

Adsorption on Platinum Single Crystals: A Review

Shamshyna MO and Ivanenko IM*

Department of Inorganic Substances Technology, Water Treatment and General Chemical Engineering, National Technical University of Ukraine, Ukraine

Volume 1 Issue 1 - 2019

Received Date: 04 Mar 2019

Accepted Date: 28 Mar 2019

Published Date: 16 Apr 2019

2. Keywords

Transition metals; Water monolayer; Heterogeneous catalysis

1. Abstract

An ideal solution to the problem of dependence on natural raw materials can become such a simple and fairly common component as water. If the water be divided into components, then hydrogen can be used as a pure energy. As is known, some transition metals, such as Pt, are good catalysts for water splitting reactions. They play a key role in understanding the basic aspects of elementary interactions occurring on the surface of catalysts. However, these surfaces contain many defects and, as a rule, it is very difficult or even impossible to control the course of reactions. Consequently, it is necessary to understand the interaction between catalysts and water to develop or create a more active, selective, stable, mechanically stable and economically advantageous catalyst.

3. Introduction

To do this, different scientific areas are combined to identify effective and less effective catalysts. For example, with the help of theoretical experiments it is possible to study the structural and dynamic properties of the reactions. They can predict the possibility of unknown catalysts, explore their active sites and study the mechanisms of reactions. However, from a theoretical point of view, it is still difficult to predict the interaction of polyatomic molecules. In addition, it is very difficult to include all possible interactions that cause discontinuities and their formation, occurring on projections, defects or steps on the surface. In particular, to understand the fundamental interaction between small molecules such as H_2 , O_2 and H_2O and Pt, the ultra-high vacuum (UHV) system can be used as a typical approach. The advantage of such a system consists in the fact that it contains considerably fewer particles per unit volume, compared with the system under atmospheric pressure. Consequently, in UHV conditions, the surface of the sample may remain clean for several hours. In addition, UHV can provide conditions under which the amount and type of adsorbates can be easily controlled.

4. Water and Water Related Adsorption

CansinBadan [1] investigated defect surfaces of Pt with the usage of such ultra-high vacuum (UHV) methods as temperature programmed desorption (TPD), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) to discover the influence of the surface defects on the adsorption of water and water related adsorbates. He claims that one of the rational

ways to study influence of the surface structure on the chemical reaction is to compare the activity of the well-organized single crystal surfaces that have high Miller indices with those that have low Miller indices under the UHV conditions. To make the experimental conditions close to real, Cansin used high-defect Pt surfaces [Figure 1], which have step and kink sites similar to nanoparticles. Among the obtained results there are some, which prove that H_2O adsorbs molecularly at all cover-ages. Below 120 K forms amorphous solid water (ASW), which changes to crystalline ice (CI) when heated. Flat Pt(111) single crystal surface is often used to study of the face transition of the ASW and CI. In the other Chapter Cansin studied the role of surface defects on crystallization process using three-atom wide Pt (111) terraces with (100) and (110) surface steps. Results show that the presence of step sited and kinks has a substantial influence on the H_2O_{ad} wetting, which makes the adsorption kinetics for ASW and CI different [1].

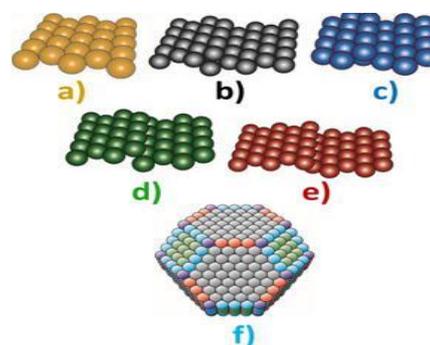


Figure 1: Diversity of Pt surface structures. a) Pt (111), b) Pt(533), c) Pt(211), d) Pt (221), e) Pt (553), f) nanoparticle [1].

*Corresponding Author (s): Iryna Ivanenko, Department of Inorganic Substances Technology, Water Treatment and General Chemical Engineering, National Technical University of Ukraine, Ukraine, E-mail: irinaivanenko@hotmail.com

While a lot of experiments were carried out to expertise the morphology of the ASW, Greg A. Kimmel et al. focused on studying the structure of the CI and researched explored the growth of the crystalline ice films on the Pt(111) and Pd(111) surface structure, using temperature-programmed desorption of the adsorbed water film and Kr on it, and came to the following conclusions [2]. Water monolayer wets the surface Pt(111) and Pd(111) at all temperature values (20-155 K for Pt(111)). However, crystalline films that were grown at higher temperatures ($T > 135$ K) do not wet monolayer. Authors obtained another results for crystalline ice films of D_2O and H_2O . Amorphous water films, that firstly wet the surface, become crystalline and then ruin the monolayer of water while annealing at higher temperatures. Thinner films become crystalline and grow at lower temperatures than thicker films. For samples with the Ex. atoms dosage, surrounded with Pt (111) surface structure, further annealing causes water molecule diffusion from ice crystals to rearrange the monolayer of water. The simple model shows that for crystalline films that were grown at higher temperatures, ice crystallites start to separate widely on the typical distances between the crystallites ~ 14 nm or more.

The main idea is that desorption temperature of the gas atom is used to determine the height of the atom above the metal surface. Temperature at which atom starts to desorb correlates with the chemical potential of the adsorption layer, which is in its turn, is set to the highest layer in the film. This approach can be used to estimate the height of a liquid gas atom (Kr for the presented results in the article) adsorbed on a thin film of water grown on a metal substrate. The interaction of the adsorbed crystal on the multilayer surface of the crystalline ice is weaker than for Kr adsorbed on Pt (111) or Pd (111), or on one layer of water on these substrates. Therefore, the peak in the Kr TPD spectra associated with crystalline ice appears at lower temperatures than the peak Kr TPD for monolayer water or for a metallic substrate.

