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The Energy Dependence of the Ratio of Step and Terrace Reactivity for H_2 Dissociation on Stepped Platinum**

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Most industrially relevant heterogeneously catalyzed reactions are carried out on small particles (1–15 nm) that consist of transition metals.[1] Surfaces of these particles consist of atomically flat terraces, step sites, and kinks. The coordination of the atoms in steps and kinks is lower than that of the atoms of the terraces. The importance of these uncoordinated sites was emphasized by Taylor as early as 1925.[2] In particular cases, it has also clearly been shown that steps and kink sites enhance reactivity, as was for example shown for hydrogenolysis on platinum[3] and ammonia synthesis on ruthenium.[4]

Recently, a state-of-the-art kinetic model based on density functional theory (DFT) calculations was presented for ammonia synthesis.[5] As it was shown that N_2 dissociation is by far the slowest step under all realistic conditions,[6] this step is treated as rate-limiting. Another assumption that is made is that steps are infinitely more reactive than terraces, and only dissociation along step sites where the active B_5 sites exist[4] are taken into account. Little experimental evidence exists that generalizes such assumptions in kinetic models. In particular, no systematic studies have appeared regarding the reactivity of step sites toward activated dissociation and their dependence on, for example, atom arrangement in the step or neighboring terrace widths. Therefore, we employ H_2 dissociation on bare stepped platinum as a test case. This system has been extensively studied before (see for example, Refs. [7–10]).

To justify that steps are indeed far more reactive than terrace sites, the different reaction mechanisms taking place at these sites must be unraveled. For H_2 dissociation, we show that we are able to attribute reaction mechanisms to step and terrace sites by varying the kinetic energy of the incident molecules. Futhermore, we determine the absolute reactivity at steps and terraces as a function of kinetic energy, and their relative importance at realistic conditions by a systematic variation of terrace widths for the first time. We convolute these absolute reactivities with site distributions as occurring on nanoparticles and show that the dynamics of dissociation leads to greatly varying contributions of different sites in producing atomically bound hydrogen.

We have experimentally determined the reaction probability as a function of the kinetic energy of H_2 for three Pt(S) (stepped platinum) surfaces; that is, Pt(211), Pt(533), and Pt(755). From the split pattern of the LEED spots,[11,12] we determine the average terrace widths to be 2.9, 4.0, and 5.9 atoms wide, in agreement with the expectation of 3, 4, and 6 atom-wide terraces. Figure 1 a shows the reaction probability for Pt(755). As no isotope effect was observed, no distinction is made between results for H_2 and D_2. Decreasing reactivity with increasing kinetic energy at low energies, and a linear increase at high energies are observed. We attribute the reactivity at low energy to an indirect, trapping-mediated mechanism.[10] The behavior at high energy is indicative of direct, activated adsorption. The data are fitted with an exponential decay at low energy, and a linear contribution at high energy.[13] This linear part of the fit intercepts the reactivity axis at a non-zero value, in contrast with reactivity at Pt(111).[14,15] This reactivity at zero kinetic energy is due to adsorption of H_2 directly impinging on the step sites. This interpretation is fully in line with theoretical studies that find no barrier to dissociation at these sites.[10] These three independent components to the overall reactivity are shown in Figure 1 b for Pt(755).

Figure 1 c shows the experimentally determined reactivity and the fits for three surfaces that differ only in the width of the (111) terrace that separates the (100) step. At low kinetic energy (0 to about 0.1 eV), Pt(211) has the highest reactivity, followed by Pt(533) and Pt(755), which is consistent with the general belief that steps enhance reactivity. In the regime of direct adsorption, the energy dependence for Pt(755) is the steepest, followed by Pt(533) and Pt(211). This results in the highest reactivity for Pt(755) at high kinetic energy.

