Absolute dissociation cross sections for D2 dissociation on Pt steps

Jansen, C.; Juurlink, L.B.F.

Chemical Physics Letters 776 (2021) 138679

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Absolute dissociation cross sections for D_2 dissociation on Pt steps

Charlotte Jansen, Ludo Juurlink *

Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, the Netherlands

ARTICLE INFO

Keywords:
Hydrogen
Platinum
Steps
Dissociation
Cross section
Molecular beam

ABSTRACT

Reaction mechanisms following gas-surface collisions may differ depending on the site of impact. On stepped Pt surfaces at least three dissociation mechanisms have been suggested to occur in parallel. Using supersonic molecular beams and a curved Pt single crystal, we unravel these site-dependent contributions and quantify absolute reaction cross sections using these mechanisms' different dependencies on kinetic energy in the range of 0.7 to 13.4 kJ/mol. A sum of three dissociation mechanism probabilities fits our data well and allows us to extract absolute cross sections for indirect and direct non-activated dissociation at steps. We find good agreement with theoretical predictions.

1. Introduction

Many bulk industrial chemical processes rely on heterogeneous catalysis. A fundamental understanding of catalytic reactions may aid in improving these processes, making them more efficient or sustainable. Different surface sites on catalytic particles are known to have different abilities toward bond breaking and bond making events. Their contributions to the total reactivity therefore vary [1]. Steps and other defects on the surface are often regarded to play a major role in these reactions due to their low coordination. Such defects, however, are challenging to study separately, as there is no surface that consists of defects alone. Experiments, therefore, often use multiple stepped single crystal surfaces, as those have a well-defined defect (step) density with atomically flat terraces in between the steps.

The dissociation of molecular hydrogen (H_2) on platinum (Pt) is a model system for catalytic reactions. Density functional theory (DFT)-based reaction dynamics studies of this reaction on Pt(211) [2,3] identified three dissociation mechanisms (see Fig. 1). On the terrace, reaction barriers exist causing one dominant mechanism: direct activated dissociation (1). At the steps, two mechanisms lead to dissociation. Indirect dissociation via a dynamic precursor happens if the molecule is briefly trapped in the cusp of the step (2). On the top of the step edge, non-activated direct dissociation occurs (3). While other mechanisms have been proposed [4,5], results of most experimental studies and the various expected dependencies fit this model very well [4,6–8].

The dissociation of molecular hydrogen on Pt(111) has been studied in even greater detail than stepped surfaces, and reactivity dependencies are well known [9–12]. The dissociation probability is isotope-independent and increases nearly linearly with incident energy over a wide collision energy range [9,12,11]. It shows a complex angle dependence with respect to the crystal's normal along both high symmetry azimuthal axes [9,4,10,11]. The relative reactivity of steps and terraces has been also studied [13] for several flat single crystal surfaces with different step densities of the A-type step (the step being a {100} facet). While collision energy dependencies were generally determined, the velocity vector for molecules incident on these stepped surfaces was mostly oriented along the surface normal. As the angle between the surface normal and the Pt(111) terraces and steps varies with step density and the angle dependence is known to be complex, disentangling contribution of steps and terraces to reactivity is far from straightforward.

Here, we cleanly separate the reactivity of steps and terraces and determine the reaction cross section of two of the suggested dissociation mechanisms shown in Fig. 1. We experimentally determine the initial reaction probability of D_2 on a continuous range of Pt surfaces using a curved Pt single crystal [8,14]. We use seeded supersonic molecular beams to vary the average collision energy between 0.7 and 13.4 kJ/mol and detect reactivity over a very small area on this crystal to circumvent convolution with the continuous range of step densities. All measurements are done under the same experimental conditions and at normal incidence with respect to the {111} terraces. Using both sides of the apex of the curved crystal, we also distinguish between A-type and B-type (i.e. {110} faceted) steps with average terrace widths ranging from 6 to hundreds of atom rows.

