces at 500 K, and the corresponding calculated difference in activation energy is 1.5 eV. The low barrier at the step is shown to be due to a combination of electronic and geometrical effects. The consequences for Ru as a catalyst for ammonia synthesis are discussed.

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It has long been realized that steps at metal surfaces may provide sites with particular reactivity. The concept of special "active sites" associated with low-coordinated surface atoms was introduced as early as 1925 by Taylor [1]. Steps are generally found to be more reactive than terraces [2] and, most recently, it was observed directly by using the scanning tunneling microscope (STM) that NO preferentially dissociates at steps on a Ru(0001) surface [3]. For the H₂/Si(100) system, experiments as well as density functional calculations have shown that the steps dominate the reactivity [4]. It is, however, usually hard to quantify the difference in reactivity between, e.g., steps and planar surfaces. The exponential dependence of the reactivity on the barrier height means that the lowest barrier process dominates completely at ordinary temperatures.

In this Letter we report thermal rate measurements and density functional calculations of the activation barriers for N₂ dissociation on the close-packed Ru(0001) surface and at steps on this surface. Both the experiments and the calculations show N₂ dissociation to take place at steps with a dissociation barrier at about 0.4 eV. In the experiments we find the rate on the planar terraces to be at least 9 orders of magnitude lower than at the steps at 500 K, corresponding to a difference in the activation barrier of at least 0.9 ± 0.3 eV. The corresponding calculated barrier difference is 1.5 eV. This enormous difference in reactivity between steps and terraces has two consequences. First, it means that the rate of N₂ dissociation on Ru(0001) is completely dominated by as little as a fraction of a percent of steps on the surface. All thermal surface science experiments of N₂ adsorption on single crystal Ru(0001) have thus been dominated by the steps on the surface. Second, it means that the ammonia synthesis reaction should be extremely structure sensitive on Ru. N₂ dissociation is rate limiting in this process and essentially all the catalytic activity is thus expected to be related to steps. For nanoparticles the step density depends strongly on the particle size, suggesting that the catalytic activity of Ru

catalysts for ammonia synthesis should be dependent on the catalyst particle size.

Because of the renewed interest in Ru as a catalyst for ammonia synthesis [5], there have been a number of recent studies of the synthesis rate and N₂ dissociation rate on Ru surfaces and catalysts. Measurements of the N₂ dissociation rate over Ru catalysts show a process with an activation barrier between 0.3 and 0.6 eV [6,7]. This is in fair agreement with a dissociation probability for nitrogen of 10^{-12} at 300 K measured over three different Ru surfaces [8]. Recent time-of-flight thermal desorption measurements shows desorbing molecules to have average kinetic energies of 0.65 eV, confirming a barrier for adsorption of this order of magnitude [9]. Contrary to this, density functional calculations have shown a dissociation barrier of 1.4 eV [10], and recent calculations using a more accurate exchange-correlation description indicate an even higher barrier [9]. Molecular beam scattering experiments also indicate a barrier between 1 and 2 eV for the N₂ dissociation [11]. One possibility of reconciling the different experiments and calculations is that the thermal experiments do not in fact measure the dissociation process on the terrace sites, but measure the rate at the few step sites on the single crystal surface. If the steps dominate for the flat surfaces they should also dominate for the nanoparticle catalysts, and the agreement between the single crystal surface thermal measurements and the catalyst kinetics becomes understandable.

The thermal experiments are performed in an ultrahigh vacuum apparatus with a base pressure of 10^{-10} mbar. The setup which is described in Ref. [12] is, apart from standard surface science tools, equipped with a high pressure cell where the sample can be exposed to gas pressures of up to 10 bars at elevated temperatures without destroying the vacuum. The nitrogen exposures are done with pure nitrogen (N60 quality further purified by passing it over a dried molecular sieve and a reduced Ni catalyst at room temperature) at pressures between 0.1 bar and

