Water Formation under Silica Thin Films: Real-Time Observation of a Chemical Reaction in a Physically Confined Space

Mauricio J. Prieto,* Hagen W. Klemm, Feng Xiong, Daniel M. Gottlob, Dietrich Menzel, Thomas Schmidt, and Hans-Joachim Freund

Dedicated to Helmut Schwarz on the occasion of his 75th birthday

Abstract: *Using low-energy electron microscopy and local photoelectron spectroscopy, water formation from adsorbed O and H_2 on a Ru(0001) surface covered with a vitreous SiO_2 bilayer (BL) was investigated and compared to the same reaction on bare Ru(0001). In both cases the reaction is characterized by moving reaction fronts. The reason for this might be related to the requirement of site release by O adatoms for further H_2-dissociative adsorption. Apparent activation energies (E_a^{app}) are found for the front motion of 0.59 eV without cover and 0.27 eV under cover. We suggest that the smaller activation energy but higher reaction temperature for the reaction on the SiO_2 BL covered Ru(0001) surface is due to a change of the rate-determining step. Other possible effects of the cover are discussed. Our results give the first values for E_a^{app} in confined space.*

The possibility of influencing chemical reactions by performing them in confined spaces has recently attracted the attention of the scientific community.[1] For instance, confinement of an aromatic halogenation reaction inside carbon nanotubes can affect the regioselectivity, thus changing the product distribution.[2] Also, theoretical calculations suggest that confinement of Diels–Alder reactions in carbon nanotubes can affect kinetic as well as thermodynamic aspects of the reaction.[3] The mechanism by which confinement can modify the reaction kinetics is an important aspect that has to be considered in order to reach a rational understanding.

Generally, the spatial confinement of a chemical reaction can affect the reaction kinetics by the modification of the transition state and/or by changing the reaction path, in particular the rate-limiting step. For example, van der Waals interactions can stabilize certain intermediate species, thus lowering the activation energy (E_a) for selected reaction paths.[4] Local electric fields can also affect the progression of a chemical reaction by favoring one transition state over another when multiple paths are possible.[5] Confinement occurs, for example, inside the voids of zeolite materials, which are well known to be active for some chemical reactions due to their acidic reactive sites.[6] However, it may also happen in the space contained between 2D films and their transition metal (TM) support. Hence, attractive and repulsive interactions between the thin film and the catalytically active TM surface can induce changes in its adsorptive properties. For this reason, molecules permeating through the film may interact with the support differently than with the uncovered support.[7] Moreover, the 2D cover may hinder the access of reactants or the removal of products by acting as size-selective molecular sieves and changing the rate-limiting step.

We report herein the results of H_2 intercalation and reaction with preadsorbed O atoms under a vitreous SiO_2 bilayer supported on Ru(0001). We show that physical confinement of the H_2 oxidation reaction influences its energetics by decreasing the apparent activation energy (E_a^{app}) and probability of the chemical process. For our experiments a vitreous bilayer was produced on a Ru(0001) surface.[8] Experimental details on the preparation can be found in the Experimental Section and in previous publications.[9] The film has proven to be inert towards H_2 chemisorption under the experimental conditions used, thus showing that the reaction takes place only on the active Ru surface. An important aspect to consider is that the SiO_2 film is decoupled from the Ru(0001) substrate and interacts with it only via van der Waals forces.[10] In this context, Emmez et al. showed that a vitreous silica bilayer can intercalate gases such as D_2, O_2 and CO, as proved by FTIR and TPD spectroscopy.[1c] The intercalation of gases into the space enclosed by the SiO_2 film opens the possibility of studying the mechanism by which confinement can undermine or boost a chemical reaction, as well as the influence of the structure of the material defining the small physical space.

