Surface-structure dependencies in catalytic reactions
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Chapter 2

Experimental set-up and techniques

2.1 The set-up

The experiments were performed using an ultra-high vacuum (UHV) apparatus named Lionfish. The main chamber has a base pressure of $< 1 \cdot 10^{-10}$ mbar during experiments and contained a LEED/Auger Electron Spectroscopy device (LK Technologies, RVL 2000/8/R), a fixed quadrupole mass spectrometer (QMS, Pfeiffer QMA 200), a sputter gun and various leak valves (experiments in chapter 6). Later, the machine was extended with a double differentially pumped supersonic molecular beam, a single differentially pumped effusive beam, and a quadrupole mass spectrometer (UTI 100C) which can be moved along the molecular beam axis for time-of-flight (TOF) measurements (for experiments in chapter 3, 4, and 5). The crystal is suspended from a liquid nitrogen cooled cryostat on an x, y, z, θ manipulator. The crystal temperature can be controlled between 84 and 1200 K with the use of liquid nitrogen for cooling and radiative heating combined with electron bombardment for heating.

A schematic side view of the supersonic molecular beam is shown in figure 2.1. The main UHV chamber (left) can be separated from the other chambers by the slide. The slide can be set to one of three orifices (diameter of 6.2 mm, 3.2 mm and 1.8 mm) or the slit (for future measurements on curved crystals).
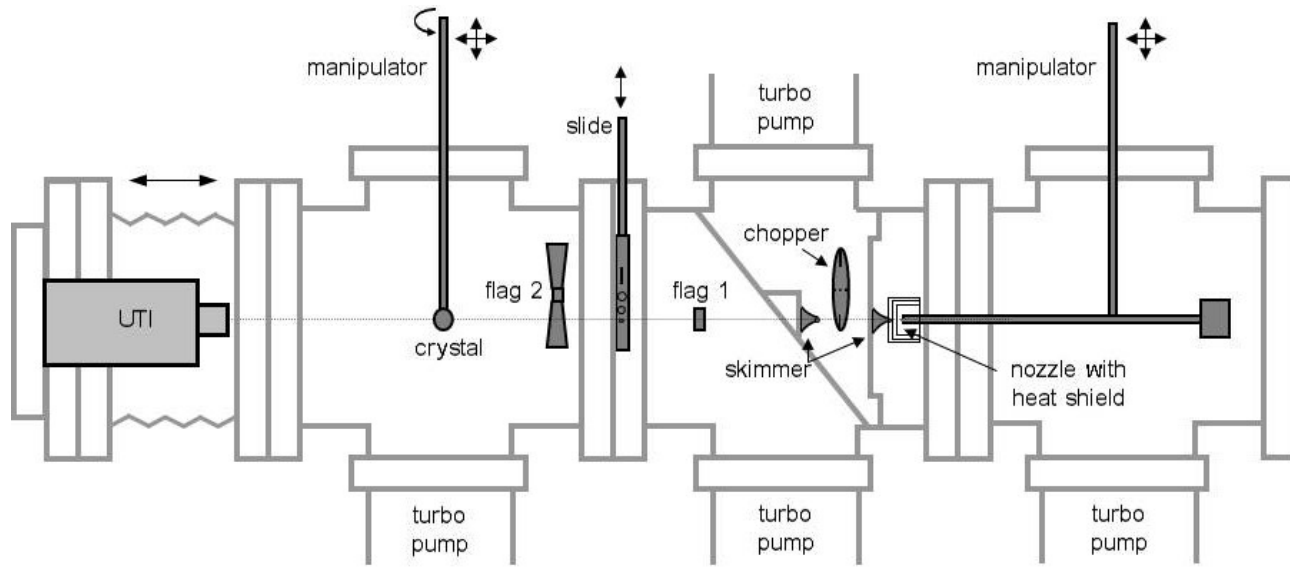
Figure 2.1: Schematic side view of the supersonic molecular beam parts.

The beam was created by continuous expansion of gas mixtures at 0.5-4.7 bar through a tungsten nozzle. The nozzle has a circular 45 μm diameter orifice and can be heated by two filaments. A heat shield protects the rest of the machine from overheating. The beam enters from the right and is shaped by a set of skimmers (diameter of 2.5 mm and 0.45 mm). Two flags (one in the second differential and one in the UHV chamber) and the chopper wheel (first differential chamber) modulate the beam. The two flags are used to determine the sticking probability with the King and Wells (KW) technique[8] (see chapter 2.2.4). The chopper wheel is a fast rotating disk ($\sim$ 250 Hz) with two broad (17 mm) and two narrow slits (0.85 mm, 16% total duty cycle). It is used to determine the kinetic energy (E_i) of the beam with the time-of-flight (TOF) technique (see section 2.2.3). The incident kinetic energy of the molecular beam was controlled by seeding or antiseeding with helium (Linde, 6.0) or argon (Air Products, 5.7) an by heating the nozzle. Exposure of the crystal to the beam is continued until the exposed surface area has reached a maximum coverage. A temperature programmed desorption (TPD) experiment was performed after each adsorption experiment.

The procedures of the crystal cleaning and the experiments are described in the experimental part of the following chapters. Cleanliness of the crystals was checked regularly by monitoring additional masses (such as $^{m}/_{e}$ = 2 (H_2), 18 (H_2O), 28 (CO or N_2), 32 (O_2), and 44 (CO_2) in desorption experiments and repeating experiments under identical conditions. Surface structure was confirmed by low energy electron diffraction (LEED, see chapter 2.2.1).