Kr TPD spectra with Pt (111) (W0), one water monolayer on the surface Pt (111) (W1), and ~ 50 monolayers of crystalline ice on Pt (111) (CI) are presented in [Figure 2]. For each TPD spectrum ~ 1 , the monolayer Kr adsorbed on the surface and the rate of the temperature drop is 1 K/s. Well-defined peaks of TPD allow to investigate the morphology of thin crystalline ice films.

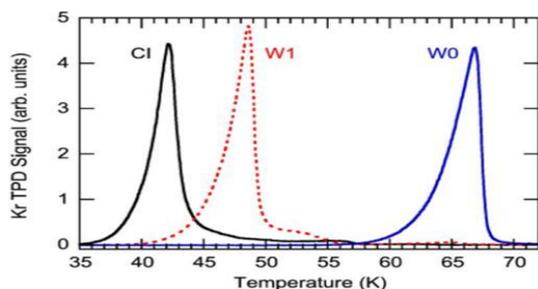


Figure 2: TPD spectra with Pt (111) (W0), one water monolayer on the surface Pt (111) (W1), and ~ 50 monolayers of crystalline ice on Pt (111) (CI) [2].

Fig.2 shows the TPD ~ 1 ML Kr spectra desorbed from Pt (111), indicated by W0 in the figure; D_2O monolayer on Pt (111) (W1) and multilayer crystalline D_2O in a form of crystalline ice. In each case, Kr is mainly desorbed in the form of one peak. Since the polarization of the film for water is less than the polarization of the substrate Pt (111), and the water film is separated by Kr from Pt (111), the desorption temperature Kr from both water levels and the multilayer films of CI is lower than for Pt (111). The differences in the Kr spectra are seen from the Fig.2, which is the basis for analyzing the growth of crystalline ice films on Pt (111). Similar results were obtained for Kr TPD water spectra on Pd (111). Researchers argue that these results are consistent with theory and experiments that suggest that molecules in a water monolayer form a surface that does not contain “dangling” OH bonds or ions of electron pair, which increases the hydrophobicity of a water monolayer on the surface of Pt (111) structure.

The interaction between H_2O and platinum is particularly interesting in the fuel cell catalysis, where OH $^-$ adsorbed on stepped platinum sites is considered a possible oxygen donor for example, for the oxidation processes of CO, methanol and ethanol at the anode. Structural sensitivity of these reactions, as a rule, is associated with activation of water, which occurs predominantly on stepped sites. Janneke van der Niet investigated in [3] that the desorption spectra of water molecules, desorbing from Pt (553) surface structure, shows three peaks. First peak at 171 K is associated with water monolayer desorption. This peak shows the characteristics of the zero order kinetics desorption and can be due to the coexistence of the condensed phase and 2D water-gas in the sub-monolayer coverage. The second peak is associated with the water multilayer desorption and starts at 154 K and increases with the temperature and coverage. TPD shows the stabilization of the water monolayer in because of the presence of steps. An additional peak is observed at ~ 188 K for (100) steps structure or at ~ 197 K for (110) steps, indicating a stronger interaction between water and (110) steps. For the surface Pt (533) with the structure Pt [4(111) \times (100)], the TPD spectra shows two peaks for the H_2O monolayer. On the coverage under 0.13 monolayers, one peak shift is observed from 194 K to 198 K, which corresponds to change in the coverage. It also corresponds to desorption from steps. At higher coverage (less than ~ 0.33 monolayers), a peak appears at 185 K, which is associated with desorption from the terrace site and is observed prior to the peak of the multi-layers. The peak corresponding to desorption from the multilayer and appears at ~ 160 K. Also, the author investigated that the ON $^-$ group always binds to the platinum substrate through an oxygen atom. All hydrogen bonds lie parallel to the surface.

Despite the fact that Pt (111) is considered to be the most stable surface structure, there are also UHV studies on less stable sur-

faces, like Pt (100) and (110). For example, Netzer and Kneringer [4] investigated adsorption of the H atom on the Pt (100) surface using such techniques as LEED, AES, and TDS. The results showed that during the adsorption of hydrogen, the surface reconstruction was not detected, and the maximum desorption temperature was about 433 K. Norton et al. [5] found that the adsorption of the hydrogen at the reconstructed Pt (100) surface at low temperatures led to the formation of a surface with a structure (1×1), then they [6] compared the stability and reactivity of (5×20) and (1×1) Pt (100) surfaces using LEED and TDS. The difference between the nature of the behavior of these two structures is due to a decrease in the energy of the heat adsorption of hydrogen. In [7], Qiaocui Shi and Rong Sun used Density Functional Theory (DFT) to study the adsorption of hydrogen on the surfaces Pt (100), (110) and (111) with different coverages. It was detected that each surface has different hydrogen adsorption and saturation ability, and the surface Pt (111) is characterized by the weakest adsorption, as well as the least saturated coverage. The researchers used the thermodynamic method to include the factor of the temperature and partial pressure of hydrogen on a stable surface area, where the built-in phase diagram clearly showed the dependence of the reaction on the concentration of the H₂ ions on the surface. Also, to calculate the tendency of adsorption of the hydrogen on a platinum catalyst, the following surface structures were used: (100), (110) and (111).

Fig.3 shows in the upper part the structures and possible adsorption centers of the hydrogen on them. For example, Pt (100) has a top (T), a bridge (B) and a 4-fold hollow (4F) sites; Pt (110) has a top (T), a bridge (B) and a 3-fold hollow (3F) sites while Pt (111) has a top (T), a bridge (B), a hexagonal close packed (hcp), and a face-cubic centered (fcc) sites [7].