[*] Dr. M. J. Prieto, Dr. H. W. Klemm, Dr. D. M. Gottlob,
Prof. Dr. D. Menzel, Dr. T. Schmidt, Prof. Dr. H.-J. Freund
Department of Chemical Physics
Fritz-Haber Institute of the Max-Planck Society
Faradayweg 4–6, 14195-Berlin (Germany)
E-mail: prieto@fhi-berlin.mpg.de

Dr. F. Xiong
Department of Chemical Physics
University of Science and Technology of China
Hefei 230026 (P. R. China)

Prof. Dr. D. Menzel
Physik-Department E20, Technical University München
85778 Garching (Germany)

As a result of the preparation procedure, the SiO₂|Ru-(0001) interface contains oxygen with an estimated coverage of $\theta_{O,nominal} = 0.75$ ML.[11] This state of the film has been described in previous publications as O-rich and corresponds to the initial stage of our reaction experiments. In the next step, H₂ is intercalated under the silica bilayer at high temperatures ($T \approx 550$–650 K) to produce atomic H by dissociative adsorption and finally form H₂O. Scheme 1 exhibits a representation of the idea behind the experiment.
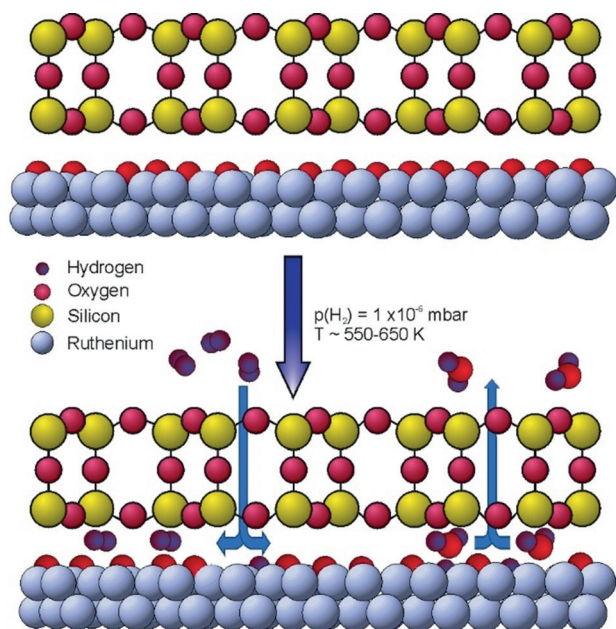
Scheme 1. Representation of the sample used to study the water formation reaction in the confined space under a vitreous SiO₂ bilayer supported on Ru (0001).

After the complete characterization of the as-prepared vitreous SiO₂ bilayer, real-time low-energy electron microscopy (LEEM) was used to follow the effect of hydrogen dosing up to 1×10^{-6} mbar at various temperatures. During the annealing, a front appearing as a sudden change in image intensity was seen moving across the sample surface. Figure 1 displays a series of snapshots showing the time evolution of the front propagation. This front movement seems not to follow specific directions on the surface when different areas were analysed (not shown), although it is clear that step bunches on the surface (red arrows in Figure 1) constitute a barrier for its propagation.

