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Surface-structure dependence of water-related adsorbates on platinum

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Chapter 1

Introduction

1.1 Catalysis

The term catalysis, proposed in 1835 by Jakob Berzelius (1779-1848), comes from the Greek words *kata*, meaning down, and *lyein*, meaning loosen. Berzelius wrote the following to clarify his definition, "*the property of exercising on other bodies an action which is very different from chemical affection. By means of this action, they produce decomposition in bodies, and form new compounds into the composition of which they do not enter*"[1]. Without literally defining what it actually is, humankind has been aware of the influences of catalysis since ancient times. In the beginning of mankind's civilization, our awareness was solely based on simple processes, e.g. producing alcohol by fermentation. With the industrialization of human society, today we can utilize and design various catalysts to make energy resources, to synthesize nearly 90 % of the products of chemical and pharmaceutical industry, and to reduce pollution from power plants and cars. Our society would not have reached its modern status without employing catalysis in our life[2–4].

There are three sub-disciplines in catalysis namely: biological, homogeneous, and heterogeneous catalysis. Enzymes are biological catalysts which can catalyze a single or multiple chemical reactions both inside and outside of living cells. In homogeneous catalysis, the catalysts occupy the same phase as the reaction mixture. A very well-known example is ozone depletion where chlorofluorocarbons (CFCs) and other halogenated molecules react with O_3 to form O_2 . For this reaction, CFCs catalyze the decomposition of ozone and remain nearly unaltered[3].

In heterogeneous catalysis, the catalyst and the reactants are in different phases. As the catalytic reaction takes place on the surface of the catalyst, it is crucial that small particles with larger surface areas (nanoparticles) are used.

Compared to other catalysts, heterogeneous catalysts are more tolerant to extreme operating conditions. Hence, they are the primary catalysts used in the chemical and petrochemical industries. A typical heterogeneous catalysis reaction starts with the adsorption of the reacting species on the surface of the (generally impenetrable) catalyst. Next, the adsorbed species react on the surface. This involves several steps where intramolecular bonds may be weakened or even broken and new bonds may be formed. With introducing some energy, the products finally desorb from the surface into the gas phase. As soon as the product desorbs, it liberates a new available adsorption site on the surface to regenerate another catalytic cycle[3, 4].

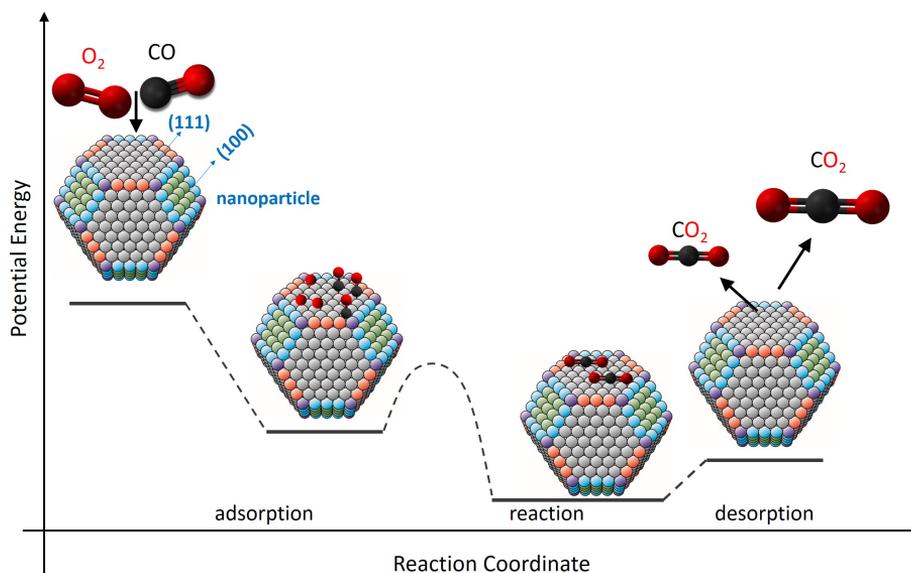


Figure 1.1: Schematic representation for the catalytic oxidation of CO by O₂ on a Pt nanoparticle.