Theoretically predicted hydrogen desorption temperatures are well consistent with the available experimental results. The authors believe that the hydrogen adsorption could also modify the morphology of the Pt catalyst based on Wolf's structures. All these calculations provide very useful information to calculate the reaction mechanism, especially for hydrogenation reactions, where the water coverage on the surface plays a significant role in the determining of the adsorption configurations of reagents, as well as the final reaction mechanisms.

Understanding the interaction of Pt surfaces and water molecules at the atomic level is important for further improving their activity and creating new cost-effective catalysts that behave like Platinum. In order to obtain a complete picture of the real catalytic surfaces, which usually consist of small particles, it is necessary not only to consider highly symmetric surfaces, but also the influence of steps and kinks on the adsorption and reactivity of catalysts. In the paper [8], set out to investigate and establish

a qualitative explanation of the results of TPD experiments by calculating the energy of adsorption of water and dissociation products such as H, O and OH⁻ on the stepped Pt (533) and Pt (553) surface structures using the DFT. These will be a reference for further studies on the interaction of water with stepped surfaces that are covered with adsorbate and will complement other studies on the catalytic activity of the step (100) and (110) structures. As a result of calculations, the authors found adsorption energy for aqueous monomers adsorbed in the plane in the upper position on the Pt (111) surface and is equal to 0.28 eV. This value is significantly different from the previous studies, none of which included vibrational entropy. The actual value for vibrational entropy varies by as much as 30% when the water molecule is rotated to a certain angle. It is also investigated that this only changes the adsorption energy by no more than 0.05 eV. The trend is that water is more associated with Pt atoms on stepped surfaces. It is also investigated that the step of the edge binds water at the upper positions with a binding energy of 0.06 eV and 0.07 eV for the surfaces Pt (533) and Pt (553) respectively (Fig. 4), compared to 0.28 eV for Pt (111) surface. According to the TPD results, the highest temperature peak corresponds to desorption from steps, since no comparable peak was observed on the Pt (111) surface. Desorption temperature for the peak corresponding to the step was ~10 K below on the surface Pt (533), relative to the surface Pt (553). Consequently, the general tendency indicates that the edge of the step with the structure of (100) on Pt (533) surface structure demonstrates stronger bonding for all studied species, while the edge of step (111)/(110) located in Pt (553) does not show a significant increase in the binding energy for H₂, a noticeable increase for OH⁻ and O⁻, although smaller for the edge of Pt (533) surface, and a similar increase for H₂O molecule compared to Pt (533) structure.

Since the last twenty years the interaction of water with metal surfaces or close-packed transition metals has been investigated. The most striking example is Pt (111) as the ideal surface, and with all defects (steps, kinks, etc.). Article [9] is devoted to the study of the influence of steps on the binding of water to Pt (111). Alexander Picolin et al. used thermo-desorption analysis to obtain results on an artificially deformed surface (with ion bombardment) consisting of close-packed (100) and (111) –micro-faceted steps. In the article, authors analyzed the effect of steps on the adsorption and desorption of H₂O. Unlike other studies, they did not use single crystals with highly symmetrical surfaces, but instead, nanostructures of the Pt (111) sample were used. Experiments with different morphologies can be compared with each other because they are obtained in one experimental series without changing the specimens. Water was adsorbed molecularly on Pt (111), and individual molecules are bonded to the upper positions through the O-Pt bonds. The sequence of creating

the monolayer at a temperature of the water effective diffusion ($T > 60$ K) leads to the formation of a hydrogen-bonded wetting layer. Structure of the film after the growth of several layers at the top of this wetting layer depends on the temperature and growth rate: at low temperature ($T < 135$ K) above the surface of the hydrophobic wetting layer amorphous solid water is formed. For high temperatures ($T > 137$ K), the crystalline monolayer functions as a template, and the first few layers adapt to this structure. When heated (or with the growth of thicker films for a crystalline monolayer), both structures crystallize into bulk ice, which is incommensurate with Pt (111).

Ball model of nanostructured surface Pt (111), representing the step arranging mechanism, used in [9], is presented in Fig. 5. Ripple resulting from ion bombardment follows the way [11]. The side walls are locally equivalent to the structure Pt (335) (on the left side) containing (100)-micro faceted steps (blue rectangles) and Pt (221) (right) containing (111)-micro faceted steps (red triangles) Fig. 5a. Mound is produced by homoeopathic growth. It is limited to (111) steps. For simplicity, this structure will be called a triangular mound Fig. 5b [9].

The authors used tunnel-scanning microscopy to determine the surface structure. It was confirmed that water binds better to (111) steps. Moreover, the authors have found that the higher the concentration of steps on the surface, the less likely that the condensed and dissolved phase coexist in the monolayer of water. It has also been found that the presence of defects slows the growth of the monolayer of crystalline ice during heating.

Greg A. Kimmel and colleagues paid more attention to the water structures on the surface of the metal in [10]. The aim of the experiment was to study the growth of crystalline water layer under gas physical sorption. The authors used temperature programmed desorption of water and Cr on adsorbed films. As expected, the aqueous monolayer wets the Pt (111) surface. However, for coverage of more than 1 monolayer, additional water molecules form ice that does not wet the water monolayer. The structure of the water monolayer on Pt (111), which has no suspended OH bonds or electron pair, is essential to understanding the trend of growth of CI films. The hydrophobic nature of the water monolayer is further confirmed by the observation that the kinetically wet, amorphous films deform when heated. The study was carried out in the temperature range of 20-155 K and found that the water monolayers wet the Pt surface over the temperature range. Under conditions of $T \leq 120$ K, the subsequent water layers wet the surface of the monolayer at the kinetic level. However, the layer of crystalline ice, which begins to grow at $T > 135$ K, does not wet the water monolayer. Researchers have confirmed that the results of experiments are consistent with recent theory and experiments that suggest that molecules with a water environ-

ment in a monolayer form a surface that does not contain dangling OH bonds or single electron pairs, which leads to the formation of a hydrophobic water monolayer.