To identify the nature of the front, its progression was stopped and both sides were characterized by means of LEEM-IV and X-ray photoemission electron spectroscopy (XPS) of the O 1s and Si 2p core levels. Results are presented in Figure 2. A thorough description of the principle of LEEM-IV measurements and their use is beyond the scope of this publication and hence the readers are referred to specific literature on this topic.[12] However, it is important to say that the oscillations in these curves depend on the state of the sample surface (electronic and structural) and they can be used as fingerprints to identify changes upon sample treat-
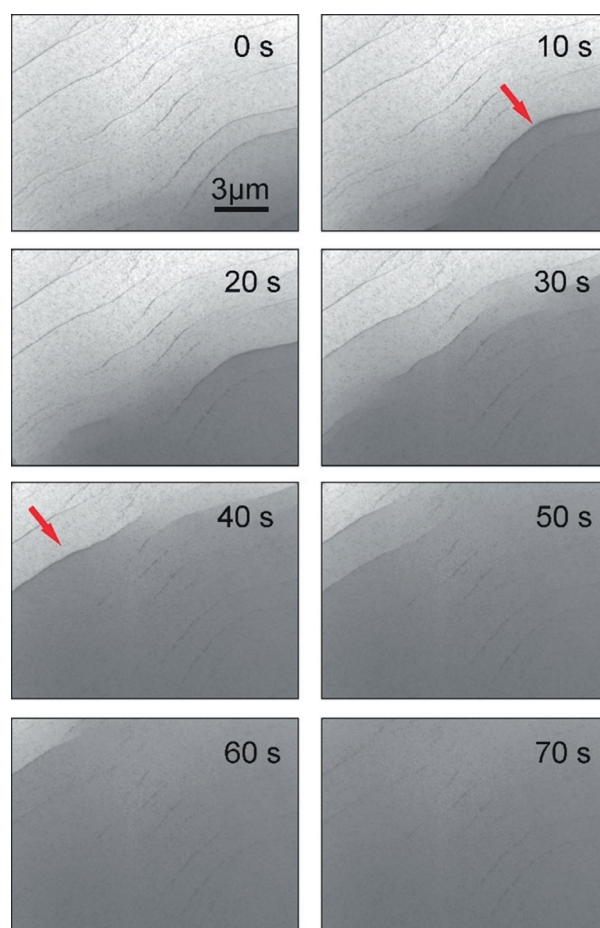

Figure 1. Snapshots of the reaction front observed during annealing in 1×10^{-6} mbar H₂ at 550 K. $E_{kin} = 14$ eV.

ment. In the case of SiO₂/Ru(0001), our group has performed a systematic study addressing the differences in LEEM-IV curves due to changes in the bilayer structure.

LEEM-IV curves collected on both sides of the front, as depicted in the inset of Figure 2a, show that within the energy range of 4–30 eV the oscillations in the reflectivity curve of the (0,0) beam are roughly the same for both sides, except for a shift in energy by about 1 eV. This suggests that the nature of the film is preserved upon H₂ exposure and is confirmed by the photoelectron spectra presented in Figure 2b. In this case, no changes in the lineshape of Si 2p are observed, thus making it possible to exclude any possibility of film degradation due to partial reduction of SiO₂ that would manifest as contributions at the lower binding energy tail. Furthermore, the possibility of extensive hydroxylation of the silica film, either by H or OH transfer to the SiO₂ bilayer or by reaction with potentially confined H₂O molecules is excluded based on the lack of changes in the XPS O 1s lineshape (Figure 2b). Additionally, earlier published reports show that the hydroxylation of silica films is a quite demanding process in terms of the experimental conditions needed. For instance, ice layers were created at 100 K and subjected to electron irradiation at energies considerably higher than those used in our experiments (100–200 eV) in order to create silanol groups on the silica surface at low concentrations.[13]
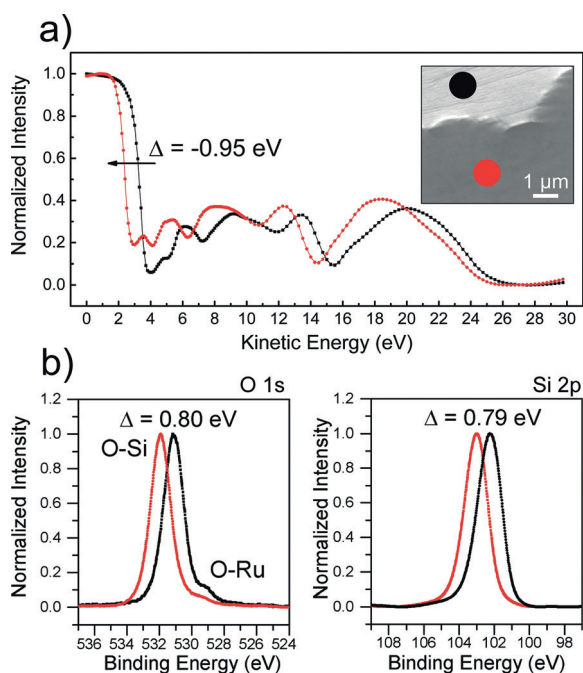
Figure 2. a) LEEM-IV curves recorded at room temperature on different areas of the H_2-treated SiO_2 vitreous BL on Ru(0001), as indicated by the inset. b) O 1s and Si 2p XPS spectra collected before and after H_2 treatment. O 1s and Si 2p lines were measured with 600 eV and 175 eV, respectively.

