Angewandte Zuschriften

Surface Chemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201500410
Internationale Ausgabe: DOI: 10.1002/anie.201500410

Zundel-like and Eigen-like Hydrated Protons on a Platinum Surface**

*Youngsoon Kim, Sunghwan Shin, and Heon Kang**

Abstract: *The nature of hydrated protons is an important topic in the fundamental study of electrode processes in acidic environment. For example, it is not yet clear whether hydrated protons are formed in the solution or on the electrode surface in the hydrogen evolution reaction on a Pt electrode. Using mass spectrometry and infrared spectroscopy, we show that hydrogen atoms are converted into hydrated protons directly on a Pt(111) surface coadsorbed with hydrogen and water in ultrahigh vacuum. The hydrated protons are preferentially stabilized as multiply hydrated species ($H_5O_2^+$ and $H_7O_3^+$) rather than as hydronium (H_3O^+) ions. These surface-bound hydrated protons may play an important role in the interconversion between adsorbed hydrogen atoms and solvated protons in solution.*

Understanding the nature of hydrated protons is important in many branches of chemical research, including acid–base reactions, enzymatic functions, and electrode processes in acidic aqueous environments. For example, proton transfer between hydrated protons and an electrode surface is a key elementary process of the hydrogen evolution reaction (HER) on Pt electrodes, $2H^+(aq) + 2e^- \leftrightarrow H_2$, which is one of the most studied electrode reactions. However, essential features of the HER are still not well understood,[1] particularly the conversion between $H^+(aq)$ in solution and atomic hydrogen adsorbed on the electrode surface. It is unclear whether the reaction involves the formation of surface-bound ion species or charge is transferred between nonspecifically adsorbed hydrated protons and the electrode surface prior to hydrogen adsorption. A central question to this issue is the stability of hydrated protons on a Pt electrode surface.

One strategy to approach this issue is to generate hydrated protons in a water film adsorbed on a metal surface in ultrahigh vacuum (UHV) and characterize their properties using surface spectroscopic measurements.[1b,2] Wagner and co-workers[1b,2c,d] studied the interaction of adsorbed hydrogen and water on a Pt(111) surface using high-resolution electron energy-loss spectroscopy (HREELS). They reported that a vibrational band at about 1150 cm^{-1} appeared after heating the surface at 150 K, which was interpreted as a signature of hydronium (H_3O^+) ions on the surface. The same feature has been observed on Pt(100)[2e] and also in reflection–absorption infrared spectroscopy (RAIRS) studies.[2g] Later, theoretical calculations of the gas-phase vibrational spectra of protonated water clusters and comparison with the vibrational feature at about 1150 cm^{-1} suggested that the corresponding surface species are more likely protonated water clusters rather than hydronium ions.[2f] Studies of the hydrogen–deuterium (H–D) exchange between coadsorbed water and hydrogen on Au(111) and density functional theory (DFT) calculations suggest protonated water clusters as an intermediate for the H–D exchange reaction.[2k] On the other hand, there is continuing doubt regarding the presence of stable hydrated proton species on a Pt surface owing to the thermodynamic endoergicity of hydronium ion formation on the surface. Recent studies of the coadsorption of water and hydrogen on stepped Pt surfaces could neither support nor disprove the existence of hydrated protons on the surfaces.[2h,i] It is yet to be clarified whether protons are adsorbed specifically or nonspecifically on Pt electrodes. In the present work, we examine the surface species formed upon coadsorption of water and hydrogen on Pt(111) using mass spectrometry and RAIRS. The study shows that adsorbed hydrogen atoms are ionized to protons directly on the Pt surface, resulting in the formation of multiply hydrated proton species of certain preferential structures ($H_5O_2^+$ and $H_7O_3^+$) rather than hydronium ions.

