

Anomalous Dependence of the Reactivity on the Presence of Steps: Dissociation of D₂ on Cu(211)

Gernot Fuchsel,^{†,||} Kun Cao,^{†,||} Süleyman Er,[‡] Egidius W. F. Smeets,[†] Aart W. Kleyn,^{§,||} Ludo B. F. Juurlink,^{*,†} and Geert-Jan Kroes^{*,†,||}

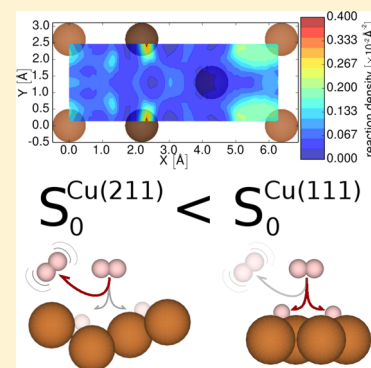
[†]Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

[‡]Center for Computational Energy Research, Dutch Institute For Fundamental Energy Research, De Zaale 20, 5612 AJ Eindhoven, The Netherlands

[§]Center of Interface Dynamics for Sustainability, Institute of Materials, CAEP, 596 Yinhe Road seventh Section, Shuangliu, Chengdu, Sichuan 610200, People's Republic of China

Supporting Information

ABSTRACT: Stepped metal surfaces are usually assumed to exhibit an increased catalytic activity for bond cleavage of small molecules over their flat single-crystal counterparts. We present experimental and theoretical data on the dissociative adsorption of molecular hydrogen on copper that contradicts this notion. We observe hydrogen molecules to be more reactive on the flat Cu(111) than on the stepped Cu(211) surface. We suggest that this exceptional behavior is due to a geometric effect, that is, that bond cleavage on the flat surface does not occur preferentially over a top site.



Structure-sensitive catalyzed reactions often proceed at edges or corners of nanoparticles. Understanding heterogeneously catalyzed processes from a microscopic perspective therefore requires a realistic modeling of complex surface structures. While the development of quantum-chemical methods is a major goal in theoretical surface science and continuously progressing,^{1,2} only a limited amount of theoretical work has focused on the description of the reaction dynamics of molecules scattering from stepped or, more generally, defective surfaces that incorporate more complex surface structures. To our knowledge, so far theoretical dynamics studies have only been performed for the dissociation reaction of H₂ on stepped Pt(211)^{3–8} and on defective Pd(111),⁹ and, very recently, for the dissociation of CHD₃ on Pt(211).¹⁰ This is contrasted by the amount of experimental work available on this subject, which established our understanding of surface imperfections and steps as usually being especially active sites in surface chemistry. Using STM experiments, Zambelli et al.¹¹ demonstrated for the first time that NO dissociation proceeds at atomic steps on a Ru(0001) surface. Molecular beam experiments yield larger sticking coefficients for H₂ reacting on stepped Pt surfaces than on flat Pt(111), particularly at low incidence energies.^{12–15} For a nickel cylindrical single crystal, similarly enhanced reactivity for low-energy incident D₂ was reported for surfaces vicinal to (111) and (100).¹⁶ The importance of steps for the promotion of surface chemistry was also demonstrated for the reactive

scattering of O₂ from platinum^{17,18} and silver¹⁹ surfaces, methane reacting with platinum,^{10,20} for N₂ dissociation on Ru(0001),^{21,22} for the hydrogenation of CO₂ on copper,²³ and also for redox reactions on functional groups of N-heterocyclic carbene molecules anchored on Pt particles.²⁴ These and other observations form the view that, in general, steps and defects constitute active sites on the surface and promote reactions by lowering reaction barriers, in particular, for direct dissociative chemisorption reactions that are highly activated on the low Miller index surfaces of the metal involved.²⁵

Theory has contributed significantly to this notion by providing details of the electronic structure of gas-surface systems obtained from first-principles calculations and by developing simplified models that explain the experimental observations described above with fundamental principles. The promotion effect can be rationalized with the d-band model of Nørskov and Hammer^{26,27} (or modifications of it²⁸), which relates the electronic interaction between the metal surface and a gas molecule to the energy of the d-band of the surface relative to the Fermi energy. For transition metals, it is generally argued that expanded surfaces, open facets, and low-coordinated surface atoms on steps reduce the width of the d-band.^{26,29} If the d-band is more than half-filled and its width

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reduced, then the d-band center shifts in energy toward the Fermi level. In principle, this results in a stronger molecule–surface interaction, larger reaction energies, and reduced reaction barriers.