Figure 1.1 illustrates the reaction cycle and potential energy diagram for the well known reaction most commonly applied to exhaust systems in cars. In this catalytic reaction CO is oxidized on the Pt catalyst, which sits between the engine and the tailpipe. Because adsorption is an exothermic process, the potential energy decreases during the associative adsorption of CO and dissociative adsorption of O₂. On a Pt surface, the dissociated O_{ad} and CO_{ad} combine to form CO_{2,ad}. Finally, the new product, CO₂, desorbs from the surface of Pt nanoparticle.

1.2 Surface science approach and the need for ultra-high vacuum (UHV)

In the last decades, petroleum and natural gas became the major natural resource (> 60%) of the main energy production for 7 billions inhabitants on earth. Because of the consequential increase in energy demand, we are expected to be even more dependent on the raw chemical materials in the upcoming decades. Due to this inevitable dependency on natural resources, many developed countries are bringing new laws which promote renewable energy sources [5].

An ideal solution to our dependency to natural resources should be forged by a simple and rather abundant component such as water. If H_2O is split to its components, H_2 can be generated and used as clean and compact energy[6]. In electrochemistry, several precious heterogeneous catalysts, e.g. Pt, Pd, Rh, and Ni, are studied in detail to perform similar reactions that potentially play a key role to bring our dependency to fossil fuels to an end. Hence, a concrete understanding of interactions between catalysts and water is needed to develop or create a more active, selective, stable, mechanically robust and economically feasible catalyst [3, 4, 7]. To accomplish this, different scientific branches are merged to identify efficient and less efficient catalysts. For instance, theoretical studies can examine the structural and dynamic properties of reactions[8]. They can predict the possibility of so far entirely unknown catalysts, their active sites and explore the reaction mechanisms[9].

From theoretical point of view, however, it still remains challenging to predict the interactions of molecules containing many atoms. In addition, it is very difficult and expensive to include all the possible interactions, involving bond breaking or bond formation, that occur at the kinks, defects or steps[10]. In this aspect, electrochemistry offers more realistic, direct or indirect insight applicable to gas-phase studies. Despite the advantages, the various type of aggressive media can influence the long-term stability and durability of the electrode very negatively. Also, the electrochemical processes undergo mass-transport limitations causing difficulties to investigate the solid-liquid interfaces[11].

Particularly to understand the fundamental interaction between small molecules (such as H_2 , O_2 , and H_2O) and Pt, a UHV system can be used as a model approach. In a UHV system, there are significantly less particles per unit volume compared to atmospheric pressure. Hence, under UHV conditions the surface of the sample can be maintained clean for a couple of hours. Moreover, UHV can provide a reproducible domain where the amount and the type of adsorbates can be easily controlled.

Especially with the advances in vacuum technology in the late 1950s, many

surface probing techniques including temperature programmed desorption (TPD), low electron energy diffraction (LEED), etc, developed (chapter 2). Most of these techniques require an optimum impingement rate and mean free path, which can be accomplished only at pressure ranges below 10^{-9} bar. Since such a low pressure range stands out as a drawback of using UHV when it is compared to real processes, more techniques are currently being developed to elucidate the fundamental aspects of catalytic surfaces under more realistic conditions[12, 13].

1.3 Surface-structure sensitivity

The electronic structure, chemical and surface properties of the catalytic surface are crucial components to thoroughly elucidate the behaviour of catalysts in all aspects, (figure 1.2). Especially in heterogeneous catalysis, the behaviour of the adsorbates depend critically on the surface topography of the metals. Since real nanoparticles (figure 1.1) have a very large variation in surface orientation, determining the active sites is crucial in understanding the role of the catalysts in a catalytic reaction[14]. One way to identify the impact of local structure on chemical reactions occurring on a catalytic surface is to compare reactivity of well-structured, high and low-Miller-index single crystals under well-controlled UHV conditions.