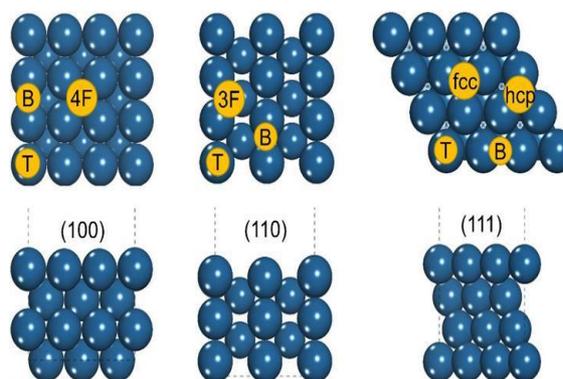


Figure 3: The structure and adsorption centers of the Pt (100), (110) and (111) surface structures [7].

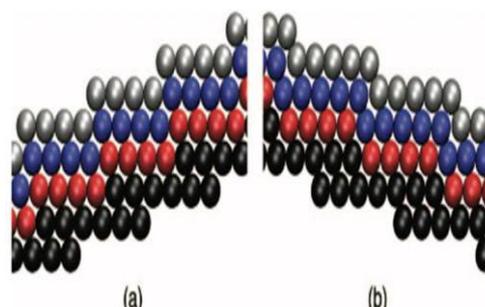


Figure 4: Side view of the surface (a) Pt (533) and (b) Pt (553) [8].

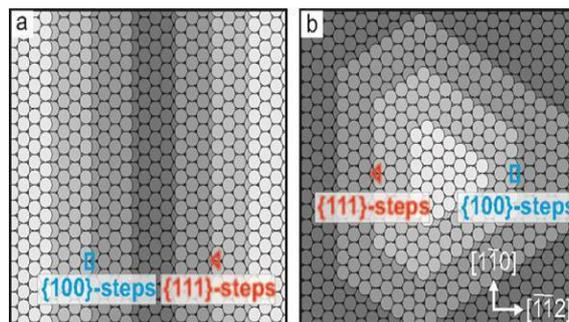


Figure 5: Ripple resulting from ion bombardment follows the way [110] (a) and a triangular mound (b) [9].

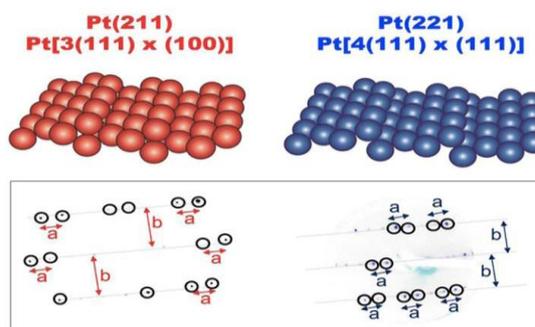


Figure 6: Schematic image and LEED scans the clean surface of Pt (211) (red) and Pt (221) (blue) to the left and right respectively [11].

4. Surface Defects

Recently, more and more attention is paid to surface defects. It is known that water molecules bond better at the steps of the Pt (111) surface. Steps also intensify the process of crystallization of amorphous solid water, control the formation of ice and affect

long-term interaction in water films. Since the structure Pt (111) is investigated as an ideal surface, scientists are trying to explore other, more defective ones.

The structure of the surfaces Pt (211) and Pt (221) is schematically depicted in the upper part of the Fig.6. They consist of terraces (three atoms in width) with (100) steps and four-atomic (111) terraces with (100) steps and four-atomic (111) terraces with (111) steps. The last description is identical to the triatomic terrace with (110) steps. The bottom of the Fig.6 depicts LEED scans from clean surfaces. From these images, we extract spot row spacing (b) to spot splitting (a) ratios of 2.38 for Pt (211) and 3.06 for Pt(221). These values correspond well with the values from the literature [12], which are 2.45 and 3.00 respectively. All experiments were carried out under UHV conditions. During the experiment, the desorption spectra showed that the wetting of the surface and the thickness of the layer have large discrepancies that depend on the step type. It was also found out that the initiation of crystallization occurs at lower temperatures than for Pt (111). The energy spectra of the Pt (211) and Pt (221) structures have higher desorption energy, and the crystalline ice layer is considered to be more stable than at Pt (111). In spite of the results, more experiments are needed to find out how the structure of different surfaces affects the water adsorption.

When water adsorbs on the surface, it reduces its energy by adopting the structure and frequency that is characteristic for this surface. How this happens and how the surface structure affects its properties is still poorly defined even for close-packed transition metals. In the paper [13], authors investigated the structure of adsorbed water at a temperature above 135 K. It is known that water forms small clusters connected by hydrogen bonds in the size of a cell ($\sqrt{37} \times \sqrt{37}$) R25°, which grows amorphous ice at $T < 120$ K. This structure is compressed to ($\sqrt{39} \times \sqrt{39}$) R16°. At higher temperatures (usually $T > 135$ K), water becomes more flexible for crystallization during the growth of ice islands. The results of LEED showed [Figure 7] that the trajectory of scattering $\sqrt{39}$ is more intense during the growth of the second layer, leaving a trace (light) for films that consist of 10-15 layers. Then,