We performed low-energy sputtering (LES) and reactive ion scattering (RIS) experiments for coadsorbed water and hydrogen on Pt(111). In this experiment, a Pt(111) surface was exposed to H_2 gas to generate atomic H coverage of 0.75 monolayer equivalent (MLE) and then to H_2O vapor to generate water coverage of 1.2 monolayer (ML) at less than 90 K. Atomic H coverage is expressed in units of MLE, where $1\,MLE = 1.5 \times 10^{15}$ atoms cm^{-2}, which is equivalent to the metal atom density of Pt(111). A H/Pt ratio of 1:1 is attained at the saturation exposure of hydrogen on Pt(111).[3] The H_2O monolayer density on Pt(111) is $1\,ML = 1.2 \times 10^{15}$ molecules cm^{-2} ($\sqrt{39}$ structure).[4] Figure 1a shows the mass spectrum of LES and RIS signals obtained on a Pt surface after H and H_2O adsorption at low temperature (< 90 K). An RIS signal of CsH_2O^+ appeared at $m/z = 151$ amu/charge, which was produced by the pickup of surface H_2O molecules by the scattering Cs^+ projectiles. No LES signal was observed on this surface.

Figure 1b shows the spectrum obtained after the surface was heated at 140–150 K. Strong LES signals appeared at $m/z = 37$ ($H_5O_2^+$) and 55 ($H_7O_3^+$) and a weaker signal at $m/z = 73$ ($H_9O_4^+$). These signals indicated the formation of multiply hydrated proton structures ($H^+(H_2O)_2$, $H^+(H_2O)_3$, and $H^+(H_2O)_4$) on the surface. Higher-mass LES signals were not detected. Interestingly, the H_3O^+ ($m/z = 19$) signal was very weak or nearly absent from the surface; the H_3O^+ intensity was usually even smaller than that of H_2O^+ ($m/z = 18$), with their relative ratio fluctuating with LES measurement conditions. The observed intensity distribution for hydrated

---

[*] Y. Kim, S. Shin, Prof. H. Kang
Department of Chemistry, Seoul National University
1 Gwanak-ro, Seoul 151-747 (Republic of Korea)
E-mail: surfion@snu.ac.kr

[**] This work was supported by the grant of the National Research Foundation (NRF) of Korea funded by the Korea government (MSIP) (No. 2007-0056095).

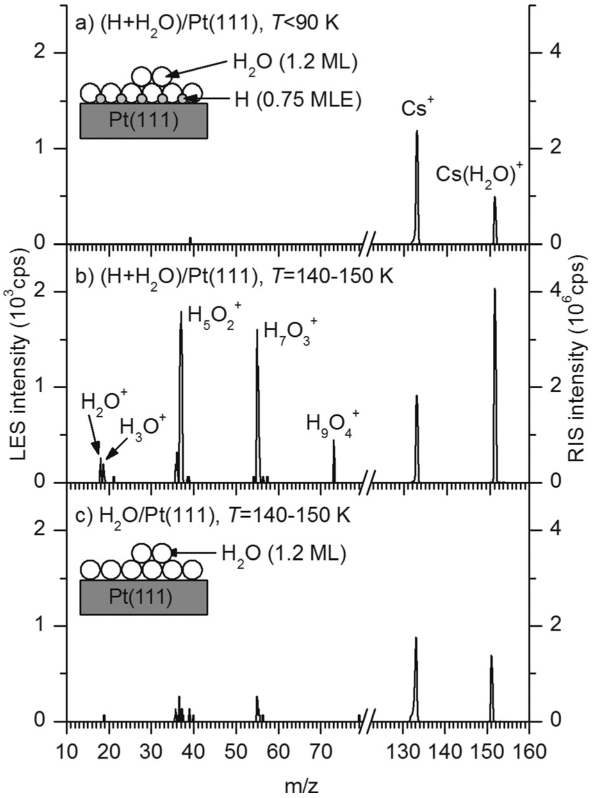

Figure 1. Positive-ion LES signals (shown for $m/z \leq 80$) and RIS signals ($m/z > 133$) obtained from various surfaces. a) A Pt(111) surface with coadsorbed H (0.75 MLE) and H_2O (1.2 ML) at ≤ 90 K. b) The sample prepared in (a) was heated at 140 K for 100 s and then at 150 K for a few seconds. c) H_2O (1.2 ML) was adsorbed on a bare Pt(111) surface and heated in the same way as for surface (b). All spectra were obtained after the sample was cooled back to ≤ 90 K. The Cs^+ beam energy was 28 eV.

proton signals is very unusual. For example, when hydrated protons are generated by acid ionization on an amorphous solid water (ASW) film and detected by mass spectrometry, the H_3O^+ signal is the strongest, and the intensities of more hydrated species decrease rapidly with increasing hydration number.[5] The contrastingly weak H_3O^+ intensity for the present surface indicates that the nature of the hydrated protons is quite different from that generated by acid ionization on ASW films.