Also, for the prototypical reaction of molecular hydrogen on Cu surfaces, previously performed density functional theory (DFT) calculations suggested that kinks, steps, and vacancies promote dissociation since lower reaction barriers were predicted at low-coordinated sites,³⁰ and recent DFT results for the H₂ dissociation on Cu(111) and Cu(211) supported this view.^{23,31} With the aid of molecular beam experiments and quasi-classical trajectory (QCT) simulations performed on an ab initio potential energy surface (PES) we show, in contradiction to previous findings, that D₂ molecules are less reactive on Cu(211) than on Cu(111).

To measure the reactivity as a function of incidence energy, we create a well-defined molecular beam from supersonic expansion of D₂ at various nozzle temperatures. The absolute initial dissociation probability is determined using the King and Wells technique³² (KW) for D₂ beams normally incident onto Cu(211) and Cu(111). Details, including the extraction of the kinetic energy distributions in the beams from time-of-flight measurements, are described in the [Supporting Information](#) (SI). For KW measurements the surface was cooled to a temperature of $T_s = 90$ K with liquid nitrogen. We achieve averaged translational energies $\langle E_i \rangle$ of 28–39 kJ/mol for D₂ corresponding to nozzle temperatures T_n of ~1300–1700 K. Surface cleanliness was regularly checked after standard cleaning procedures with Auger electron spectroscopy. Surface structure was verified with low-energy electron diffraction (LEED), showing expected patterns with a clear and crisp spot-splitting ratio of 2.47, in good agreement with the theoretical value of 2.45.³³ Our QCT simulations model the experimental beam conditions and are carried out on a new potential energy surface (PES), which accounts for the six molecular degrees of freedom of D₂. In accordance with previous work on the D₂ + Cu(111) reaction,³⁴ we employ the Born–Oppenheimer static surface approximation; that is, surface atom motion and electron hole pair excitation are not considered in the dynamics. Our very accurate PES is based on ~116 000 periodic DFT energy points that have been calculated using the Vienna Ab Initio Simulation (VASP) computer package^{35–38} and a specific reaction parameter (SRP) functional,³⁴ called SRP48.³⁹ The semiempirical SRP48 functional is a mixture of the PBE⁴⁰ and the RPBE⁴¹ functionals fitted to reproduce measured sticking probabilities of H₂ on Cu(111).³⁹ Sementa et al. showed that the SRP approach is transferable among systems in which H₂ interacts with low-Miller index Cu surfaces.⁴² Migliorini et al. very recently demonstrated the transferability of the SRP approach among systems in which the same molecule interacts with a low-index and a stepped surface of the same metal.¹⁰ These findings inspire the use of the SRP approach for the system at hand because Cu(211) consists of Cu(111) terraces and Cu(100) steps.

In [Figure 1a](#), we present newly measured and computed results on sticking of D₂ on Cu(111) and Cu(211) for incidence energies of $\langle E_i \rangle \in [28, 39]$ kJ/mol. Experiment and theory agree in that they yield D₂ sticking coefficients S_0 that are roughly twice to thrice as large on Cu(111) than on Cu(211). There are quantitative differences between experiment and theory, for instance, regarding the dependence of S_0 on E_i , in particular, for D₂ + Cu(211). We note that previous