* Corresponding author.
E-mail address: l.juurlink@chem.leidenuniv.nl (L. Juurlink).

https://doi.org/10.1016/j.cplett.2021.138679
Received 11 January 2021; Received in revised form 15 April 2021; Accepted 19 April 2021
Available online 28 April 2021

2. Methods

The model proposed by Baerends and coworkers [2] is illustrated in Fig. 1. The initial reaction probability (s_0) of H_2 on Pt behaves like the weighted average of the reaction probabilities on the step and on the terrace [8]:

$$s_0 = f_{step} s_{0step} + f_{terrace} s_{0terrace} \quad (1)$$

where f_{step} and $f_{terrace}$ are the fractions of the surface covered in steps and terraces. We express the fraction of steps in terms of step area (A_{step}), step width (w_{step}), i.e. the unit step length along the edge, and step density (d_{step}):

$$f_{step} = \frac{A_{step} d_{step}}{w_{step}} \quad (2)$$

Thus, we can find the step reaction cross section, defined as $s_{0step} A_{step}$, if we know the step width, the step density of the surface and the contribution of the terrace to s_0:

$$A_{step} s_{0step} = \frac{s_0 - f_{terrace} s_{0terrace}}{d_{step}} w_{step} \quad (3)$$

The site-dependent reaction probabilities are characterized by different collision energy dependencies. We extract the terrace contribution to s_0 by investigating the kinetic energy dependence of s_0. The reaction probability of H_2 on Pt(111) for normal incidence is approximately proportional to its kinetic energy over a wide energy range up to at least 25 kJ/mol [9–12], due to the activated direct dissociation mechanism on Pt(111) with a range of small reaction barriers [15]. The reaction probability on the steps has two components: one that decays with increasing kinetic energy (indirect mechanism, illustration 2 in Fig. 1) and and one that is energy independent (non-actived direct mechanism, illustration 3 in Fig. 1). It has been shown before that a function with an exponential and linear component (Eq. 4) fits the energy dependence of H_2 reaction on stepped Pt surfaces well in our energy range [4,6,7].

$$s_0\left(E\right) = \overbrace{ae^{-E/b} + c}^{step} + \underbrace{dE}_{terrace} \quad (4)$$

Here, a, b, c and d are constants. We assume that the exponential and constant components are only due to reaction on the steps, and therefore constants a and c are proportional to the fraction of the surface covered in steps. We assume the proportional component is only due to reaction on the terraces, and therefore d is proportional to the fraction of the surface covered in terraces. If we isolate and remove the proportional component, and thereby the full contribution of the terrace, we can calculate the step reaction cross section with Eq. 3.

3. Results

Fig. 2a and b show s_0 of D_2 on Pt as a function of average kinetic energy, measured over a range of step densities. s_0 is measured using the King&Wells method [16]. A molecular beam hits a small rectangular section along the curved surface of our *c*-Pt(111)[1$\bar{1}$0]-31° [17] crystal in vacuum, which is kept at 150 K. The reaction probability is determined by measuring relative partial pressure of D_2 in the vacuum chamber. The kinetic energy of the molecules in the beam is controlled by the expansion temperature and anti-seeding with argon. For each individual section of the curved surface with a certain step density, the kinetic energy dependence is fitted with Eq. 4. The resulting fits are also shown in Fig. 2a and b. In Fig. 2c, the data analysis process is exemplified for a single data set. The black dots show the s_0 data for a surface with step density of 0.62 nm^{-1} and B-type steps. The dashed line shows the initial fit with Eq. 4. The solid black line shows only the linear part of this fit. To eliminate the terrace contribution from s_0, the part of the fit proportional to E is removed. This results in the gray data points. It is illustrated by the difference between the black and gray line. Fig. 2d shows the kinetic energy distribution in the molecular beam, for each experiment. This distribution is a fit of data obtained by Time of Flight measurements [18]. The energy distributions are too broad to resolve any small details, such as resonances, in the energy dependence of s_0. However, if the energy dependence follows Eq. 4, the convolution with the energy distributions in the beam has no significant effect on the measured s_0 (see Appendix A).

Fig. 3 shows the calculated reaction cross section as a function of kinetic energy. A full-size image is also included at the end of Appendix A. Some values of the cross section are visualised in the inset, and compared to the potential energy surface (PES) of Pt(211) as calculated