The measurements of the reaction probability of H_2 dissociation on three stepped surfaces enable us to confirm the reaction mechanisms proposed by theory,[10] and their trend related to step density. The data also validate Equation (1):

$$P^{\mathrm{total}} = P^{\mathrm{step}}_{\mathrm{indirect}} + P^{\mathrm{step}}_{\mathrm{direct}} + P^{\mathrm{terrace}}_{\mathrm{direct}} \qquad (1)$$

Here, P is used for calculated reaction probabilities (for details, see the Supporting Information). This separation of

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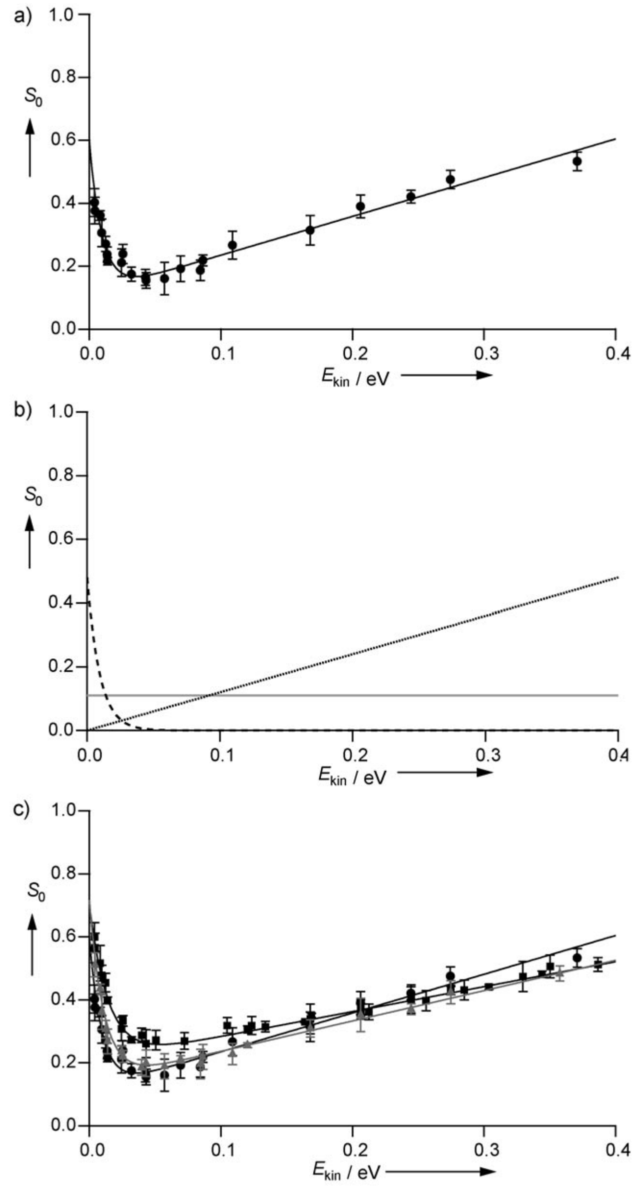

Figure 1. a) Reactivity curve for Pt(755); b) deconvolution of the overall reactivity of Pt(755) in direct dissociation at step (——) and terrace sites (•••••) and indirect dissociation at step sites (-----); c) comparison of the reactivity of Pt(211) (■), Pt(533) (▲), and Pt(755) (●). The measured data points (error bars: 2 s.d.) and the fits to experimental data are shown.

the contributions to reactivity by the three reaction mechanisms allows us to calculate the fractions of the dissociation reaction taking place at step and terrace sites, and to estimate their relative contribution at catalytically interesting conditions. Figure 2 shows the fraction of the dissociative reactivity that we can strictly attribute to the step sites as a function of kinetic energy for normal incidence. From this figure, it is immediately clear that the contribution of steps and terraces in the dissociation of H_2, which is an elementary step in many heterogeneously catalyzed reactions, is strongly dependent on kinetic energy. At zero kinetic energy, dissociation only occurs at step sites, and the steps are infinitely more reactive than the terraces. With increasing kinetic energy, dissociation occurs increasingly on terrace sites, and becomes dominant at a kinetic energy which depends on step density. For reference, we also show Maxwell distributions in Figure 2 at 300 and 1000 K, calculated using Equation (2):