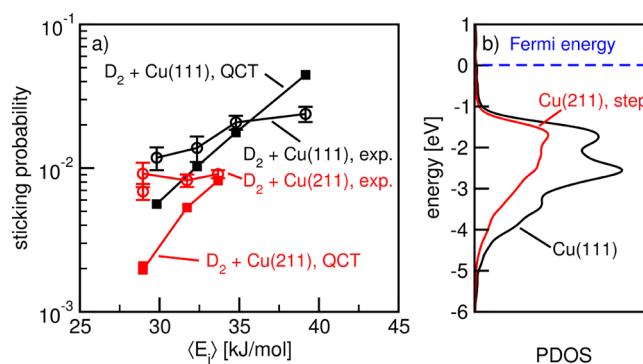


Figure 1. Left, experimental (exp., circles) and calculated (QCT, squares) sticking probabilities for D₂ on Cu(111) (black) and D₂ on Cu(211) (red). Vertical error bars indicate standard deviations from 10 measurements. Beam energy distributions are broad as specified in the [SI](#). Right, site-projected densities of states (PDOS) of the d-band for the first layer Cu(111) surface atoms and the Cu(211) step atoms.

theoretical work on D₂ + Cu(111) suggests the computational approach used here to be accurate down to $E_i \approx 33$ kJ/mol.³⁴ Below this energy, the accuracy of this approach may become limited by the neglect of quantum effects and of surface atom motion. At the same time, the King and Wells method used here to measure the sticking probabilities is being pushed to its limits in the measurement of sticking probabilities ≤ 0.01 . Because measured sticking coefficients are generally small here ($S_0 < 2.5 \times 10^{-2}$), we characterize the agreement between theory and experiment for both surface reactions as semi-quantitative, suggesting also that the following theoretical analysis is appropriate.

The observed lower reactivity of D₂ on Cu(211) is unexpected and conflicts with observations usually made on the catalytic activity of stepped surfaces. To determine reactive sites and barrier energies, we have performed transition-state (TS) search calculations on our PES and, additionally, nudged elastic band (NEB) calculations using VASP. Reaction barrier energies E^\ddagger and the corresponding geometries of D₂ are summarized in [Table 1](#) for Cu(211), Cu(111),⁴³ and Cu(100).⁴² The corresponding impact sites are specified in [Figure 2b](#), where optimized reaction barriers for the entire Cu(211)(1 × 1) unit cell are drawn, according to our PES. The activation energies suggest a reactivity order of Cu(111) > Cu(211) in contradiction to previous theoretical studies.^{23,30,31} There, ~100 meV lower barriers on Cu(211) were calculated, while we find 30–90 meV higher barriers. As discussed in the [SI](#), the calculations with the PW91 and the SRP48 functional used here suggest that an SRP approach is needed to obtain the correct order of the reactivity of the flat and the stepped surface. Moreover, the erroneous sign of the difference in barrier heights obtained in the previous theoretical studies^{23,30,31} (as suggested by the present experiment) and the extent of the deviations may also be due to shortcomings of the computational setups used in these works (e.g., the use of too few layers to model the surface³⁰). Interestingly, our lowest NEB barrier value on Cu(211) is associated with the t₂b position at the step edge. This is different from the (111) and (100) surfaces that provide reactive sites located at the midpoint between two adjacent Cu atoms called the bridge (brg) position. In summary, our static analysis of the PES suggests that the lower reactivity of Cu(211) is due to the higher barriers to H₂ dissociation on Cu(211). This could, in

Table 1. Reaction Barrier Energies E^\ddagger Calculated with the SRP48 Functional for D_2 on Various Cu Surfaces, Corresponding Geometries, and Azimuthally Averaged Barriers \bar{E}_ϕ^\ddagger with the Corrugation Measure σ^a