On the other hand, changes are seen in the LEEM-IV curves at energies below 4 eV in the feature known as MEM-LEEM transition.[12b] It defines the energy at which the incoming electrons have sufficient kinetic energy to overcome the surface potential and interact with the unoccupied electronic states on the sample. Thus, the position of the transition can be directly related to the vacuum level, tracking work function (Φ) changes of the surface. Figure 2a clearly shows that, upon H_2 treatment, there is a decrease in Φ on moving from the bright side of the front (black circle) to the darker side (red circle). Moreover, a closer look at the O 1s line reveals that the lower binding energy component ascribed to the interfacial oxygen adsorbed on the Ru surface under the silica film follows the same trend as the work function, both indicating removal of O_{ads} from the Ru surface. It is important to stress that the change seen on the work function (-0.95 eV) relative to that in the XPS line positions (0.8 eV) can be explained by the fact that data acquisition is performed at different sample positions and the O content under the SiO_2 film may slightly differ across the surface. The change in work function and energy shifts of the core level peaks in XPS for this system were previously reported and ascribed to the removal of the oxygen-Ru dipoles at the silica | Ru interface;[10,14] in Ref. [15] the work function change has served for accurate measurement of the oxygen removal by water formation. The possibility of O_{Ru} loss due to thermally induced molecular desorption of O_2 is rejected based on TPD data published by Madey et al.,[16] reporting an onset for O_2 desorption from Ru(0001) above 1000 K.

It is important to point out that because the front is seen on both bare and SiO_2-covered Ru (0001), we exclude any

effects on contrast formation by SiO_2 lift-off. Instead, a change on the surface work function due to O_{Ru} removal during H_2O formation is proposed to be responsible for the intensity change. Koch et al.[15a] concluded from kinetic analysis that the reaction of $O_{ads} + H_{ads}$ is rate limiting, with extremely low H_2 and H_2O coverages on bare Ru under reaction conditions (H_2 coadsorbed with O desorbs completely at 400 K[17] and H_2O at 220 K[18]). Also, they saw that the reaction propagates by the emptying O sites, required for further H_2 dissociative adsorption. This finding, derived from an unexpected dependence on starting O_{Ru} coverage and nonequilibrium effects, explains the formation of reaction fronts.

To find the temperature dependence of the front velocity (v_{front}) and extract its E_a^{app}, its movement was recorded in real time at different temperatures. The v_{front} values were calculated from the intensity evolution over time, to average out local differences. The values are presented in the Arrhenius plot in Figure 3. The Arrhenius analysis yields an E_a^{app} for the
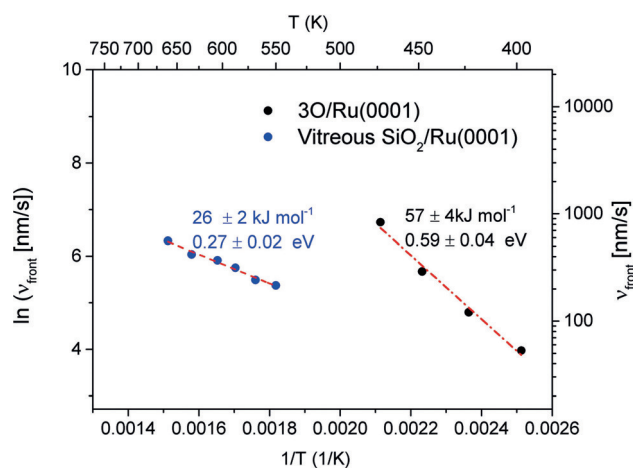

Figure 3. Arrhenius plots of the temperature-dependent velocities of the H_2 oxidation front on SiO_2/Ru(0001) (blue dots) and 3O/Ru(0001) (black dots).