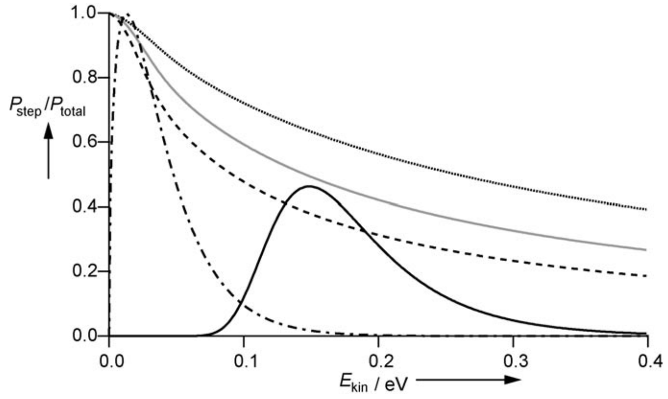

Figure 2. Fraction of reactivity at the step sites versus kinetic energy. ••••• Pt(211), —— Pt(533), ----- Pt(755). Maxwell–Boltzmann distributions for gas temperatures of 300 (–•–•) and 1000 K (——) are also shown. See text for details.

$$g(E) = 4\left(\frac{1}{\sqrt{kT}}\right)^{1.5}\frac{\sqrt{E}}{\sqrt{\pi}}e^{\frac{-E}{kT}} \qquad (2)$$

where k is the Boltzmann constant, T is the gas temperature, and E is the kinetic energy.

For ideal nanoparticles that minimize surface tension, we calculate the ratio of atoms located in steps and terraces (see Supporting Information for details). If we assume that all (100) and (111) facets of such truncated octahedra have similar reactivity, and that all edges between facets have similar reactivity, but different from the terrace (100) and (111) facets, we can now estimate the relative contributions of steps and terraces to producing surface-bound hydrogen at relevant conditions for any particle diameter. Furthermore, as no subsurface hydrogen is expected for Pt single crystals,[16] we assume that no subsurface hydrogen is present when modeling the nanoparticle. Figure 3 shows the contribution to H_2 dissociation by steps for gas temperatures of 300 and 1000 K and particle diameters up to 20 nm. Three lines close together are calculated using the parameters determined from the (211), (533), and (755) surfaces individually. Their near-coincidence justifies our approach. However, implicit in our calculations is the assumption that the same mechanisms for dissociation occur on our single crystal and on the platinum particle. On a truncated octahedron, edges occur between surface planes, but no steps are present as they occur on our single crystal. It is likely that the direct dissociation mechanisms on the steps and terraces of a single crystal do not deviate from direct dissociation on the corners, edges, and planes of a particle. However, the indirect mechanism requires a hollow geometry of several Pt atoms that is absent on the ideal truncated octahedron, but is present on our single crystal surface. Of course, such geometries may be present on real catalytic particles. We create a lower boundary

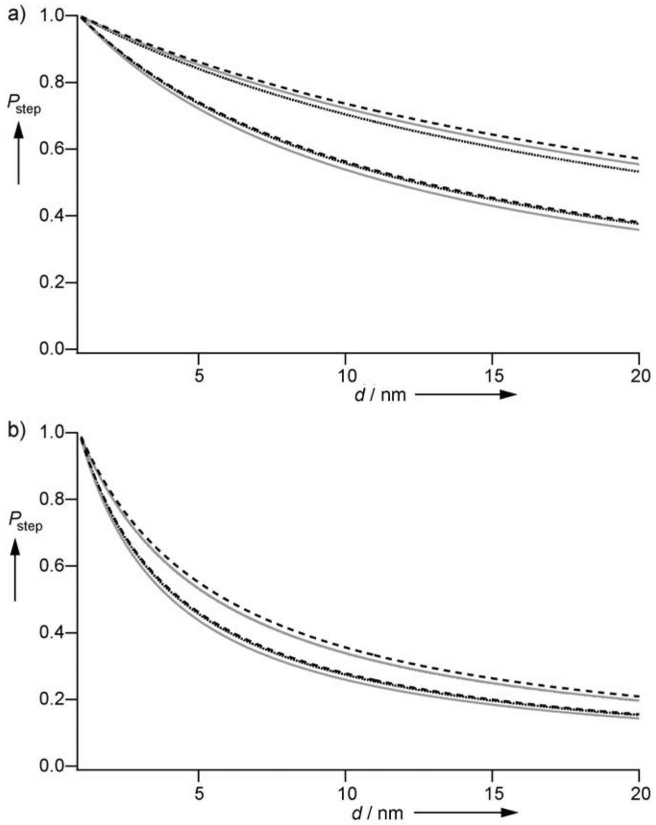

Figure 3. The percentage of dissociation at step sites for industrially used nanoparticles up to 20 nm at a gas temperature of a) 300 K and b) 1000 K. A comparison is made for inclusion (top sets of curves) and exclusion (bottom) of the indirect mechanism at the steps. ••••• Pt(211), —— Pt(533), ----- Pt(755).