The appearance of weak H_2O^+ and H_3O^+ signals can be attributed to fragmentation of larger protonated water clusters, such as $H_5O_2^+$ and $H_7O_3^+$. It is difficult to imagine that H_2O^+ exists on a metal surface because the ionization energy of H_2O is very high (12.6 eV). When large protonated water clusters are ejected from the surface in the LES process, their unimolecular dissociation in the gas phase may produce H_2O^+, such as by reaction (1):

$$(H_5O_2^+)^* \rightarrow (H_3O^+)^* + H_2O \rightarrow H_2O^+ + H + H_2O \tag{1}$$

Here, $(H_5O_2^+)^*$ and $(H_3O^+)^*$ denote the energized species in the gas phase. Only the lowest-energy decomposition channel is shown in reaction (1). Note that reaction (1) will produce both H_3O^+ and H_2O^+ signals, with their intensity ratios depending on the lifetime of $(H_3O^+)^*$ inside a mass spectrometer. The observed fluctuations of the H_3O^+ and H_2O^+ intensities are consistent with this interpretation. A small $H_4O_2^+$ peak appearing at $m/z = 36$ may also be explained by similar unimolecular dissociation reactions from $H_7O_3^+$.

A control experiment was performed to examine whether hydrated protons could be formed without adsorbed H atoms. Figure 1c shows the spectrum obtained when only H_2O was adsorbed on a Pt(111) surface. The $H_5O_2^+$ and $H_7O_3^+$ signals were very weak as compared to those observed in Figure 1b. Owing to the difficulty of eliminating atomic hydrogen impurities from the Pt surface completely, it was difficult to judge whether these hydrated protons originated from the impurity hydrogen atoms or formed in the pure H_2O layer. However, it was clear that most of the $H_5O_2^+$ and $H_7O_3^+$ signals observed in Figure 1b resulted from the coadsorbed H and H_2O layer.

In previous work,[2c–g] coadsorption of H and H_2O on Pt surfaces at 150 K produced a vibrational band at about 1150 cm^{-1} in HREELS and RAIRS, and this feature was assigned as the symmetric bending mode of "hydronium" ions. We performed RAIRS experiments to compare with these reports. In Figure 2, spectrum (a) was measured after H and H_2O coadsorption at low temperature, the same condition as that used for Figure 1a. The spectrum showed vibrational bands at 3700 cm^{-1} (free O–H stretching), ca. 3400 cm^{-1} (hydrogen-bonded O–H stretching), ca. 1640 cm^{-1} (scissoring), and ca. 900 cm^{-1} (librational mode; almost buried in the cut-off region). The "hydronium" band was not observed. When this sample was heated at 150 K, shown as spectrum (b), a new band appeared at about 1130 cm^{-1}, which closely resembled the "hydronium" band in the previous reports.[2c,g] This band did not appear on a pure H_2O layer on Pt(111). The correlation between the RAIRS and LES results indicates that the circa 1130 cm^{-1} band is the result of multiply hydrated proton species on the surface.

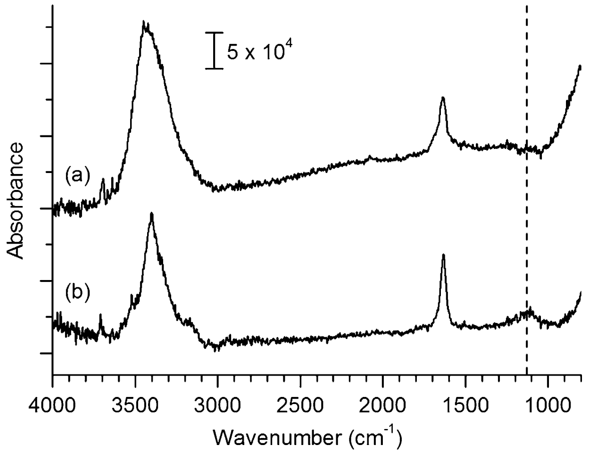

Figure 2. a) RAIR spectrum of a Pt(111) surface with coadsorbed H (0.75 MLE) and H_2O (1.2 ML) at 90 K. b) Spectrum measured after heating the sample at 140–150 K and cooling at 90 K, as was done for Figure 1b. The dotted line marks the position of the hydrated proton band (ca. 1130 cm^{-1}).