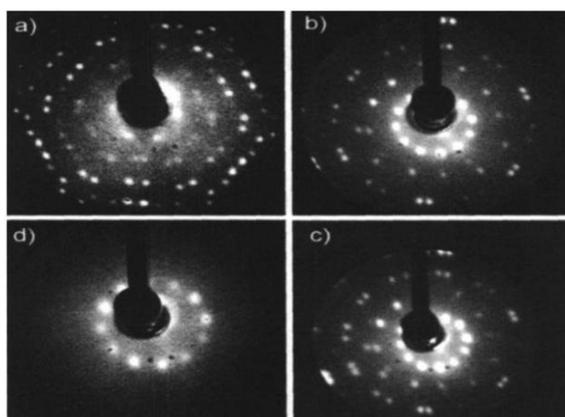


Figure 7: LEED pictures for structure (a) ($\sqrt{37} \times \sqrt{37}$) R25°

it fades out and disappears for films that consist of about 40 layers.

LEED pictures for structure (a) ($\sqrt{37} \times \sqrt{37}$) R25°, where the water coverage is 0.65 ML ($E = 27$ eV); (b) ($\sqrt{39} \times \sqrt{39}$) R16° for 1 ML of water ($E = 15$ eV); (c) 10 ml of ice after desorption of 55-65 ML ASW at 148 K ($E = 15$ eV); (d) 41 ML of ice formed by desorption of 24 ML from 65 ML of ASW layer at 148 K show spots $\sqrt{39}$ of the first order ($E = 7$ eV). The growth of the crystalline ice films at $T > 135$ K shows an identical LEED path for (c) and (d) for same coverages [13].

Moreover, results confirmed that the ice multilayer consists of $\sqrt{39}$ ordered wetting layers, on which the ice grows as a crystalline film, which is no longer a wetting layer. Ice films (over 50 layers) form a hexagonal LEED trajectory, which indicates a reorientation of the film and wetting layers in order to form solid ice. All these changes affect the vibrational spectrum, which reflects changes in the shape and intensity of the line associated with different ice structures. Researchers may argue that thin films of amorphous solid water crystallize to form the same phases observed during growth. From this, it follows that these structures are thermodynamically stable, not the kinetic phases, through which they pass during growth. Consequently, it was investigated that the transition from structure $\sqrt{39}$ to extremely bulk ice (approximately 50 layers) is associated with a change in the kinetics of crystallization.

In the article [14], investigated how is Pt (211) representative for the surfaces Pt [$n(111) \times (100)$] in the adsorption / desorption behavior of water, hydrogen, and oxygen by temperature-programmed desorption. Unlike terraces with $n > 3$, where n is the number of atoms, it has been found that H₂O molecules are adsorbed below the amorphous solid water crystallization temperature (ASW). For D₂ molecule, scientists have investigated that desorption from (100) steps does not depend on the length of the terrace $n > 3$. However, desorption from neighboring (111) terraces varies. There is a pattern: the longer the terraces, the more variations in energy and, as a result, the decrease in adsorption ability is closer to the step edge. For the O₂ molecule, more dissociation was observed with Pt (211). The results of the TPD showed the formation of 1D PtO₂ structures, which are formed only for $n = 3$ with (100) steps. Consequently, the researchers concluded that Pt (211) cannot be regarded as representing of Pt (111) with (100) steps.

The chemical interaction between water and metal surface is important in many practical fields, especially when studying corrosion, electrochemistry and heterogeneous catalysis. Thus, there are a large number of studies on adsorption of water on metal surfaces. Hirohito Ogasawara, along with a research team, did experiments with the D₂O molecule. Article [15] is devoted to the study of the adsorption properties of water on the Pt surface

with the absorption spectroscopy of infrared radiation method. The sample was prepared by heating and cooling in the temperature range of 25-165 K. The authors first discovered that the molecules of adsorbed water at 25 K exist not only in the form of monomers, but also in dimers. After heating up to 40 K, the dimers dissociate and formed monomers stick to the two-layer ice on the surface, and at 105 K, a liquid phase is formed on the stepped surface. Further, when heating up to 125 K, there are two phases simultaneously: two-layer ice and liquid-like phase. At higher temperatures, such as 155 K, it is found that the two-layer ice melts, and the residual molecules melt and move to the stepped surface.

Water interactions with a clearly defined metal surface are becoming more and more interesting issues for research because of their importance in surface physics and the interaction type water/surface in nature. The structure of water was also studied on surfaces of close-packed metals by a number of methods, such as LEED, STM, infrared astronomy satellite (IRAS) and others. In the article [16], investigated adsorption, desorption and mechanism of adhesion of H₂O molecule to Pt (111) by helium scattering. The supersonic helium beam was produced by expanding the pure gas (air liquid) through a hole with a diameter of 100

mm at a pressure of 1000Torr and a temperature of 300 K. The quasieffusive H₂O beam was formed through a hole with a diameter of 1 mm. The results of the experiment indicate that water adsorbed on the Pt (111) surface at 60 K is subjected to a phase transition from the chaotic distribution of molecules to the state of clustered islands. They also determined that the kinetics of the desorption for a water sub monolayer is $n=0$ at a temperature of 145-172 K. Researchers concluded that the desorption kinetics of zero order is possible for the existence of 2D-phase coexistence of H₂O in the condensed phase in the form of clustering islands and in 2D-gas phase on the Pt surface. Moreover, in the condensed phase there are more H₂O molecules than in the gaseous.