	site	E^\ddagger (eV)	r^\ddagger (Å)	Z^\ddagger (Å)	θ^\ddagger (deg)	ϕ^\ddagger (deg)	$\bar{E}_\phi^\ddagger \pm \sigma$ (eV)
Cu(111) ⁴³	brg	0.636	1.03	1.17	90	90	
Cu(111) ³⁴	t ₂ b	0.837	1.38	1.34	107	0	
Cu(100) ⁴²	brg	0.740	1.24	0.99	90	90	
Cu(211)	t ₂ b	0.678(0.663)	1.41(1.41)	1.33(1.31)	102(106)	86(87)	0.876 ± 0.142
Cu(211)	t ₁	0.696(0.694)	1.44(1.43)	1.37(1.37)	90(90)	90(90)	0.924 ± 0.155
Cu(211)	t ₂	0.721(0.727)	1.19(1.13)	0.28(0.26)	98(98)	0(0)	0.886 ± 0.120
Cu(211)	b ₁	0.707(0.727)	1.21(1.17)	0.97(0.98)	92(77)	0(0)	1.066 ± 0.228
Cu(211)	b ₂	0.671(0.673)	1.05(1.06)	0.86(0.89)	84(85)	62(62)	1.006 ± 0.234

^aData in brackets are obtained from NEB-SRP48 calculations, while the other data are derived from PESs. Reaction sites on Cu(211) are indicated in Figure 2. The azimuthal and the polar angle at the barriers are denoted by ϕ^\ddagger and θ^\ddagger , where $\theta = 90^\circ$ and $\phi = 0^\circ$ describe the molecular axis aligned perpendicular to the macroscopic surface normal and parallel to the X axis, respectively (see the SI). The X and Y axes are as indicated in Figure 2b.

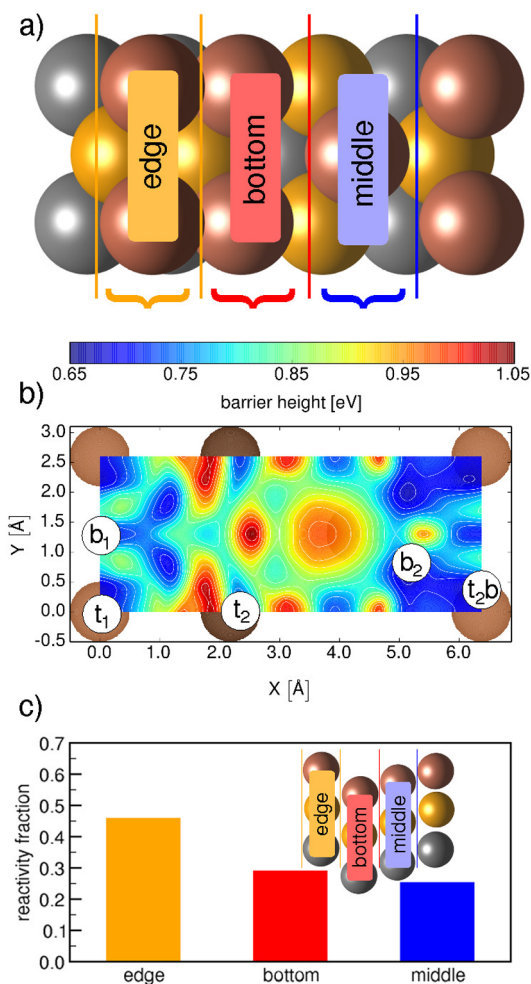


Figure 2. Shown are (a) top view on the (1 × 1) unit cell of Cu(211), (b) optimized barrier heights as a function of the impact site according to the 6D PES, and (c) reactivity fraction for different surface areas together with a side view on Cu(211). The reactivity fraction was resolved over 290 000 reactive trajectories of D_2 initially approaching Cu(211) with $\langle E_i \rangle = 33.67$ kJ/mol.

principle, have been compensated somewhat by increased vibrational promotion of reaction of $\nu = 1$ D_2 ⁴⁴ (population 4–8% at the values of T_n used) on Cu(211), as the barriers on Cu(211) are all later (occur at a larger value of r) than at the minimum barrier geometry on Cu(111) (see Table S4). However, the experiments and dynamics calculations pre-

sented here clearly show that if such a compensating effect occurs, it is too small to offset the effect of the higher barriers on Cu(211).