3.5 bars and at temperatures between 300 and 700 K. The reduced Ni catalyst exposes roughly 10 m^2 of metallic Ni to the gas meaning that impurities such as H_2 , O_2 , CO , and most hydrocarbons, if present, would be adsorbed and removed prior to N_2 entering the high pressure cell. No sign of impurities could be observed by x-ray photoelectron spectroscopy (XPS) or temperature programmed desorption (TPD) after prolonged exposures, except at 300 K, where small amounts of hydrogen were observed. The relatively high gas pressures ensure that the impinging gas molecules are in thermal equilibrium with the surface. The nitrogen coverage was measured with XPS or TPD monitoring both mass 14 and 28 to distinguish between CO and N_2 . The maximum coverage was determined to be 0.25 ML (monolayer) by comparing the N_2 TPD area to the CO saturation coverage at 300 K (see also Ref. [8]). Gold is deposited on the surface by evaporation; the coverage is measured with ion scattering spectroscopy (ISS) or XPS. CO was found to be adsorbed from the background when the crystal was kept below 500 K for a prolonged time. In order to avoid this, the crystal was in general kept above 500 K. In the cases where the exposures were given below 500 K the crystal was kept above 500 K until isolated in the high pressure cell. In this manner the CO adsorption could also be eliminated for the low temperature experiments. It should be mentioned that leaving the crystal above 500 K for a prolonged time was found to reduce the reactivity, probably due to dissociation of CO at the steps.

The density functional calculations have been performed by expanding the wave functions in plane waves and describing the ion cores by nonlocal ultrasoft pseudopotentials [13]. Plane waves with kinetic energies up to 25 Ry and 18 special \mathbf{k} points have been used to sample the first Brillouin zone. Exchange and correlation effects are described within the generalized gradient approximation [14,15]. The self-consistent electron density is determined using the PW91 (Perdew-Wang-91) exchange-correlation functional by iterative diagonalization of the Kohn-Sham Hamiltonian, Fermi population of the Kohn-Sham states ($k_B T = 0.1 \text{ eV}$), and Pulay mixing of the resulting electronic density [15]. All total energies have been extrapolated to $k_B T = 0 \text{ eV}$. Complete structural relaxation is performed for each configuration studied. The structures and electron density have then been used to calculate the interaction energies using the more accurate RPBE (revised Perdew-Burke-Ernzerhof) functional [15]. The use of the non-self-consistent electron densities introduces a negligible error due to the variational principle [15]. The same method gives an excellent description of N_2 adsorption and dissociation on $\text{Fe}(111)$ [16]. The $\text{Ru}(0001)$ surface is modeled by a three layer slab repeated periodically with a (2×2) , (2×3) , or (2×4) unit cell parallel to the surface.

The measured dissociative sticking probability for N_2 on a $\text{Ru}(0001)$ single crystal surface is shown in Fig. 1. The activation energy is determined to be $0.4 \pm 0.1 \text{ eV}$ and it

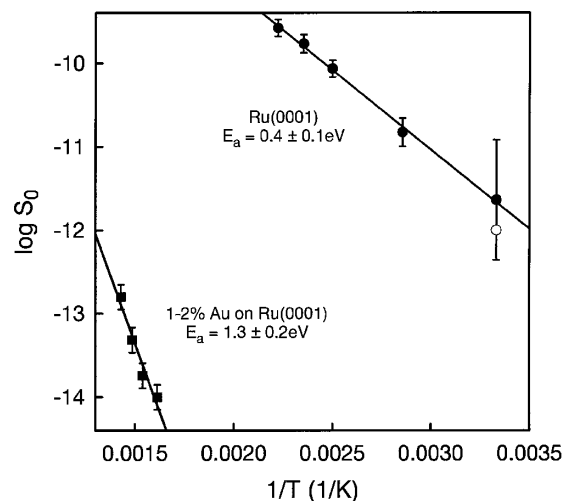


FIG. 1. Arrhenius plot of measured thermal sticking coefficients of N_2 on a clean $\text{Ru}(0001)$ surface and the same surface covered with 0.01–0.02 ML of gold. The open circle is the result from a similar measurement at room temperature by Dietrich *et al.* [8].

is seen that at room temperature the measured dissociation rate agrees well with the room temperature measurement by Dietrich *et al.* [8]. Kinetic models for ammonia synthesis using this dissociation rate predicts well the ammonia synthesis rates over a Ru single crystal [12].

The calculated potential energy diagram for N_2 dissociation on a $\text{Ru}(0001)$ surface using the RPBE functional is shown in Fig. 2. The barrier is 1.9 eV and even if we correct for the zero-point energy in the N-N coordinate, the barrier will still be higher than 1.75 eV, in sharp contrast to the measurements.