5. Enantioselective Surfaces of Metals

Surface studies of metals, and especially precious ones, are very important in the materials science. The main focus during experiments is on defect surfaces, those that contain a lot of steps, kinks that can be rebuilt during heat treatment, etc., since such surfaces almost fully reproduce the structure of a real industrial catalyst. Authors Andrew J. Gellman et al. in [17] refer to the chemistry of the Enantioselective surface. This is an extraordinary example of a structural sensitivity, since enantioselectivity can occur only on surfaces with chiral structures that do not have mirror symmetry. Interestingly, enantioplastic superficial chemistry is more widely studied on natural chiral surfaces of single crystals Cu and Pt than in any other metals. The researchers used the combination of photoemission of adsorbed Xe(PAX)

and TPD to study the distribution of adsorption sites on Pt(111), Pt(221) and Pt(531) surfaces. PAX is a great tool for studying adsorption sites, because the Xe 5p binding energies are sensitive to the work function on the surface on which they are adsorbed, and therefore, differ depending on the structure (terraces, steps, edges). Using TPD, adsorption sites can be determined, on condition that the adsorption energy Xe is sensitive to the structure at the adsorption site.

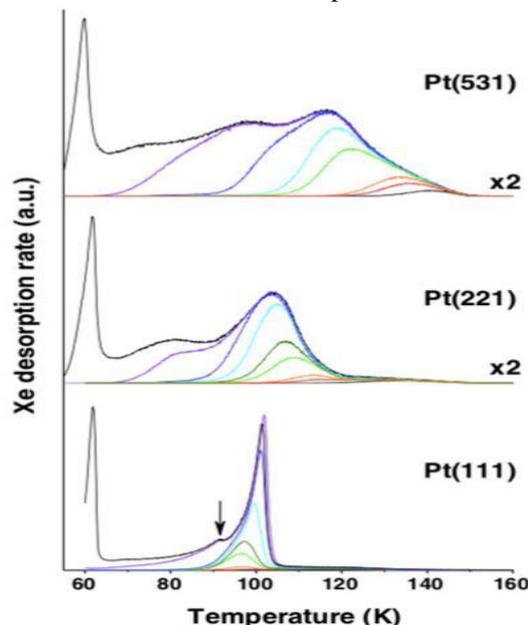


Figure 8: Xe TPD spectra on Pt (111), Pt (221) and Pt (531)

Figure 8 depicts TPD spectra taken from Pt (111), Pt (221) and Pt (531) with Xe coverage, whose thickness varies within $\theta_{\text{Xe}} \sim 0.02 > 0.41$ Xe/Pt (saturated monolayer on Pt (111)). The desorption characteristics of low temperatures ($T \sim 60$ K) are associated with the Xe desorption from the multilayer coverage and does not demonstrate structural sensitivity. Monolayer with the coverage $\theta_{\text{Xe}} = 0.41$ is defined as the Xe layer at which the multilayer desorption is observed and is equivalent to the area (integrated over $T = 65-160$ K) with the highest coverage of the Xe TPD spectra, shown for each surface on Fig.8. This definition of the coverage is reliable for the Pt (111) surface, it should be noted that for Pt (221) and Pt (531) θ_{Xe} is based on the atoms ranges density on the surface Pt (111). In other words, in absolute terms, the fractional value of the coating $\theta_{\text{Xe}} = 1$ corresponds to the real coating of $1.50 \cdot 10^{15}$ atoms Xe/cm². The results of PAX and TPD measurements on the surfaces Pt (111), Pt (221) and Pt (531) gave a quantitative description of the distribution on the terraces, steps and kinks on these surfaces while Xe adsorption for coverages up to $\theta_{\text{Xe}} = 0.33$ relative to the density of Pt atoms on the Pt(111). The areas measured by the Xe adsorption on Pt (221) have almost equal amount of the terrace and steps, since the coverage is increased with $\theta_{\text{Xe}} = 0.05-0.33$. PAX and TPD indicate the presence of irregularities on the surface of Pt (531). On Pt (531) there is data on the successive filling on the steps, kinks and terraces in order to increase the coverage of Xe.

The way water molecules join the platinum surface is challenging not only in catalysis, but also in electrochemistry. Of particular interest is the nature of the adsorbed species, bonds with the surface as a result of chemisorption, as well as the molecular orientation and area, which is responsible for adsorption. At present time, there are few works, related to the adsorption of water on clean single crystals. In the article [18], Brett A. Sexton, using in-fared and Raman spectroscopy, obtained data indicating that hydrogen bonds and clustering occur in the sub monolayer region, and that a complete isotope exchange of hydrogen occurs at 100 K. However, the transition between the first and the second layers of water (exposure >1.5 layer) creates a new translational frequency near $\sim 250 \text{ cm}^{-1}$. This peak appears simultaneously with the crystalline ice peak during thermal desorption. The vibrational values of all the bands were compared with the adsorption spectra of D_2O . In order to determine the molecular orientation and adsorption centers of adsorbed water, it is necessary to understand the kind of electron scattering, involved in the system. There are two techniques: dipole scattering [19] and scattering in a collision

[20]. In the article [18], the study of water on the Pt (111) surface was carried out without energy dependent measurements, so the scattering mechanism remains unknown.

Fig.9a shows the number of vibrational states for gaseous and adsorbed water. In the gas phase, 3 normal modes are IR active, but on the surface 9 states can be active. Fig.9b shows possible symmetry of the bond on the surface. The highest symmetry is C_{2v} . The local symmetry is C_{2v} , or as low as C_1 can be observed depending on the angle at which the molecule is oriented to the surface.