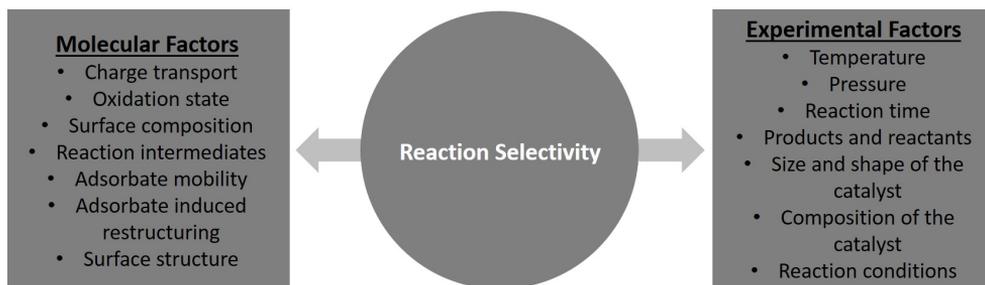


Figure 1.2: Schematic representation of main factors influencing a catalytic reaction[5, 6].

Figure 1.3 shows flat, curved and cylindrical crystals, which are used in surface science studies in our laboratory. The image in the left bottom panel demonstrates the surface orientations adapted from a face centered cubic (fcc) unit cell. [100] and [110] planes occur at angles from the [111] surface of 54.7° and 35.3° , respectively (image in the right bottom panel). Moving away from [111] plane, (100) (clockwise) or (110) (counterclockwise) stepped (111) terraces can be obtained. On flat single crystals, only one particular surface structure is present whereas

on curved or cylindrical crystals, multiple facets can be used in the same vacuum environment.

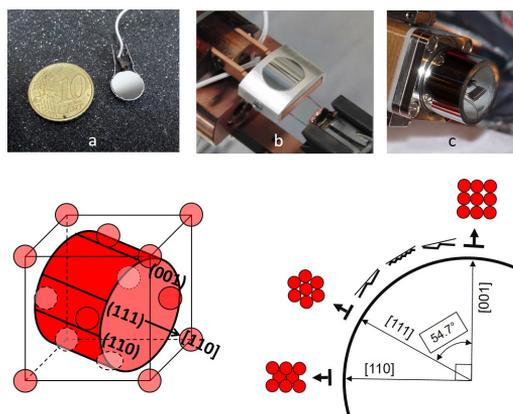


Figure 1.3: a) Flat, b) curved, and c) cylindrical crystals can be used to perform surface science experiments under well-controlled UHV conditions. The schematics in the bottom panel illustrates surface orientations on a curved or cylindrical crystal.

Pt(111) has been the focus of experimental and theoretical surface science studies for the last decades because of its simplicity, figure 1.4a. An ideal (111) plane has an infinite hexagonal structure without any kinks, steps or other defects. On the other hand, real nanoparticles have large number of defect sites, which are more active in bond breaking and making reactions[15], as compared to the (111) plane. This difference between real nanoparticles and well-defined catalysts is known as the materials gap. This drawback in surface science studies can be partially overcome when surfaces with higher step densities, such as Pt(211), Pt(221), Pt(553), Pt(533), are used, as shown in figure 1.4[16]. Therefore, from an experimental point of view, highly stepped surfaces are considered as appealing model systems for a nanoparticle catalyst.

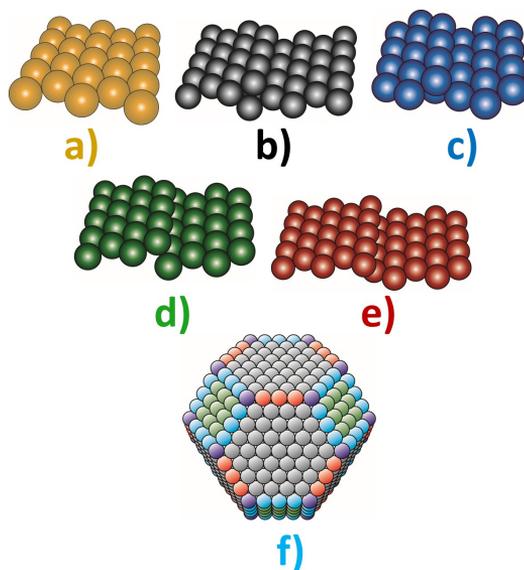


Figure 1.4: a)Pt(111), b) Pt(533), c) Pt(211), d) Pt(221), e) Pt(553) and f) a catalyst nanoparticle.