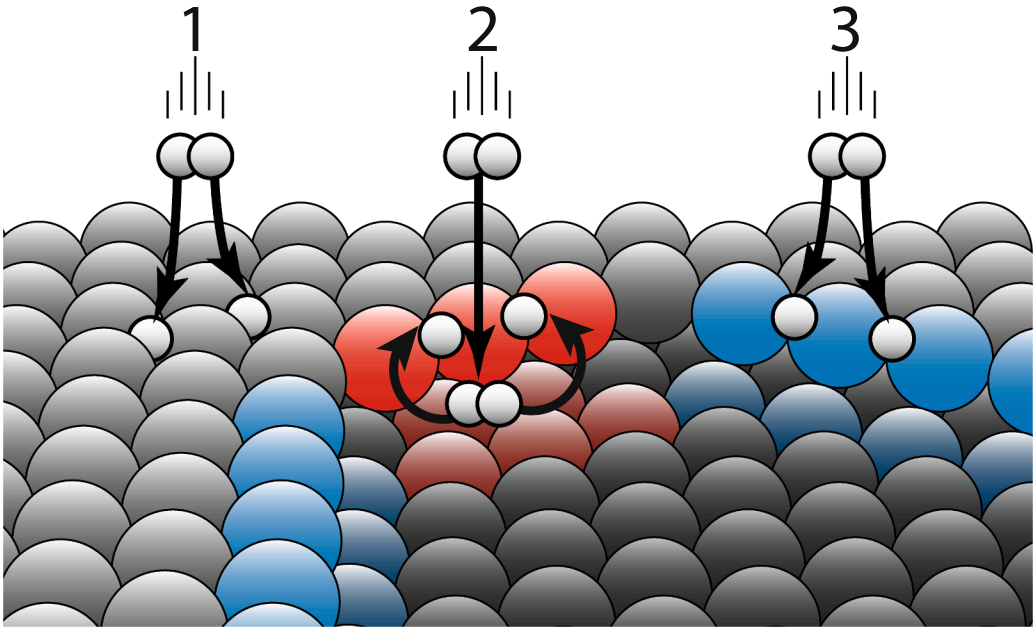

Fig. 1. The three dissociation mechanisms of H_2 on Pt determined by [2]. 1) Direct, activated dissociation on the Pt(111) terrace. 2) Indirect dissociation on the steps. 3) Direct non-activated dissociation on the steps. Blue: A-type {100} step. Red: B-type {110} step.

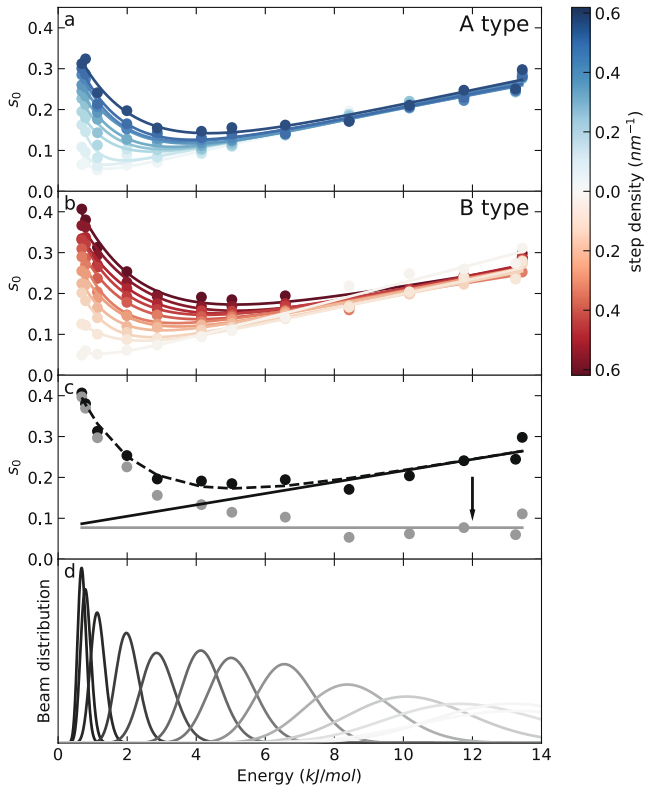

Fig. 2. a), b) The s_0 data as a function of kinetic energy, obtained by King & Wells measurements. Fitted with Eq. 4. Data for a) all surfaces with A-type steps and b) all surfaces with B-type steps. c) Data set for a single surface with step density of 0.62 nm^{-1}, with B-type steps. The fit is shown as a dashed line. The linear part of the fit is shown as the solid black line. The terrace contribution to s_0 is subtracted from the data points, resulting in the contribution of the steps only (gray data points). The same transformation is done on the black line, resulting in the gray line. d) The kinetic energy distribution of the molecular beam for each measurement.

by [19]. Two trends are apparent. First, the cross section decreases with kinetic energy and levels out at a non-zero value. Second, with decreasing step density the cross section increases. The two reaction mechanisms on the step can be distinguished on the basis of the first trend. The energy-dependent indirect mechanism dominates for energies below 6 kJ/mol. The energy-independent direct mechanism remains as the only mechanism contributing significantly for higher energies. We note that there are some outliers for low step density surfaces. The step contribution to s_0 is very small on a surface with few steps, resulting in a large relative error. There may also be a small contribution from unintended remaining defects near the apex [20].