front motion under SiO_2 of 0.27 ± 0.02 eV. The value reported here is, to the best of our knowledge, the first reported for a chemical reaction in a space confined by a 2D material. We then performed the same experiment on a bare Ru(0001) surface, precovered with a 3O layer,[11] to clearly define the effect of the cover and to make use of the previously obtained knowledge of this reaction without cover.[15a] Also in this case we found moving reaction fronts with characteristics similar to those observed on the SiO_2-covered Ru surface. The Arrhenius analysis yields a value of 0.59 ± 0.04 eV for the E_a^{app}, in excellent agreement with the value reported by Koch et al.[15a] for the water formation on basal and vicinal Ru surfaces, albeit at lower starting θ_O.

The agreement of the E_a^{app} values for bare Ru with literature values suggests that most likely the front motion indeed is identical to that of the $(O + H)_{Ru}$ reaction. However, with a complete, immobile 3O layer, the reaction would not be possible at all, because H_2 cannot dissociate on it (first step of the reaction mechanism). Therefore, we suggest that the

reaction starts at defects on the surface, where local fluctuations on the disordered 3O layer can allow H_2 dissociation, and then spreads across the surface.

Two main factors should be considered on this discussion. First, a strong decrease of E_a^{app} is found and, also, a strong decrease of the preexponential factor (by a factor of $\approx 10^4$) is observed for the undercover reaction. This behavior suggests that the energetically favored path under the SiO_2 cover has only very small phase space, compared to that on the free surface. Then, a change of the rate-limiting step may become likely. However, the overall water formation reaction is a complex process, where many parameters can be accessed. The origin of the difference between the activation energies obtained for the reaction on the uncovered and covered Ru(0001) surfaces is still not completely clear. Nonetheless, we can give some hints on the processes that could be affected by the presence of the SiO_2 cover. In principle, the following reaction steps can lead to water formation on Ru(0001) [Eqs. (1)–(5)]:

$$H_{2(g)} \rightleftharpoons 2H_{(ads)} \tag{1}$$

$$H_{(ads)} + O_{(ads)} \rightleftharpoons OH_{(ads)} \tag{2}$$

$$OH_{(ads)} + H_{(ads)} \rightleftharpoons H_2O_{(ads)} \tag{3}$$

$$2\,OH_{(ads)} \rightleftharpoons H_2O_{(ads)} + O_{(ads)} \tag{4}$$

$$H_2O_{(ads)} \rightleftharpoons H_2O_{(g)} \tag{5}$$

We emphasize that, under our experimental conditions, both directions of each step are fast.

On uncovered Ru(0001), reactions 1–3 and 5 have been described as part of the mechanism, with reaction 2 being the rate-determining step.[15a,19] In confined space, according to Hacarlioglu et al.,[20] a SiO_2 BL is essentially freely penetrated by H_2, thus leaving step 1 unaltered or only slightly modified. On the other hand, it seems reasonable to assume that the presence of the SiO_2 bilayer can strongly interfere with reaction (5) by impeding water diffusion away from the confined space, thus increasing its residence time on Ru. In this case, water diffusion through the SiO_2 film or on the Ru surface within the confined space are processes that need to be considered. For instance, Kostinski et al.[21] have reported that water diffusion through silica is thermally activated, with $E_a \approx 0.3$ eV for seven-membered rings. Since the H_2O formed has to be removed in the vicinity of the reaction front in order to regenerate the adsorption sites and propagate the front, one possibility is that the rate-limiting step for the reactions under confinement is its removal instead of reaction 2. Thus, the prerequisite of the highest E_a for the rate-determining step can be overruled by a lower preexponential factor for the process, here interpreted as the probability for water to find the right position on the SiO_2 film to escape.