Altogether, these observations show that hydrated protons can be stabilized on the Pt surface. However, they exist mostly as multiply hydrated $H_5O_2^+$ and $H_7O_3^+$ species and, to a smaller extent, as $H_9O_4^+$ rather than as monohydrated species (H_3O^+).

According to theoretical studies,[6] the most prevalent structure of hydrated protons in bulk liquid water is a triply coordinated hydronium ion, $H_3O^+(H_2O)_3$, often called an Eigen cation. $H_5O_2^+$ (a Zundel cation) plays an important role in proton transport through interconversion between different proton solvation structures. In the case of water and hydrogen coadsorption on Pt(111), water molecules form a two-dimensional H-bonding network on the surface, and hydrogen atoms occupy the fcc threefold-hollow sites of Pt(111).[2b,7] The two-dimensional structure of the water layer will suppress the formation of $H_3O^+(H_2O)_3$ and larger water clusters, which have a bent geometry. On the other hand, $H_5O_2^+$ and $H_7O_3^+$ can adapt a planar geometry and thus be stabilized in the water layer. In this respect, $H_5O_2^+$ and $H_7O_3^+$ species formed on the surface may be regarded as two-dimensional analogues of Zundel and Eigen cations, respectively.

We further characterized the properties of hydrated protons present on the Pt surface by investigating their H–D exchange behavior with water. For this experiment, a Pt(111) surface was first adsorbed with D atoms and then with H_2O. Figure 3 a shows the LES and RIS spectra obtained from this surface as prepared at a temperature below 90 K, where no hydrated proton signals appeared. Upon heating the sample at 150 K, shown as spectrum (b), LES signals appeared for $H_5O_2^+$ and $H_7O_3^+$ and their D-substituted isotopologues. The RIS spectrum showed $Cs(HDO)^+$ as a new signal. The isotopologue intensity ratio for $H_5O_2^+/H_4DO_2^+/H_3D_2O_2^+$ was 0.60:0.29:0.11, and the ratio for $H_7O_3^+/H_6DO_3^+/H_5D_2O_3^+$ was 0.58:0.25:0.16. These ratios indicated a H/D abundance ratio of 0.91:0.09 in these protonated water clusters. A close H/D abundance ratio was estimated for the surface water molecules from the $Cs(H_2O)^+/Cs(HDO)^+$ intensity ratio of 5:1. Desorbing water molecules exhibited a similar H/D ratio in temperature-programmed desorption (TPD) experiments (not shown). Without hydrated protons, the H–D exchange reaction of water did not occur, as shown in Figure 3 a. These observations indicate that hydrated protons undergo rapid proton (deuteron) transfer with water to establish a H–D exchange equilibrium between the hydrated protons and water.

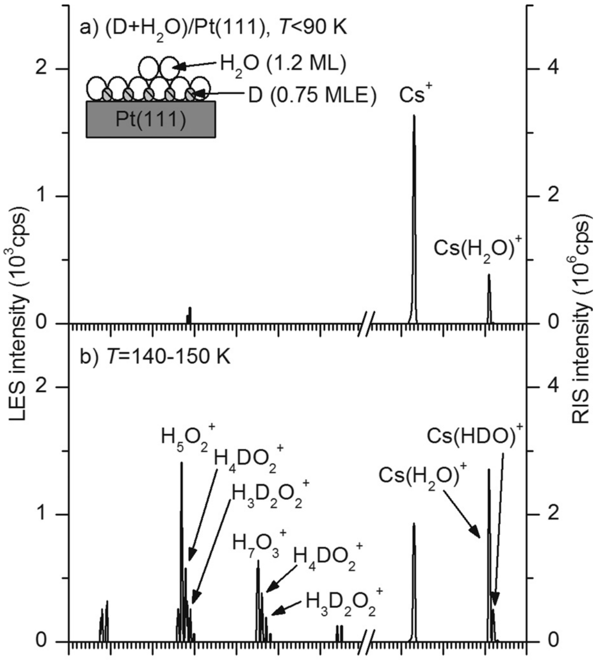

Figure 3. a) LES and RIS spectra obtained from a Pt(111) surface with coadsorbed D (0.75 MLE) and H_2O (1.2 ML) at < 90 K. b) The sample was heated at 140 K for 100 s and briefly at 150 K. The LES and RIS measurements were conducted below 90 K with a Cs^+ beam energy of 28 eV.