The anomalous reactivity and the higher barriers found on the stepped surface are in stark contrast with expectations based on the d-band model. In Figure 1b, the projected densities of states (PDOS) of the first layer Cu(111) atoms and of the atoms forming the step on Cu(211) are drawn. We find that the energy of the d-band center of the latter ($\epsilon_d = -2.434$ eV) is indeed 0.12 eV shifted toward the Fermi energy compared to (111) atoms ($\epsilon_d = -2.556$ eV). The stabilization of the transition state for $D_2(H_2)$ on Cu due to the interaction of the d-band with the antibonding σ_u^* orbital can be approximately calculated according to⁴⁵

$$\delta E_{ts} \approx -2 \frac{V^2}{\epsilon_{\sigma_u^*} - \epsilon_d} + \alpha V^2 \quad (1)$$

Using $V^2 = 2.42$ eV² for the coupling matrix element, $\alpha = 0.42$ eV⁻¹, and $\epsilon_{\sigma_u^*} = 1$ eV for the renormalized energy of the σ_u^* orbital of $D_2(H_2)$ as reported in refs 26 and 45, we find that the TS on Cu(211) should be stabilized by 50 meV over Cu(111). This is in qualitative agreement with the energy of the t₂b geometry on Cu(211) being lower than that of Cu(111) (175 meV, see NEB results in Table 1). This suggests that the d-band model correctly predicts variations of the reactivity of different facets for the dissociation of $H_2(D_2)$ if (A) like geometries are considered and if (B) the TS is located near a top site. The reaction of molecular hydrogen on a low-index Cu surface is, however, not a typical on-top reaction, and, as presented in Table 1, the barrier geometries vary with the facets, explaining the observed mismatch between the actual reactivity and results of the d-band analysis. The observations made above are fully consistent with previous calculations that revealed for the $H_2 + Cu(100)$ system higher barriers than for $H_2 + Cu(111)$, although the computed d-band upshift on Cu(100) would suggest the opposite.⁴⁶ This difference was attributed to geometrical effects,⁴⁵ that is, the breach of condition A above. Specifically, as noted in ref 45, on Cu(100) H_2 needs to be more stretched at the bridge-to-hollow TS than on Cu(111), where the adjacent fcc and hcp hollow sites are more closely spaced than the four-fold hollow sites on Cu(100).

It is clear that the electronic structure affects the activation energy and the overall topology of the adsorbate–substrate interaction. The latter, however, directly affects the reaction

dynamics in that certain geometrical configurations of D_2 are favored for dissociation. The influence of these configurational effects on the outcome of the dynamics is the subject of the following analysis. The reduced symmetry of Cu(211) leads to an increased complexity in the molecule–surface interaction potential in comparison with Cu(111). For example, Cu(111) provides three indistinguishable bridge sites associated with the lowest barrier. On the contrary, when considering the bridge-type sites relevant for reaction, Cu(211) has two indistinguishable bridge sites similar to those on Cu(111), indicated by b_2 in Figure 2b, and one bridge site (b_1) that is similar to the bridge site on Cu(100). There are also three different top sites associated with Cu atoms of different coordination numbers. They are located at the step edge (t_1), at the bottom of the step (t_2), and, analogously to Cu(111), in the middle of the terrace. In Figure 2b, we plot the lowest reaction barrier energies obtained from our PES as a function of the impact coordinate. From the step atoms (t_1) to the Cu(111)-like b_2 site, the reaction barrier energy varies only slightly by ~ 30 meV. This is similarly true for the barriers between the t_1 site and the Cu(100)-like b_1 site. At the bottom of the step a valley emerges localized at the t_2 site, which appears as being surrounded by four “hills” when taking the periodicity of the PES into account.

The complexity of the interaction potential revealed in Figure 2b makes it difficult to ascertain the actual reaction site beyond doubt. We therefore determined the reaction density on Cu(211)(1×1) from our QCT simulations. A detailed analysis on this is given in the SI and reveals that reaction predominantly takes place in an area near the b_2 site, similar to Cu(111), but also clearly separated from this strongly localized at the t_2 site at the bottom of the step. The analysis also suggests that reaction occurs without the formation of long-lived molecular trapped states prior to dissociation.