The structural properties of liquid water and ice were the subject of several studies. Better understanding of the wetting mechanism, the micro porosity of ice, the structure of liquid water and other properties of surfaces and adsorbents would allow us to find answers to questions related to the removal of organic molecules from water, adsorption of proteins on surfaces, the formation and structure of amphiphilic monolayers and the hydration of proteins. Article [21] investigates the relationship between the thermal desorption of thin layers of condensed D_2O and the wetting properties on the surface of the supporting substrate. As sample surfaces, $\text{HS}(\text{CH}_2)_{16}\text{OH}$ and $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ were used. IR spectroscopy was used to characterize structural transformations during TPD. During short IRAS measurements, when passing a single TPD scan, authors received an idea of what happens to the water when the temperature of the sample increases.

Fig.10 shows the results of one of such measurement with the use of the CN_3 surface, which clearly indicates that the adsorbed water, firstly, in an amorphous solid form, becomes polycrystalline during the TPD measurement. The temperature intervals on

which the spectra were taken are shown on the Fig. 10a and the actual spectra are plotted on the Fig. 10b. Spectra "120 K" and "140 K" are marked for comparison of the received data. The heating rate was 0.33 K/s. The precipitation temperature of the D_2O molecule was 120 K [21]. The results of the spectroscopy showed that amorphous ice is formed at sufficiently low temperatures ($T < 100 \text{ K}$) at all self-ordered layers, regardless of their wettability. The structural transition from amorphous to polycrystalline D_2O is observed above 100 K. The author investigated that the exact transition start strongly depends on the wettability of the surface and varies from $\sim 110 \text{ K}$ to a strongly hydrophobic (CH_3) substrate to 145-150 K on a hydrophilic (OH) substrate.

Commercial metallic catalysts for heterogeneous processes contain many surface defects, such as kinks, steps and adatoms. For several major industrial processes, it is determined that monatomic steps on catalyst particles are crucial for the kinetics of the whole process. In the article [23], investigated the properties of a curved Pt (111) crystal by means of infrared spectroscopy during the CO adsorption on the surface. Authors argue that, unlike flat single crystals, continuous variation of the structure provided by curved crystals gives many advantages to the study of physical and chemical processes on the surface. However, the curvature of the crystal itself creates a lot of inconveniences during the experiment. The experiments were carried out under a UHV conditions in one of the UHV chambers. For infrared spectroscopy, adsorbates on metal samples are usually investigated at the reflective-absorption frequency of the incidence of infrared rays. During this analysis, curved crystal acts as a mirror surface. Researchers also described the experimental difficulties caused by the cylindrical surface, and the ways to solve them by means of reflection adsorption infrared spectroscopy (RAIRS). An additional mirror was installed under the curved crystal inside the chamber in order to minimize the difference in values given by the crystal. While passing infrared focus through a sample (Figure 11), they investigated adsorption vibrational spectrum as a function of the step type and its depth.

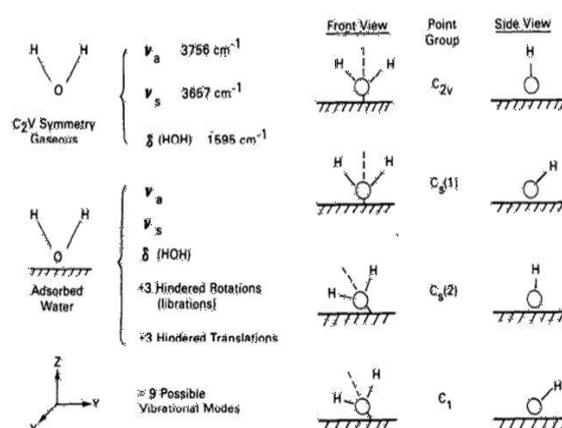


Figure 9: The number of vibrational states for water in the gas and adsorbed state (a). Possible symmetries of adsorbed water on Pt (111) (b) [18].

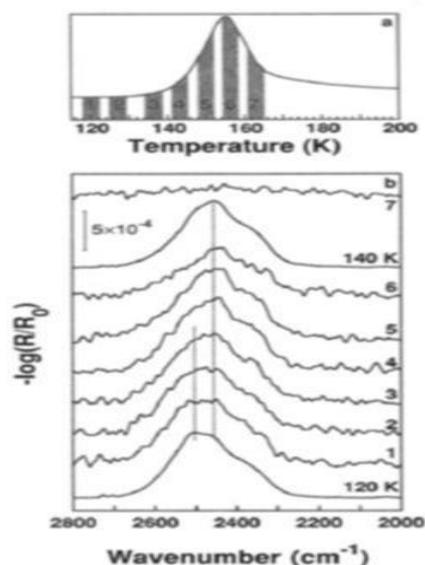


Figure 10: Simultaneous TPD (a) and IRAS (b) measurements of the methyl substrate desorption show that the structural transition occurs in an aqueous overlayer on substrate during the TPD [21].

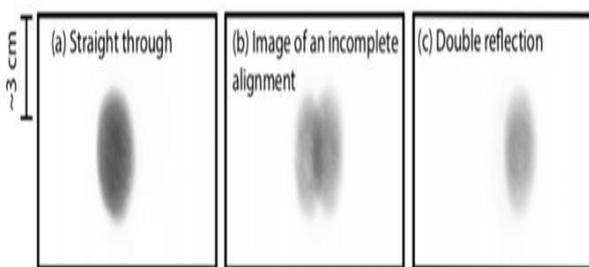


Figure 11: A gray scale image created on white paper is located 2.5 m. —

A gray scale image created on white paper is located 2.5 m from the parabolic mirror in the camera exit window when (a) the light passes directly through the surface, (b) when the light begins to display both surfaces, (c) clear double reflection. The light source is a slit, located in front of a standard tungsten filament of the spectrometer [23].