4. Discussion

4.1. Energy dependence of indirect mechanism

There are several explanations for the decay of the reaction cross section for the indirect mechanism. Since the cross section is the product of the area of the active site and the sticking probability (Eq. 3), a change in either of these parameters results in a change in the cross section. For indirect dissociation, the molecule needs to be trapped in the potential well in the cusp of the step (see Fig. 1) prior to dissociating at the top of the ledge. Quantum mechanical effects, such as rotationally mediated selective adsorption, could play a role. Predictive calculations show resonances in this energy regime [21,3]. These are not likely to show in our data, as the kinetic energy distributions in our measurements are rather broad, our beams contain multiple rotational states, and the surface temperature is substantial. A simple hard cube model [22], used for predicting trapping probabilities in a square potential well, predicts the energy dependence very well (see Appendix A). This suggests that the sticking probability, s_{0step}, may be energy dependent. On the other hand, if the depth of the potential well is not of a single value, but varies across the surface, low-energy molecules can be trapped on a larger surface area than high-energy molecules. Hence, the active area (A_{step}) may also be energy dependent. While the potential calculated by Baerends and coworkers suggests a variable depth of this well, our experiments cannot unravel whether one or both are energy dependent.

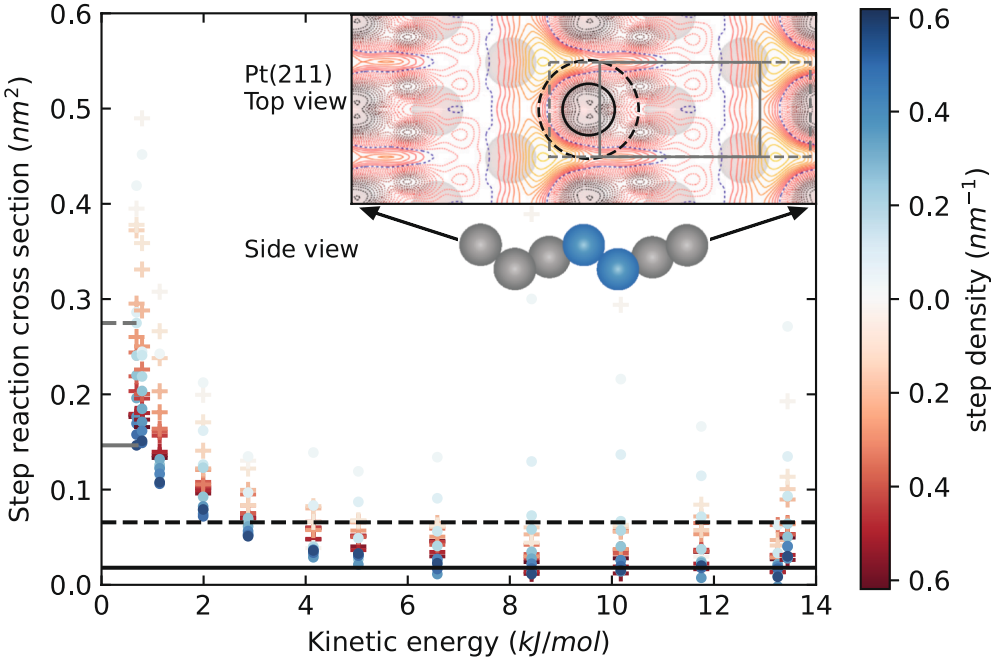

Fig. 3. The step reaction cross sections calculated with Eq. 3 for each surface and kinetic energy. A-type steps (·) and B-type steps (+). We found for the direct mechanism an average reaction cross section of 0.018 nm^2 for a step density of 0.57 nm^{-1} and energies above 6 kJ/mol. This is shown as the solid horizontal line, and as a circle in the inset. The reaction cross section for the indirect mechanism at 0.7 kJ/mol is included as a line in the plot and rectangle in the inset. We also included the reaction cross sections for both mechanisms for a step density of 0.15 nm^{-1} as the dashed circle and rectangle. The inset shows a top view of 4 unit cells of the Pt(211) surface. Our calculated cross sections are shown as circular and rectangular areas on the surface. Below the inset, a side view of the top atoms of the surface is given. In the inset, the potential energy surface (PES) from Ref. [19] is shown as well. Repulsive potentials are shown ranging from yellow to red, attarctive potentials range from red to dark blue. The dashed line shows where the potential energy switches from attractive to repulsive.

4.2. Cross section for indirect mechanism

Although we can not distinguish between potential origins for the energy dependence of s_{0step}, we can semi-quantitatively compare the reaction cross section for our highest step density surface with the calculated potential energy surface (PES) from Ref. [19] for Pt(211). This PES shows the potential energy of a H_2 molecule 0.2 nm above the Pt(211) surface. The potential energy is minimized with respect to the rotation and stretch of the molecule. In the calculations, the molecule does not vibrate or rotate, and Van der Waals interactions are not taken into account. The solid line rectangle