In Figure 2c, we show the reactivity fraction associated with three different surface areas called edge, bottom, and middle, as indicated in Figure 2a. Almost 50% of reacting molecules react at the step edge, and the remaining reacting molecules react with almost equal probability at the terrace and the bottom of the step. In the latter case, 25% of molecules react over the t_2 site (see Figure S4 in the SI), while the associated surface area makes up only $\sim 4\%$ of the total area. One can therefore speak of a top-site supported process and a domination of t_2 in terms of efficacy. This is also a consequence of configurational effects on the dynamics associated with the ability of a surface area to be “azimuthally open” and the specific interatomic distance assumed at the barrier by transient D_2 . In Table 1, we quantify the former feature by the effective azimuthally averaged activation energy \bar{E}_ϕ^\ddagger and the associated azimuthal corrugation of the PES represented as standard deviation σ . According to \bar{E}_ϕ^\ddagger , reaction is facilitated at the t_2 site at the bottom of the step because: (i) t_2 is associated with a small effective barrier and the lowest azimuthal corrugation, making it the site that is azimuthally most open to reaction and (ii) at t_2 , reaction occurs far earlier (at a smaller value of r , see Table 1) than at the t_2b site, which appears to compete in terms of activation energy but is less important in the dynamics; see Figure S4 in the SI. On the contrary, the larger effective barriers and azimuthal corrugation unfavorable for reaction found in the vicinity of the b_2 site are compensated by a larger reactive surface area and the generally low reaction barriers that show only small variations along the surface. This makes the step-

edge area toward the terrace quantitatively the most reactive region on Cu(211).

The observed lower reactivity on Cu(211) may have implications for our understanding of methanol synthesis from CO_2 as catalyzed industrially by Cu/ZnO/ Al_2O_3 .^{23,47} The formation of atomic, surface-bound hydrogen is generally not explicitly considered or discussed in any detail for this important industrial process, while elementary reactions that influence the overall rate contain its surface concentration. For example, hydrogenation of bidentate formate and subsequent intermediates have been suggested to be rate-limiting.^{47,48} Our results may imply that the dissociation of H_2 participates more strongly in the multistep dynamics than assumed so far because defects do not lead to lower barriers for hydrogen dissociation on copper. This may become particularly relevant for very small Cu particles, where a Wulff construction would not include t_2 type sites (small metal nanoparticles are octahedral in shape and have edge-like sites but not the t_2 bottom sites¹⁴).

A lesser point concerns the quantitative differences remaining between theory and experiment in the determined sticking coefficients, as shown in Figure 1a. In the SI, we address the influence of the DFT functional on the computed reaction barrier heights. Here we mention only that, as already stated before, the PW91 functional yields a somewhat lower TS energy on Cu(211) than on Cu(111), suggesting that an SRP functional is necessary to properly describe the interaction potential.

In summary, we have reported on the dissociation reaction of molecular hydrogen on Cu(111) and Cu(211), and we showed by experiments and theory that sticking is less likely on the stepped surface. The observed anomalous reactivity order cannot be explained on the basis of the d-band model because the dissociation of molecular hydrogen on low-index Cu surfaces is not a typical top site reaction. Finding other systems with an anomalous dependence of the reactivity on the presence of steps or other defects might help ascertain if such a dependence usually arises from a geometric effect as found here or whether other effects may also be important.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b03097.

Details of experiments and beam parameters, the DFT calculations, the PES construction, and the QCT simulations. (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*L.B.F.J.: E-mail: ljuurlink@chem.leidenuniv.nl. Tel: +31 (0) 71 527 4221.

*G.-J.K.: E-mail: g.j.kroes@chem.leidenuniv.nl. Tel: +31 (0)71 527 4396.

ORCID

Gernot Füchsel: 0000-0001-6062-5254

Aart W. Kleyn: 0000-0002-0772-6133

Geert-Jan Kroes: 0000-0002-4913-4689

Author Contributions

^{||}G.F. and K.C. contributed equally.

Notes

The authors declare no competing financial interest.

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