The observed H/D ratios, however, indicate that only some of the adsorbed D atoms participated in the H–D exchange reaction. For example, from the H_2O/HDO abundance ratio of 5:1, it can be deduced that 15 % of surface D atoms were incorporated into water to form HDO (heating the sample at 150 K reduced the surface coverage of water to 0.8 ML and that of D and H atoms to 0.7 MLE, according to TPD results). This, in turn, indicates that only 15 % of surface D (or H) atoms were ionized to D^+ (or H^+) by charge transfer to Pt, while the rest remained as neutral atoms.

The next stage of the investigation involved the migratory behavior of protons in the vertical direction through a water layer. For this experiment, hydrated protons were generated on Pt(111) by H and H_2O coadsorption, as was done above, and then an ASW layer was overlaid on this surface by depositing H_2O vapor at 90 K. The ASW film buried the hydrated protons completely when the film thickness exceeded about 3 ML, as evidenced by the disappearance of the hydrated proton signal in LES, shown in Figure 4 I-a. The difference IR spectrum, Figure 4 II-a, shows that the vibrational feature of hydrated protons moved from about 1130 cm^{-1} to about 1260 cm^{-1}. The latter position was close to the symmetric bending frequency of hydrated protons in ASW.[8] This change indicated that hydrated protons with two-dimensional structure in the coadsorbed H and H_2O layer changed to different structures in the three-dimensional environment of a thick water film. The absence of hydrated proton signals in LES indicated that protons were trapped inside the ASW film at this stage, without migrating all the way to the film surface.

We then adsorbed NH_3 molecules on top of the ASW overlayer. Here, the thickness of the ASW overlayer was increased to 20 ML prior to NH_3 adsorption. Figure 4 b shows the appearance of LES signals for NH_4^+ ($m/z = 18$), NH_4^+-(NH_3) ($m/z = 35$), and $NH_4^+(H_2O)$ ($m/z = 36$). A new RIS signal appeared for $CsNH_3^+$ ($m/z = 150$). These signals indicate the formation of ammonium ions on the surface via protonation of NH_3 adsorbates. We confirmed that the ammonium ion signals were not generated by secondary ionization of neutral NH_3 adsorbates through control experiments without hydrated protons.[9] The difference RAIR spectrum (Figure 4 II-b) shows a vibrational feature at about

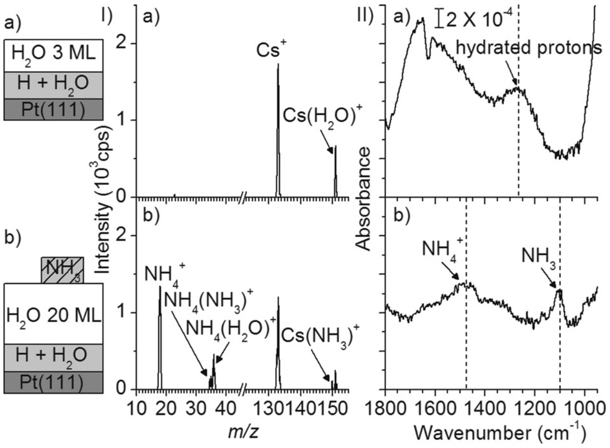

Figure 4. I) LES and RIS spectra and II) difference RAIR spectra measured for an ASW/hydrated proton/Pt(111) sample. In sample (a), hydrated protons were generated on the (H + H_2O)/Pt(111) surface, and then an H_2O ASW film was overlaid for circa 3 ML thickness at 90 K. In sample (b), the thickness of the H_2O ASW overlayer was increased to 20 ML, and then NH_3 (ca. 0.2 ML coverage) was adsorbed onto the ASW film surface. The Cs$^+$ beam energy for LES and RIS was 30 eV.

1100 cm^{-1} corresponding to the ν_2 band of NH_3 and a feature at about 1470 cm^{-1} corresponding to the ν_4 band of NH_4^+,[10] conforming with the LES and RIS signals. These observations indicate that the hydrated protons formed on a Pt substrate migrate through an ASW film over a substantially long distance (ca. 20 ML) to reach ammonia adsorbates on the surface and protonate them. Excess protons in ASW produced by acid ionization also migrate over a comparably long distance (ca. 25 ML).[11] Therefore, as far as proton transfer ability is concerned, hydrated protons formed on Pt(111) behave similarly to those formed in ASW.