The new technique to adsorb carbon monoxide on curved Pt (111) crystal and to investigate the effect of the step type and its depth on the CO radiation as a function of the coverage was used. The strong evidence supporting, that appropriately codosed surfaces in UHV at low temperatures can mimic in some detail the vibrational spectroscopic properties of the analogous ambient temperature metal-solution interface was provide [23].

6. Conclusions

Thus, the great efforts of many groups of scientists have been made to understand the nature of the adsorbed species, bonds with the surface as a result of chemisorption, as well as the molecular orientation and area, which is responsible for adsorption.

Very extensive experimental data and promising results were obtained relating the influence of the surface defects of platinum catalysts on the adsorption of different matters. And, despite the huge successes achieved, it was possible only a little closer to un-

derstand the active centers on the surface structure and the optimizing ways of catalysts' activity.

References

1. Badan C. Surface-structure dependence of water-related adsorbates on platinum, Doctoral thesis, Leiden University, 2016.
2. Kimmel GA, Petrik NG, Dohnálek, Z, Kay BD. Crystalline ice growth on Pt (111) and Pd(111): Nonwetting growth on a hydrophobic water monolayer, *J Chem Phys.* 2007; 126(11): 1-4.
3. Niet MJTC, Van der. A surface science view on the reactivity and localization of water on nano-structured platinum, Doctoral Thesis, Leiden University. 2010.
4. Netzer FP, Kneringer G. The adsorption of hydrogen and the reaction of hydrogen with oxygen on Pt (100). *Surf Sci.* 1975; 51: 526-538.
5. Norton PR, Davies JA, Jackson DP, Matsumani N. A study of the phase transition and relaxation of a Pt(100) surface by MeV ion back scattering and channeling., *Surf Sci.* 1979; 85: 269-275.
6. Norton PR, Creber DK, Davies JA. Stability and reactivity of (5×20) and (1×1) Pt(100) surfaces, *J. Vat. Sci. Technol.* 1980; 17: 149-1953.
7. Shi Q, Sun R. Adsorption manners of hydrogen on Pt (100),(110) and (111) surfaces at high coverage, *Computat. Theoret. Chem.* 2017; 02: 43-49.
8. Kolb MJ, Calle-Vallejo F, Juurlink LBF, Koper MTM. Density functional theory study of adsorption of H₂O, H, O, and OH on stepped platinum surfaces. *J Chem.* 2014; 140(13): 134708.
9. Picolin A, Busse C, Redinger A, Morgenstern M, Michely T, Institut IIP, et al. Desorption of H₂O from Flat and Stepped Pt (111). *J Phys Chem C.* 2009; 113(2): 691-7
10. Kimmel GA, Petrik NG, Dohnálek Z, Kay BD. Crystalline ice growth on Pt (111) and Pd(111): Nonwetting growth on a hydrophobic water monolayer. *J Chem.* 2007; 126(11): 114702.
11. Badan C, Heyrich Y, Koper MTM, Juurlink LBF. Surface structure dependence in desorption and crystallization of thin interfacial water films on platinum. *J Phys.* 2016; 7(9): 1682-1685.
12. Vanhove M, A Somorjai. New microfacet notation for high-Miller-index surfaces of cubic materials with terrace, step and kink structures. *Surf Sci.* 1980; 92: 489-518.
13. Zimbitas, G., Haq, S., Hodgson, A., The structure and crystallization of thin water films on Pt(111). *J Chem.* 2005; 123(17) : 174701.
14. Badan C, Koper MTM, Juurlink LBF. How well does Pt (211) represent Pt[(111) × (100)] surfaces in adsorption/desorption. *J Phys Chem.* 2015; 119(24): (13551-60).

15. Ogasawara H, Yoshinobu J, Kawai M. Clustering behavior of water (D₂O) on Pt(111). *J Chem Phys.* 1999; 111(15) : 7003 - 9
16. Daschbach JL, Peden BM, Smith RS, Kay BD. Adsorption, desorption, and clustering of H₂O on Pt(111). *J Chem Phys.* 2004; 120(3) : 1516-1523.
17. Gellman AJ, Baker L, Holsclaw BS, Xe. adsorption site distributions on Pt(111), Pt(221) and Pt(531). *Surf Sci.* 2016; 646 : 83-89
18. Sexton BA. Vibrational spectra of water chemisorbed on platinum (111), *Surf. Sci.* 1980; 94(2-3): 435-445.
19. Ibach H, Hopster H, Sexton BA. Analysis of surface reactions by spectroscopy of surface vibrations. *Appl Surface Sci.* 1977; 1: 1 - 24
20. Ho W, Willis RF, Plummer EW. Observation of nondipole electron impact vibrational excitations: H on W(100). *Phys Rev.* 1978; 40: 1463-1466.
21. Engquist I, Lundström I, Liedberg B. Temperature-programmed desorption and infrared studies of D₂O ice on self-assembled alkanethiolate monolayers: Influence of substrate wettability. *J Phys.* 1995; 99(32): 12257-12267.
22. Walsh AJ, van Lent R, Auras SV, Gleeson MA, Berg OT, Juurlink LBF. Step-type and step-density influences on CO adsorption probed by reflection absorption infrared spectroscopy using a curved Pt(111) surface. *J Vacuum Sci Technol.* 2017; 35(3): 03E102.
23. Feibelman PJ, Kimmel GA, Smith RS, Petrik NG, Zubkov T, Kay B.D. Unique vibrational signature of rotated water monolayers on Pt(111): Predicted and observed. *J Chem Phys.* 2011; 134: 204702.
24. Kizhakevariam N, Jiang X, Weaver MJ. Infrared spectroscopy of model electrochemical interfaces in ultrahigh vacuum: The archetypical case of carbon monoxide/water coadsorption on Pt(111). *J Chem. Phys.* 1994; 100(9): 6750 - 64.