In order to investigate whether steps might be responsible for the low barrier dissociation process in Fig. 1 we exploit the results of a recent STM study by Behm and co-workers [17]. Here it has been shown that small amounts of Au deposited on a $\text{Ru}(0001)$ surface will preferentially decorate the steps. Metal surfaces are not flat on the macroscopic scale; there will always be a small concentration of steps. The $\text{Ru}(0001)$ surface used in this study is oriented to within 0.5° and has therefore an average step density of 1% or less. We therefore add Au to our $\text{Ru}(0001)$ surface, and monitor the nitrogen coverage after a fixed thermal N_2 dose as a function of the amount of Au added. Less than 1% of a monolayer of Au suppresses the nitrogen coverage and therefore the N_2 dissociation rate, substantially (Fig. 3). The only reasonable interpretation of this is that the N_2 dissociation observed before was dominated by less than 1% steps which are blocked by Au deposition.

To quantify this difference in the N_2 dissociation rate we have measured the dissociation probability of nitrogen on the gold passivated surface (Fig. 1). We find an activation barrier of $1.3 \pm 0.2 \text{ eV}$ much closer to the calculated barrier on the terrace, cf. Fig. 2. The rate on the Au passivated surface is about 7 orders of magnitude lower at

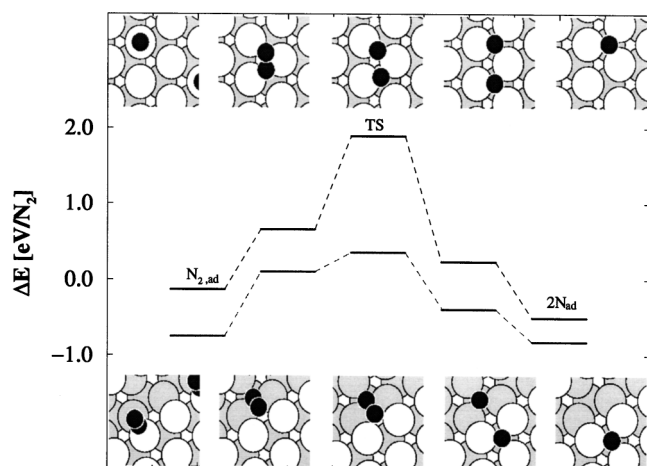


FIG. 2. Results from density functional calculations comparing N_2 dissociation on a terrace and at a step on Ru(0001). The upper curve shows the adsorption and transition state (TS) energies for the dissociation on the terrace, whereas the lower curve shows the same energies at the step. The configuration is shown in each case. The Ru(0001) terrace calculations have been performed using a (2×2) unit cell. The step is modeled by using a (2×3) or (2×4) unit cell, removing one or two rows of Ru atoms. The large cell is used to avoid interaction with the adjacent step in the cases where a N atom is adsorbed at the bottom of the step. The energy zero is taken to be the energy of the N_2 molecule in the gas phase.

500 K, and considering that there are less than 1% step sites on the surface the rate at the terrace is at least 9 orders of magnitude lower than at the step. The results are still upper bounds on the rate of dissociation on the terraces of the Ru(0001) surface. We cannot rule out the possibility that, e.g., thermally induced Au vacancies at the steps expose Ru step sites that could be responsible for the chemical activity even for the Au passivated sample.

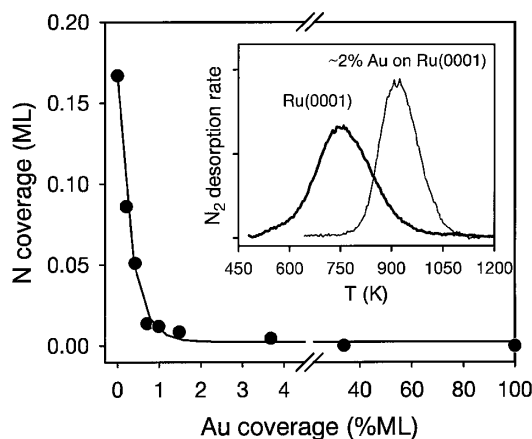


FIG. 3. The N coverage on Ru(0001) after a fixed dose of N_2 (0.1 bar, 1 min, 500 K) as a function of Au coverage on the surface. The inset shows TPD spectra from a clean Ru(0001) surface and the same surface covered with 0.01–0.02 ML of gold; the heating rate was 4 K/s. The coverage of N was 0.15 ML for both spectra.