In summary, the mass spectrometric detection of protonated water clusters on the surface, the IR absorption band at about 1130 cm^{-1}, and the proton transfer ability of these ions together provide convincing evidence that adsorbed hydrogen atoms on Pt(111) can ionize to protons assisted by hydration of adsorbed water. The resulting surface protons are stabilized only in multiply hydrated forms of preferential structures ($H_5O_2^+$ and $H_7O_3^+$) rather than as hydronium ions. This finding may clear up some disputes about the stability of hydrated protons on Pt, which might have arisen from an inability to distinguish different forms of hydrated protons. There is no reason to expect that the stability of surface-bound hydrated protons is specific to Pt(111), and it will be interesting to explore other high work-function metal surfaces for a similar behavior.

Although $H_5O_2^+$ and $H_7O_3^+$ are stable in the monolayer environment of H and H_2O on Pt(111), a thick ASW overlayer transforms these ions to a different structure that resembles hydrated protons in the bulk phase. Furthermore, the hydrated protons donate a proton to ammonia located some distance away, and this process occurs via a proton-hopping mechanism in ASW.[11] These phenomena resemble the proton transfer process at an electrolyte/electrode interface. For example, adsorbed H atoms on a Pt electrode are in electronic equilibrium with hydrated protons that are considered to be in the diffuse layer.[1] Proton transfer occurs from these solvated protons in solution to base molecules via a proton hopping mechanism.[12] Close correspondence between the proton transfer phenomena at an electrochemical interface and the present model system suggests the possibility that surface-bound hydrated protons may play an important role in the electrochemical interconversion between hydrogen atoms and solvated protons.

Experimental Section

The experiment was conducted in a UHV surface analysis chamber equipped with instrumentation for LES, RIS, TPD, and RAIRS.[13] H, D, and NH_3 were adsorbed on a Pt(111) substrate surface by dosing H_2, D_2, and NH_3 gases, respectively, through separate tube dosers. H_2O was adsorbed by a back-filling method at an H_2O pressure of about 1×10^{-8} Torr. The coverages of atomic hydrogen, H_2O, and NH_3 adsorbates were estimated from TPD measurements.[14] LES and RIS methods were used to identify chemical species present on the sample surface.[13a,15] In these methods, a Cs$^+$ ion beam collided with a sample surface at an incident energy of 28–30 eV, and the ions emitted from the surface were detected by a quadrupole mass spectrometer with its ionizer filament switched off. In RIS, neutral species (X) on the surface are picked up by the scattering Cs$^+$ projectiles to form Cs$^+$-neutral clusters (CsX$^+$). In LES, preexisting ionic species (Y$^+$) on the surface are ejected by the Cs$^+$ impact. Thus, RIS and LES signals reveal the identities of neutral (X) and ionic species (Y$^+$), respectively, on the surface. The Cs$^+$ impact under these conditions did not cause secondary ionization of water molecules. The Cs$^+$ beam current density was maintained below 0.6 nA cm^{-2} to avoid surface contamination by Cs$^+$ ions. RAIRS monitored the chemical species on the surface or in the interior of ASW film through the detection of vibrational bands.[16] The RAIRS experiment was performed in a grazing angle (84°) reflection geometry using an FTIR instrument equipped with a mercury-cadmium-telluride detector. The incident IR beam was linearly p-polarized using a wire-grid polarizer.

Keywords: hydrogen evolution reaction · platinum · protons · surface chemistry · water monolayers

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 7626–7630
Angew. Chem. **2015**, *127*, 7736–7740

---

[1] a) W. Schmickler, *Interfacial Electrochemistry*, Oxford, New York, **1996**; b) F. T. Wagner in *Structure of Electrified Interfaces* (Ed.: J. L. P. N. Ross), VCH, New York, **1993**.