in the inset in Fig. 3 represents the cross section for indirect dissociation at the step for the lowest collision energy and highest step density (0.57 nm^{-1}). It has a value of 0.13 nm^2, and is compared to the PES. For comparison, the attractive area in the PES is 0.12 nm^2. Note that this area also includes the terrace and top of the step. The PES was calculated for Pt(211), which has A-type steps and a step density of 1.56 nm^{-1}, hence representing a higher step density than our data. We consider the agreement quite reasonable. The reaction cross section for a step density of 0.15 nm^{-1} is included as a dashed rectangle. The step-density dependence of this part of the reaction cross section suggests that the area capturing molecules at the cusp increases with lowering step density.

4.3. Cross section for non-activated direct dissociation at the step

Since the direct dissociation mechanism occurring for impingement on the upper edge of the step is non-activated, a molecule landing in the active area has a dissociation probability of 1. Therefore its reaction cross section is equal to the area of the active site. We calculate this area for a step density of 0.57 nm^{-1} and A-type steps by taking the average value of the cross section for kinetic energies above 6 kJ/mol. We find that it is 0.018 nm^2. This value is shown in Fig. 3 as the solid black line passing horizontally through our data. In the inset, we compare the area to the PES as the (solid line) circle with the calculated area over the active site on top of the step. We find very good agreement between our data and the theoretical model. Our calculated area covers the area on the PES below the level of the two saddle points near the bottom of the step. At the same time, for much lower step densities, the same cross section appears larger (dashed line through our data and the inset). This suggests that the PES of lower step density surfaces not only has an enlarged area for indirect dissociation, but also a larger barrier-free area on top of the edge atom as compared to the PES calculated for Pt(211).

4.4. Step density dependence of cross section

There are a few explanations for the step density dependence of the reaction cross section for A- and B-type steps. A first consideration is that along the curvature of the crystal, the step arrays show both decreasing terrace width and decreasing terrace width variation with increasing step density. Auras and Juurlink recently reviewed such effects for a curved single crystal surface [17]. As molecules are either reflected or adsorbed to the surface, we need to consider how reflection by diffraction into the gas phase and adsorption by diffraction into a physisorbed state are affected by these variations. While the diffraction intensities for scattering of atoms from corrugated surfaces has been examined [23], we are not aware of studies that quantify integrated diffracting intensities for molecular scattering on the dependence on these two variables. On the other hand, the increased scattering angles caused by the smaller grating at increased step density, could only increase scattering into the physisorbed state. This would also increase the measured S_0, not decrease it as we observe. Hence, diffractive scattering is unlikely the origin of the observed variation of the reaction cross section with step density.