We have also compared the reactivity of the clean and the gold passivated Ru(0001) surfaces in molecular beam experiments, where N_2 molecules with kinetic energies of 0.9–1.1 eV and in highly excited vibrational states are beamed onto the surface. In these experiments the clean Ru(0001) surface is only about 2 times more efficient in dissociating N_2 than the gold passivated surface. This suggests that the high energy N_2 molecules in the beam mostly measure the activity of the flat terraces even when the more active steps are not passivated. This is reasonable since for the high energies used in the beam experiment the activity of the step sites and the terrace sites is comparable and the terrace sites will dominate through the higher number of sites. In agreement with Romm *et al.* [11] our beam experiments show that N-N vibrational energy is more efficient than translational energy in promoting the dissociation rate. Hence the N_2 dissociation on the terraces might be dominated by the reaction of vibrationally excited N_2 molecules. Comparison between the calculated barrier and the experiments is therefore not straightforward, and only direct simulations of the dissociation dynamics can connect the two.

We have also calculated the potential energy diagram for N_2 dissociation at a step. The simple geometry we have used is shown in Fig. 2. We have attempted to dissociate N_2 both parallel to the step and perpendicular to it. Both geometries gave a lower barrier than for the flat surface, but the perpendicular geometry shown in Fig. 2 gave by far the lowest energy path. The path is found by first varying the N-N distance and minimizing all other N_2 degrees of freedom. At the local minima and at the transition state we also included the effect of relaxations of the Ru substrate. The barrier we find at the step is very close to the experimentally observed value without Au. This strongly supports the interpretation that the N_2 dissociation is dominated by steps.

The calculations show that the difference in the binding energy of atomic nitrogen at the step sites and the terrace sites is quite small. This agrees with the STM observation that atomic nitrogen does not block the step sites on Ru(0001) after the adsorption of NO at room temperature [3]. Thus the steps act as a low barrier channel for populating the terraces. This is also in agreement with our observation that nitrogen desorption occurs at a lower temperature on the clean Ru(0001) surface than on the Au passivated surface; see TPD curves in the inset of Fig. 3. The step sites also offer a low barrier route for desorption for all of the nitrogen on the surface. Simulations of the desorption kinetics show that the calculated barrier for desorption at the step is in agreement with the measurements when the low number of active step sites is taken into account. We note that in the N_2 desorption experiments of Murphy *et al.* [9] the low kinetic energy molecules must be interpreted as coming from desorption from the step sites as well.

Comparing the two transition state configurations in Fig. 2, one can see that they have important similarities.

In both cases, one N atom is positioned close to the most stable hcp site while the other N atom is at a bridge position. The property favors the step site so strongly because here the two N atoms will not have to share any Ru atoms as nearest neighbors. The difference in barrier is therefore partly due to the fact that five Ru atoms are associated with the transition state complex at the step site rather than four on the terrace. In this way the transition state configuration at the step avoids the indirect repulsive interactions that are responsible for the high barrier on the terrace [10]. The step atoms are also generally more reactive than the terrace atoms [18]. This gives an additional lowering of the barrier, the size of which can be judged from the effects of the step on the molecularly and atomically adsorbed states.

The efficiency of an ammonia synthesis catalyst is normally limited by two factors: (i) the rate by which it can dissociate nitrogen and (ii) the blocking of the surface by adsorbed nitrogen atoms. Usually there is a roughly linear relation between the adsorption energy of nitrogen and the activation energy of nitrogen dissociation [19]; a lower barrier for N₂ dissociation will normally be accompanied by a stronger surface nitrogen bond. This results in the well-known volcano curves for catalytic activity as a function of *d*-band occupancy for a transition metal row in the periodic table [19]. The effect of the steps in the present study is an exception to this picture. Here the dissociation barrier is lowered without a similar increase in adsorption energy and this is the reason why the steps are so effective. The steps promote dissociation and ammonia synthesis without being blocked by the reaction products. The ammonia synthesis reaction should therefore be very structure sensitive on Ru. In particular, we would expect that small particles would be relatively more active than larger ones since the relative number of edge sites of supported metal particles increases with decreasing particle size. This assumes that the edges have both the low-coordinated metal atoms with high reactivity and the five-member sites needed for the geometrical effect. The former is always the case and the latter is true, for instance, on the hcp (11 $\bar{2}$ 1) plane and on the less open hcp (10 $\bar{1}$ 0) plane. There there are five-member sites containing a threefold hcp site and a bridge site close to each other, but in a slightly different geometry. The fact that the activation energy for N₂ dissociation measured on the small particles agrees with the step value provides additional evidence for this.

In summary, we have shown both experimentally and theoretically that steps will totally dominate N₂ dissociation even on a "flat" Ru(0001) surface. The reason for this is a high barrier on the terraces and a combined electronic and geometric effect which favors dissociation at steps on the surface.

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