[2] a) P. A. Thiel, T. E. Madey, *Surf. Sci. Rep.* **1987**, *7*, 211–385; b) A. Hodgson, S. Haq, *Surf. Sci. Rep.* **2009**, *64*, 381–451; c) F. T. Wagner, T. E. Moylan, *Surf. Sci.* **1988**, *206*, 187–202; d) D. Lackey, J. Schott, J. K. Sass, S. I. Woo, F. T. Wagner, *Chem. Phys. Lett.* **1991**, *184*, 277–281; e) N. Kizhakevariam, E. M. Stuve, *Surf. Sci.* **1992**, *275*, 223–236; f) N. Chen, P. Blowers, R. I. Masel, *Surf. Sci.* **1999**, *419*, 150–157; g) Y. Shingaya, M. Ito, *Surf. Sci.* **1996**, *368*, 318–323; h) M. J. T. C. van der Niet, I. Dominicus, M. T. M. Koper, L. B. F. Juurlink, *Phys. Chem. Chem. Phys.* **2008**, *10*, 7169–7179; i) A. den Dunnen, M. J. T. C. van der Niet, M. T. M. Koper, L. B. F. Juurlink, *J. Phys. Chem. C* **2012**, *116*, 18706–18712; j) P. P. Olivera, A. Ferral, E. M. Patrito, *J. Phys. Chem. B* **2001**, *105*, 7227–7238; k) M. Pan, Z. D. Pozun, W. Y. Yu, G. Henkelman, C. B. Mullins, *J. Phys. Chem. Lett.* **2012**, *3*, 1894–1899.

[3] a) S. C. Badescu, K. Jacobi, Y. Wang, K. Bedurftig, G. Ertl, P. Salo, T. Ala-Nissila, S. C. Ying, *Phys. Rev. B* **2003**, *68*, 205401;

b) B. Poelsema, K. Lenz, G. Comsa, *J. Phys. Condens. Matter* **2010**, *22*, 304006.

[4] G. Zimbitas, S. Haq, A. Hodgson, *J. Chem. Phys.* **2005**, *123*, 174701.

[5] S. C. Park, J. K. Kim, C. W. Lee, H. Kang, *ChemPhysChem* **2007**, *8*, 2520 – 2525.

[6] G. A. Voth, *Acc. Chem. Res.* **2006**, *39*, 143 – 150.

[7] a) S. Schnur, A. Gross, *Catal. Today* **2011**, *165*, 129 – 137; b) T. Roman, A. Gross, *Catal. Today* **2013**, *202*, 183 – 190.

[8] P. Parent, J. Lasne, G. Marcotte, C. Laffon, *Phys. Chem. Chem. Phys.* **2011**, *13*, 7111 – 7117.

[9] a) Y. Kim, E. S. Moon, S. Shin, H. Kang, *Angew. Chem. Int. Ed.* **2012**, *51*, 12806 – 12809; *Angew. Chem.* **2012**, *124*, 12978 – 12981; b) Y. Kim, S. Shin, E. S. Moon, H. Kang, *Chem. Eur. J.* **2014**, *20*, 3376 – 3383.

[10] a) H. Ogasawara, N. Horimoto, M. Kawai, *J. Chem. Phys.* **2000**, *112*, 8229 – 8232; b) C. J. Pursell, M. Zaidi, A. Thompson, C. Fraser-Gaston, E. Vela, *J. Phys. Chem. A* **2000**, *104*, 552 – 556; c) W. A. Schutte, R. K. Khanna, *Astron. Astrophys.* **2003**, *398*, 1049 – 1062; d) T. Takaoka, M. Inamura, S. Yanagimachi, I. Kusunoki, T. Komeda, *J. Chem. Phys.* **2004**, *121*, 4331 – 4338.

[11] E. S. Moon, Y. Kim, S. Shin, H. Kang, *Phys. Rev. Lett.* **2012**, *108*, 226103.

[12] M. Eigen, *Angew. Chem.* **1964**, *3*, 1 – 19.

[13] a) H. Kang, *Bull. Korean Chem. Soc.* **2011**, *32*, 389 – 398; b) J. Cyriac, T. Pradeep, H. Kang, R. Souda, R. G. Cooks, *Chem. Rev.* **2012**, *112*, 5356 – 5411.

[14] a) S. Haq, J. Harnett, A. Hodgson, *Surf. Sci.* **2002**, *505*, 171 – 182; b) J. L. Gland, E. B. Kollin, *Surf. Sci.* **1981**, *104*, 478 – 490.

[15] H. Kang, *Acc. Chem. Res.* **2005**, *38*, 893 – 900.

[16] M. Trenary, *Annu. Rev. Phys. Chem.* **2000**, *51*, 381 – 403.

Received: January 16, 2015