Another explanation is that the effective size of the step in its contribution to dissociation is so large that two separate step edges overlap at higher step densities. This is possible when there is some diffusion of the D_2 molecules across the surface. The standard model for precursor-mediated dissociation, e.g. as applied in recent studies of CH_4 dissociation on Ir(111) [24–26], includes the possibility of diffusion. Jiang and coworkers include diffusion as originally described by Comsa et al. for hydrogen dissocation on Pt [5,27]. This approach was already shown to predict the opposite temperature dependence for our system [8]. Jackson and coworkers omit specific description of diffusion and define the probability to dissociative sticking as the product of the incident energy-dependent trapping probability, P_{trap}, and the fractional chemisorption rates out of the trapped state, $k_c/(k_c+k_d)$ [24,25]. A surface temperature independence, as we observe, could reflect similar barriers to desorption and chemisorption from the trapped state. However, McCormack et al. [2] have shown that there is only fast, short-range diffusion of trapped molecules on Pt(211), mainly from the potential wells at the cusp to the top of the step. Their work did not yet include a Van der Waals correction to the DFT-based PES. It may require such interactions to fully address whether short-range diffusion on the (111) terraces contributes to dissociation. Another point of discrepancy between H_2 and heavier molecules may be that the trapping mechanism for H_2 seems to rely to a significant extent on T → R energy transfer due to a lack of strong coupling to phonons. Heavier gas phase molecules may rely more on phonon excitation to get trapped [28]. We cannot completely rule out diffusion as an explanation for the step density dependence of the indirect mechanism. However, we can for the direct mechanism. Diffusion requires trapping, and trapping probabilities decrease with increasing collision energy. The cross section of the direct mechanism is constant with collision energy, so diffusion does not play a role there.

A third possibility is that the shape of the potential energy surface changes such that the area of the active sites decreases with increasing step density. Smaller active sites for higher step densities would explain the lower reaction cross section. We used a simple hard cube model to predict the trapping probability of a molecule in a potential well on a Pt surface. We find that the energy dependence of the reaction cross section for different step densities matches the hard cube predictions for different potential well depths (see Appendix A). This suggests that the potential energy surface of the step may be step density dependent. We think that this is the most plausible explanation for the step density dependence of the reaction cross section. For the indirect mechanism, diffusion could also play a role.

4.5. A- and B-type steps

Fig. 3 and additional figures in Appendix A also show that there is a difference in cross section between the A- and B-type steps. This is not surprising for the low kinetic energies, where the indirect mechanism is dominant. The potential well causing the indirect mechanism lies at the bottom of the step. The bottom of the A type step consists of the atoms neighbouring the top atoms. The bottom of the B-type step consists of the atoms neighbouring the top atoms, plus one extra row of atoms, resulting in a larger step area. Therefore it is not surprising that the potential well of the B-type step is larger. However, the difference in A- and B-type steps also appears at higher kinetic energies, where only the direct mechanism plays a role. For each kinetic energy, we have calculated the average ratio of the cross sections of the A- and B-type steps. We find values ranging from 1.1 to 2.5, with a ratio of approximately 1.2 for the lowest energies (see Appendix A). The ratio of the reactivity of A- and B-type steps has been determined before at 0.9 kJ/mol and was found to be approximately 1.5 [8,14] This is larger than our value, and the difference is possibly due to differences in data analysis methods.

5. Conclusions and outlook

In conclusion, we have used the model from Ref. [2] shown in Fig. 1 to calculate the reaction cross section of D_2 dissociation on two types of steps on Pt. We find that the reaction cross section of the direct

dissociation mechanism on the top of the step agrees very well with the PES from Ref. [19]. The reaction cross section of the indirect mechanism on the bottom of the step is larger than the active area on the PES. This is in line with the general trend we observe in our data, where the reaction cross section decreases with increasing step density. Comparison of the results with hard cube model predictions reinforces the hypothesis that the PES of the step may depend on step density. For the indirect mechanism, diffusion may also play a role. Theoretical calculations of highly stepped surfaces, such as Pt(211), may not be sufficient to predict reactivity at lower step densities. We also find that the reaction cross section differs between the two step types, which agrees with previous research [8,14]. It is important to keep in mind that these results were obtained with a relatively simple model that assumes no interaction between steps and terraces (see Eqs. 1 and 4). Although the model fits the data well, there is no guarantee that it is correct. There may be some short-range diffusion around the steps that does not show a strong temperature dependence. Theoretical calculations for larger unit cells and longer terraces could help us gain a better understanding.

CRediT authorship contribution statement

Charlotte Jansen: Conceptualization, Investigation, Formal analysis, Writing - original draft. **Ludo Juurlink:** Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is part of the research programme Materials for Sustainability with project number 739.017.008, which is (partly) financed by the Dutch Research Council (NWO).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cplett.2021.138679.