On the other hand, the confinement of water, due to its slow removal in step 5), implies that the probability of reacting with O_{ads} (step 4) increases, thus providing an additional path for OH formation. In this case, a disproportionation path that is originally missing on bare Ru but that has been reported on metals such as Pt[22] could come into

play. Although it has been reported that the H_2O dissociative adsorption is inhibited by O_{ads} at $\theta_o > 0.2$ ML on bare Ru,[23] the possibility of opening a new reaction path due to water confinement cannot be discarded based on the present data set and, hence, should be considered as a potential explanation for the different E_a^{app} observed. For instance, it has been reported by Santiburcio and Marx,[24] based on ab initio molecular dynamics calculations, that confinement of water molecules at high temperatures (ca. 500 K) can lead to an unexpected enhancement of self-dissociation, independent of the material used to define the confined space.

In conclusion, we have shown that, although it is not possible to irrefutably explain the origin of the differences at this moment, the confinement of a chemical reaction can have an impact on the reaction mechanism by either modifying existing reaction steps or adding new ones not present for reaction in a nonconfined space. Whether this is a consequence of product confinement or an intrinsic change in the reaction mechanism is still an open question and, in order to thoroughly understand the nature of the rate-limiting process, we need the aid of further theoretical calculations, which are now in progress.

Experimental Section

The experiments were carried out in the SMART microscope operating at the UE49-PGM beam line of the synchrotron light source BESSY II of the Helmholtz Centre Berlin (HZB). The aberration corrected and energy filtered LEEM/PEEM instrument combines microscopy, diffraction, and spectroscopy techniques for comprehensive characterization. The base pressure of the system is 10^{-10} mbar.

The Ru(0001) single crystal was prepared by cycles of Ar^+ sputtering at room temperature and annealing in oxygen at 1170 K. Cleaning cycles were repeated until no contamination could be detected by XPS, with a few 100 nm wide terraces and a sharp (1×1) LEED pattern. Sample temperature was measured either by a W26%Re/W5%Re thermocouple or by a pyrometer (IMPAC IGA 740) with an absolute accuracy of ≈ 10 K. Oxygen (99.999%) and hydrogen (99.999%) were dosed directly into the experimental chamber; Si was sublimated from a 4 mm thick rod (99.999%) using a commercial evaporator (Omicron EFM3) under grazing incidence of 20°.

For the H_2 intercalation and oxidation experiments, the as prepared $SiO_2/Ru(0001)$ sample was heated typically up to 540 K in UHV and only after T stabilization H_2 was dosed into the experimental chamber up to 1×10^{-6} mbar. Once the reaction front was observed, the temperature dependent measurements were done by adjusting the sample temperature by resistive heating of a filament from the backside.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

[1] a) H. Li, J. Xiao, Q. Fu, X. Bao, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 5930–5934; b) E. Emmez, J. Anibal Boscoboinik, S. Tenney, P. Sutter, S. Shaikhutdinov, H.-J. Freund, *Surf. Sci.* **2016**, *646*, 19–25; c) E. Emmez, B. Yang, S. Shaikhutdinov, H. J. Freund, *J. Phys. Chem. C* **2014**, *118*, 29034–29042.

[2] S. A. Miners, G. A. Rance, A. N. Khlobystov, *Chem. Commun.* **2013**, *49*, 5586–5588.

[3] N. M. Smith, K. Swaminathan Iyer, B. Corry, *Phys. Chem. Chem. Phys.* **2014**, *16*, 6986–6989.

[4] A. J. Jones, S. I. Zones, E. Iglesia, *J. Phys. Chem. C* **2014**, *118*, 17787–17800.

[5] Y.-Z. Chen, L.-Z. Wu, L.-P. Zhang, C.-H. Tung, *J. Org. Chem.* **2005**, *70*, 4676–4681.

[6] J. Sauer, *Faraday Discuss.* **2016**, *188*, 227–234.

[7] a) R. T. Mu, Q. Fu, L. Jin, L. Yu, G. Z. Fang, D. L. Tan, X. H. Bao, *Angew. Chem. Int. Ed.* **2012**, *51*, 4856–4859; *Angew. Chem.* **2012**, *124*, 4940–4943; b) L. Jin, Q. Fu, A. Dong, Y. Ning, Z. Wang, H. Bluhm, X. Bao, *J. Phys. Chem. C* **2014**, *118*, 12391–12398.