1.4 Scope

Water is one of the most extensively studied molecules due to its intriguing properties and relevance to many different fields in biology, astrophysics, chemistry, and physics. It is evidently present at many interfaces involving solid surfaces. In this thesis, we focus on the surface structure dependence of water and water-related interfaces on bare and D_2 pre-and-post-covered Pt surfaces. To carry out a more realistic approach, we perform our experiments on highly corrugated Pt surfaces which have similar surface step densities to real nanoparticles. In this research, we use single crystal surfaces and UHV techniques (TPD, LEED and scanning tunneling microscope (STM)) to explore the influences of surface structure on adsorption and desorption of water and related adsorbates.

H_2 , O_2 , and H_2O are known to be excellent molecules in surface science studies. They represent dissociative (O_2 and H_2)[17, 18] and non-dissociative (H_2O)[19] adsorption with different ranges of activation barriers. In chapter 4, we discuss the adsorption and desorption behaviour of these molecules on a very corrugated surface, Pt(211), (Pt[n(111)x(100)], $n = 3$). Pt(211) is used as a model surface in many theoretical studies because it has the smallest unit cell containing the (100) step edge. We compare our results on Pt(211) with stepped surfaces with $n > 4$.

The results provide deeper insights in how extreme corrugation on a Pt surface influences the adsorption and desorption characteristics of O₂, H₂ and H₂O. We show that it is crucial to be cautious in extrapolating results from theoretical studies when using Pt(211) as a model substrate to represent Pt[n(111) x (100)] surfaces.

The interaction of water with late transition metals has been reviewed multiple times in great detail[19–21]. It is known that H₂O dosed on Pt(111) below 180 K leads to molecular adsorption without dissociation even when exposed to X-rays[22]. When water is adsorbed on colder surfaces (< 120 K), it forms metastable amorphous solid water (ASW) which crystallizes into crystalline ice (CI) when heated[23, 24]. Recent studies show that the kinetics of this transition significantly depends on the substrate structure. These studies mainly focus on the influence of different metal substrates at very high (50 - 100 ML) coverages[25–27]. In chapter 5, using very thin interfacial water films, we show the significant differences in crystallization kinetics of very similar substrates, Pt(211) and Pt(221). Our results indicate that the thickness of the CI layers depends on the substrate surface. In chapter 6, we compare the crystallization kinetics and isotopic partitioning of D₂ pre-and-post-covered Pt(211), H₂O/D₂/Pt(211) and D₂/H₂O/Pt(211), respectively. We find that isotopic partitioning does not depend on the sequence of dosing. However, the order of dosing influences the crystallization kinetics significantly. D₂ is found to provide a 'smoothing effect' on the corrugated surface when it is dosed first. Also, Pt(211) shows hydrophobic behaviour when D₂ is pre-dosed onto surface. However, the hydrophobicity of the surface does not change when the H₂O covered surface is exposed to hydrogen.

In chapter 7, we study molecular and recombinative O₂ desorption from (110) and (100) stepped Pt(111) surfaces using TPD and STM. We find that (110) stepped Pt(111) terraces trigger dissociative adsorption upon impact at a temperature as low as 100 K. A combination of atomically and molecularly adsorbed oxygen doubles total oxygen coverages for (110) stepped Pt(111) terraces as compared to Pt(111) and Pt(211). (100) stepped Pt also boosts O₂ dissociation by comparison to Pt(111). This, however, results from a trivial geometry effect brought by the steps due to the increased surface area, meaning that the (100) steps provide no extra reactivity.

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