References

[1] L. Savio, L. Vattuone, M. Rocca, Role of steps and of terrace width in gas-surface interaction: O2 / Ag(410), Phys. Rev. Lett. 87 (27) (2001) 276101, https://doi.org/10.1103/PhysRevLett.87.276101. ISSN 0031-9007, 1079-7114.
[2] D.A. McCormack, R.A. Olsen, E.J. Baerends, Mechanisms of H2 Dissociative Adsorption on the Pt(211) Stepped Surface, J. Chem. Phys. 122 (19) (2005) 194708, https://doi.org/10.1063/1.1900087. ISSN 0021-9606, 1089-7690.
[3] R.A. Olsen, D.A. McCormack, M. Luppi, E.J. Baerends, Six-Dimensional Quantum Dynamics of H2 Dissociative Adsorption on the Pt(211) Stepped Surface, J. Chem. Phys. 128 (19) (2008) 194715, https://doi.org/10.1063/1.2920488. ISSN 0021-9606, 1089-7690.
[4] A.T. Gee, B.E. Hayden, C. Mormiche, T.S. Nunney, The Role of Steps in the Dynamics of Hydrogen Dissociation on Pt(533), J. Chem. Phys. 112 (17) (2000) 7660–7668, https://doi.org/10.1063/1.481360, ISSN 0021-9606, 1089-7690.
[5] B. Poelsema, K. Lenz, G. Comsa, The Dissociative Adsorption of Hydrogen on Defect-'Free' Pt(111), J. Phys.: Condens. Matter 22 (30) (2010) 304006, https://doi.org/10.1088/0953-8984/22/30/304006. ISSN 0953-8984, 1361-648X.
[6] A. Gee, B. Hayden, C. Mormiche, T. Nunney, The Blocking of the Step-Mediated Indirect Channel to Hydrogen Dissociation by Oxygen on Pt(533), Surf. Sci. 512 (3) (2002) 165–172, https://doi.org/10.1016/S0039-6028(02)01733-8. ISSN 00396028.
[7] I.M.N. Groot, K.J.P. Schouten, A.W. Kleyn, L.B.F. Juurlink, Dynamics of Hydrogen Dissociation on Stepped Platinum, J. Chem. Phys. 129 (22) (2008) 224707, https://doi.org/10.1063/1.3040268. ISSN 0021-9606, 1089-7690.
[8] R. van Lent, S.V. Auras, K. Cao, A.J. Walsh, M.A. Gleeson, L.B.F. Juurlink, Site-Specific Reactivity of Molecules with Surface Defects—the Case of H2 Dissociation on Pt, Science 363 (6423) (2019) 155–157, https://doi.org/10.1126/science.aau6716. ISSN 0036-8075, 1095-9203.
[9] A.C. Luntz, J.K. Brown, M.D. Williams, Molecular Beam Studies of H2 and D2 Dissociative Chemisorption on Pt(111), J. Chem. Phys. 93 (7) (1990) 5240–5246, https://doi.org/10.1063/1.459669. ISSN 0021-9606, 1089-7690.
[10] E. Nour Ghassemi, M. Wijzenbroek, M.F. Somers, G.-J. Kroes, Chemically Accurate Simulation of Dissociative Chemisorption of D2 on Pt(111), Chem. Phys. Lett. 683 (2017) 329–335, https://doi.org/10.1016/j.cplett.2016.12.059. ISSN 0009-2614.
[11] K. Cao, R. van Lent, A. Kleyn, L. Juurlink, A Molecular Beam Study of D2 Dissociation on Pt(111): Testing SRP-DFT Calculations, Chem. Phys. Lett. 706 (2018) 680–683, https://doi.org/10.1016/j.cplett.2018.07.024. ISSN 00092614.
[12] P. Samson, A. Nesbitt, B.E. Koel, A. Hodgson, Deuterium Dissociation on Ordered Sn/Pt(111) Surface Alloys, J. Chem. Phys. 109 (8) (1998) 3255–3264, https://doi.org/10.1063/1.476916. ISSN 0021-9606, 1089-7690.
[13] I.M.N. Groot, A.W. Kleyn, L.B.F. Juurlink, The Energy Dependence of the Ratio of Step and Terrace Reactivity for H2 Dissociation on Stepped Platinum, Angew. Chem. Int. Ed. 50 (22) (2011) 5174–5177, https://doi.org/10.1002/anie.201007093. ISSN 1521-3773.