on the contribution of edges and corners by excluding the indirect mechanism in our calculations. From Figure 3, it is clear that the fraction of H_2 dissociating at these "steps" is strongly dependent on gas temperature and particle size. For a gas temperature of 300 K, and inclusion of the indirect mechanism, it varies between 1 and 0.55, and for 1000 K between 1 and 0.20. The exclusion of the indirect mechanism significantly lowers the importance of "steps". The effect is strongest at a low gas temperature, as a lower average kinetic energy increases the fraction of molecules relying on impinging on a location with no or a very small activation barrier.

Our results are of significance to kinetic modeling of chemical reactions. We have shown that detailed knowledge of the reaction dynamics is required to determine which sites dominate reactivity. Models based solely on a minimum activation barrier may underestimate contributions from other sites, especially when a continuous distribution of (low) barriers is present that may be surmounted by a continuous distribution of energies. Our analysis of the H_2/Pt model system shows that on a particle the contribution of steps to dissociation is extremely dependent on particle size. We believe that this is caused by the modest change in the activation barrier distribution owing to the steps. Whereas dissociation occurs predominantly at step sites for smaller particles and lower temperatures, this is not true for larger particles and higher temperatures. Although the assumptions made for ammonia production on ruthenium[4] may be valid owing to a high activation barrier for N_2 dissociation, such assumptions can therefore not be justified in a general sense. Dynamical studies are required for adequate insight. When considering the possible effects of coadsorbates, such as recently studied in detail for H_2 on O- and CO-covered Pt,[17,18] it seems even less likely that in a kinetic model steps may be taken to be the sole contributor to producing atomically bound species from a diatomic molecule.

Experimental Section

Experiments were performed in a vacuum system.[19] A well-defined supersonic molecular beam was created by expansion of H_2 from about 1–4 atm through a 43 or 60 μm nozzle and subsequent collimation by skimmers and orifices into the ultrahigh vacuum chamber (base pressure $< 10^{-10}$ mbar). This chamber contains the stepped Pt single crystal surfaces, cut and polished from the same boule (5.5N) to within 0.1° of the (211), (533), and (755) faces, respectively.

Cleaning procedures consist of repeated cycles of Ar^+ bombardment, followed by annealing in 2×10^{-8} mbar O_2 at 900 K to remove carbon and sulfur impurities. Subsequent annealing at 1200 K removes remaining O_2 and restores surface order. Surface quality was tested by low-energy electron diffraction (LEED) and temperature-programmed desorption (TPD) spectroscopy of CO, NO, H_2, and O_2.[9,20–22] Cleaning cycles were repeated until no evidence for impurities was found and clear LEED images appeared. From the split pattern of the LEED spots,[11,12] we determined the average terrace widths to be 2.9, 4.0 and 5.9 atoms wide, in agreement with the expectation of 3, 4, and 6 atom-wide terraces, respectively.

The molecular beam energy was controlled by both the temperature of the nozzle (300–1700 K) and (anti)seeding techniques. We determined the kinetic energy of H_2 and D_2 for all expansion conditions using time-of-flight (TOF) spectrometry. For details, see the Supporting Information.

The initial reaction probability (S_0) is determined using the King and Wells technique.[23] For details, see the Supporting Information. Using the described techniques we determined S_0 at a surface temperature of 300 K. We also measured the reactivity between 100 and 300 K in steps of 50 K for Pt(211) and Pt(533), but found no measurable differences from the data presented herein. When going to higher surface temperatures, desorption begins to compete with adsorption. The fact that no surface temperature-dependence is observed, although the low energy mechanism is attributed to a trapping mediated adsorption mechanism, is due to the fact that the wells that are present at the bottom of the steps are very shallow. Consequently, our experiments are always done at the high-temperature (short residence time) limit.

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