[8] M. Heyde, S. Shaikhutdinov, H. J. Freund, *Chem. Phys. Lett.* **2012**, *550*, 1–7.

[9] a) B. Yang, W. E. Kaden, X. Yu, J. A. Boscoboinik, Y. Martynova, L. Lichtenstein, M. Heyde, M. Sterrer, R. Wlodarczyk, M. Sierka, J. Sauer, S. Shaikhutdinov, H. J. Freund, *Phys. Chem. Chem. Phys.* **2012**, *14*, 11344–11351; b) H. W. Klemm, G. Peschel, E. Madej, A. Fuhrich, M. Timm, D. Menzel, T. Schmidt, H. J. Freund, *Surf. Sci.* **2016**, *643*, 45–51.

[10] R. Włodarczyk, M. Sierka, J. Sauer, D. Löffler, J. J. Uhlrich, X. Yu, B. Yang, I. M. N. Groot, S. Shaikhutdinov, H. J. Freund, *Phys. Rev. B* **2012**, *85*, 085403.

[11] M. Gsell, M. Stichler, P. Jakob, D. Menzel, *Isr. J. Chem.* **1998**, *38*, 339–348.

[12] a) E. Bauer, *Surface Microscopy with Low Energy Electrons*, Springer, New York, **2014**; b) E. Bauer, *Rep. Prog. Phys.* **1994**, *57*, 895; c) J. I. Flege, E. E. Krasovskii, *Phys. Status Solidi RRL* **2014**, *8*, 463–477.

[13] a) W. E. Kaden, S. Pomp, M. Sterrer, H.-J. Freund, *Top. Catal.* **2017**, *60*, 471–480; b) X. Yu, E. Emmez, Q. Pan, B. Yang, S. Pomp, W. E. Kaden, M. Sterrer, S. Shaikhutdinov, H.-J. Freund, I. Goikoetxea, R. Wlodarczyk, J. Sauer, *Phys. Chem. Chem. Phys.* **2016**, *18*, 3755–3764.

[14] M. Wang, J.-Q. Zhong, J. Kestell, I. Waluyo, D. J. Stacchiola, J. A. Boscoboinik, D. Lu, *Top. Catal.* **2017**, *60*, 481–491.

[15] a) M. H. Koch, P. Jakob, D. Menzel, *Surf. Sci.* **1996**, *367*, 293–306; b) D. Menzel, *Surf. Sci.* **2016**, *650*, 187–195.

[16] T. E. Madey, H. A. Engelhardt, D. Menzel, *Surf. Sci.* **1975**, *48*, 304–328.

[17] A. Schiffer, P. Jakob, D. Menzel, *Surf. Sci.* **2000**, *465*, 198–210.

[18] N. S. Faradzhev, K. L. Kostov, P. Feulner, T. E. Madey, D. Menzel, *Chem. Phys. Lett.* **2005**, *415*, 165–171.

[19] M. Schick, J. Xie, W. J. Mitchell, W. H. Weinberg, *J. Chem. Phys.* **1996**, *104*, 7713–7718.

[20] P. Hacarlioglu, D. Lee, G. V. Gibbs, S. T. Oyama, *J. Membr. Sci.* **2008**, *313*, 277–283.

[21] S. Kostinski, R. Pandey, S. Gowtham, U. Pernisz, A. Kostinski, *IEEE Electron Device Lett.* **2012**, *33*, 863–865.

[22] S. Völkening, K. Bedürftig, K. Jacobi, J. Wintterlin, G. Ertl, *Phys. Rev. Lett.* **1999**, *83*, 2672–2675.

[23] M. J. Gladys, A. Mikkelsen, J. N. Andersen, G. Held, *Chem. Phys. Lett.* **2005**, *414*, 311–315.

[24] D. Muñoz-Santiburcio, D. Marx, *Phys. Rev. Lett.* **2017**, *119*, 056002.