[14] S.V. Auras, R. van Lent, D. Bashlakov, J.M.P. Bastidas, T. Roorda, R. Spierenburg, L.B.F. Juurlink, Scaling Platinum-Catalyzed Hydrogen Dissociation on Corrugated Surfaces, Angew. Chem. 132 (47) (2020) 21159–21165, https://doi.org/10.1002/ange.202005616. ISSN 1521-3757.
[15] R.A. Olsen, G.J. Kroes, E.J. Baerends, Atomic and Molecular Hydrogen Interacting with Pt(111), J. Chem. Phys. 111 (24) (1999) 11155–11163, https://doi.org/10.1063/1.480473. ISSN 0021-9606, 1089-7690.
[16] D.A. King, G. Wells, Molecular Beam Investigation of Adsorption Kinetics on Bulk Metal Targets: Nitrogen on Tungsten 29 (2) (1972) 454–482.
[17] S.V. Auras, L.B.F. Juurlink, Recent advances in the use of curved single crystal surfaces, submitted.
[18] D.J. Auerbach, in: G. Scoles (Ed.), Atomic and Molecular Beam Methods, Oxford University Press, 1988, pp. 362–379.
[19] R. Olsen, D. McCormack, E. Baerends, How Molecular Trapping Enhances the Reactivity of Rough Surfaces, Surf. Sci. 571 (1–3) (2004) L325–L330, https://doi.org/10.1016/j.susc.2004.08.018. ISSN 00396028.
[20] T. Roorda, S.V. Auras, L.B. Juurlink, Chiral Surface Characterisation and Reactivity Toward H-D Exchange of a Curved Platinum Crystal, Top. Catal. (2020) 1–11.
[21] E.N. Ghassemi, E.W.F. Smeets, M.F. Somers, G.-J. Kroes, I.M.N. Groot, L.B. F. Juurlink, G. Füchsel, Transferability of the Specific Reaction Parameter Density Functional for H2 + Pt(111) to H2 + Pt(211), The Journal of Physical Chemistry C 123 (5) (2019) 2973–2986, https://doi.org/10.1021/acs.jpcc.8b11018. ISSN 1932-7447, 1932-7455.
[22] R.M. Logan, R.E. Stickney, Simple Classical Model for the Scattering of Gas Atoms from a Solid Surface, J. Chem. Phys. 44 (1) (1966) 195–201, https://doi.org/10.1063/1.1726446. ISSN 0021-9606.
[23] W.W. Hayes, J.R. Manson, Classical Theory of Atom Scattering from Corrugated Surfaces (2013) 31.
[24] B. Jackson, Direct and Trapping-Mediated Pathways to Dissociative Chemisorption: CH4 Dissociation on Ir(111) with Step Defects, J. Chem. Phys. 153 (3) (2020) 034704, https://doi.org/10.1063/5.0012252. ISSN 0021-9606.
[25] R. Moiraghi, A. Lozano, E. Peterson, A. Utz, W. Dong, H.F. Busnengo, Nonthermalized Precursor-Mediated Dissociative Chemisorption at High Catalysis Temperatures, The Journal of Physical Chemistry Letters 11 (6) (2020) 2211–2218, https://doi.org/10.1021/acs.jpclett.0c00260.
[26] X. Zhou, Y. Zhang, H. Guo, B. Jiang, Towards Bridging the Structure Gap in Heterogeneous Catalysis: The Impact of Defects in Dissociative Chemisorption of Methane on Ir Surfaces, PCCP 23 (7) (2021) 4376–4385, https://doi.org/10.1039/D0CP06535H.
[27] B. Poelsema, K. Lenz, G. Comsa, The Dissociative Adsorption of Hydrogen on Pt (111): Actuation and Acceleration by Atomic Defects, J. Chem. Phys. 134 (7) (2011) 074703, https://doi.org/10.1063/1.3530286. ISSN 0021-9606, 1089-7690.
[28] M. Luppi, D.A. McCormack, R.A. Olsen, E.J. Baerends, Rotational Effects in the Dissociative Adsorption of H2 on the Pt(211) Stepped Surface, J. Chem. Phys. 123 (16) (2005) 164702, https://doi.org/10.1063/1.2087467. ISSN 0021-9606.