2.2 Techniques

2.2.1 Low energy electron diffraction

Low energy electron diffraction is a technique that can be used to determine the surface structure. The low energy electrons hit the surface, the electrons are scattered back elastically in all directions. The well-ordered structure of the surface creates an interference pattern, which can be visualized on the fluorescent screen. The pattern on the screen is a reciprocal lattice. Small interatomic distances show up as a large distance between the fluorescent spots, and the other way around.

Stepped surfaces show splitted spots on the screen. The direction of the multiplet is perpendicular to the steps[10]. The spot row to spot splitting ratio is a measure

of the average terrace length on the crystal. The step height can also be determined by LEED[11]. Depending on the electron energy, the (00) spot shows either as a singlet or as a doublet. A fit for the first singlet or doublet should be compared to the theoretical energy. The best fit indicates if the steps are of single atomic height, or of double atomic height.

A good LEED device can also be used to determine the structure of ordered adsorbate layers. Unfortunately, the quality of the available LEED on our system is such that we were only able to use it to confirm the surface structure of our crystals and the azimuthal orientation relative to the plane containing the surface normal and the molecular beam.

2.2.2 Temperature programmed desorption

Temperature programmed desorption is a simple, yet very useful surface science technique. It can provide information about the binding energy of the molecule to the surface, the order of the reaction, and the surface coverage. For TPD experiments, molecules are adsorbed to the surface by background dosing (chapter 6) or by using the supersonic molecular beam (chapter 3-5). The sample is heated with a linear temperature ramp:

$$T_s = T_0 + \beta t \tag{2.1}$$

where T_s is the surface temperature, T_0 the initial surface temperature, β the heating rate, and t the time. The heating rate in this thesis varies between 1 and 4 K/s and is mentioned in the upcoming chapters when necessary. At a certain temperature, the bonds between the surface and the adsorbates are broken, the molecules desorb and are detected by the mass spectrometer.

The desorption process can be described by the Polanyi-Wigner equation[12]:

$$r(\theta) = -\frac{d\theta}{dt} = \nu(\theta)\theta^n e^{-E_d(\theta)/RT} \tag{2.2}$$

where r is the rate of desorption, θ the surface coverage, ν the pre-exponential Arrhenius factor, n the order of desorption, E_d the activation energy, and R the gas constant.

The binding energy depends on the type of adsorbed molecules, the type of metal of the crystal, the surface structure, the presence of defect sites and co-adsorbates, and the adsorbate coverage. A higher binding energy results in a higher desorption temperature. The broadness of the desorption peak is indicative of the attractive or repulsive interaction between the adsorbed molecules. The order of the reaction can be determined by dosing different amounts of molecules on the surface[13]. Zeroth-order reaction kinetics can result from an equilibrium between a condensed phase and a 2-dimensional gas phase, from which molecules can desorb. The TPD spectra are characterized by overlapping onsets with a maximum peak temperature that shifts to higher temperatures with increasing coverage. First-order reaction kinetics show no temperature shift when the coverage increases. The desorption rate is proportional to the surface concentration. Second-order kinetics (recombinative desorption) show a peak that shifts to lower temperatures with increasing coverage. The involvement of two atoms leads to a desorption rate that depends on the coverage squared. The relative number of molecules that was present on the surface (coverage) can be determined by integrating the TPD spectrum. TPD can also be used to check if the surface was clean, as the shape of the TPD spectrum often changes when other molecules are present on the surface[14].

2.2.3   Time-of-flight

The time-of-flight method is used to determine the kinetic energy of the molecules in the supersonic molecular beam. TOF spectra are measured with the quadrupole mass spectrometer (UTI 100C). The QMS can be moved along the beam axis in order to vary the distance to the chopper wheel. The chopper wheel spins at a frequency of ~ 250 Hz and has two broad and two narrow slits. The optical sensor triggers a multichannel scaler card (turbo MCS, EG&G Ortec) when a slit passes the sensor. During the measurements, the chopperwheel is rotated 15/8 turns before starting a new scan, resulting in 3 or 4 large and small peaks (depending on the timing of the trigger). Usually 10000 to 30000 scans are summed to obtain a spectrum as shown in figure 2.2.

The QMS is moved along the beam axis over a distance of 46 mm in 6 steps. When the QMS is moved further away from the chopper wheel, it takes a longer time for the molecules to reach the detector. The peaks shift to the right. The difference in flight path vs. flight time can be used to determine the average speed and kinetic
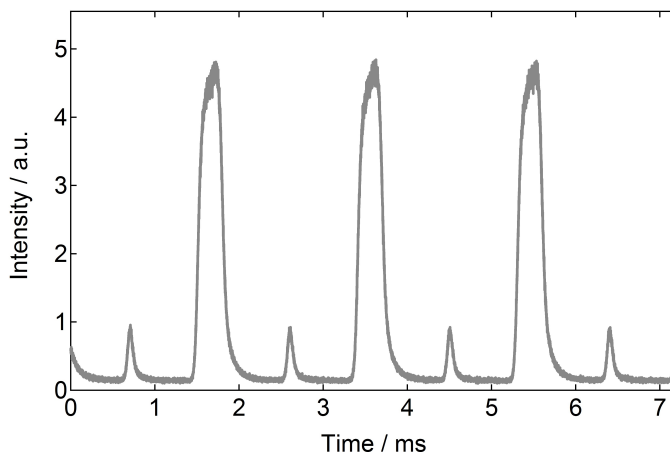
Figure 2.2: A typical time-of-flight spectrum of O_2 in the supersonic molecular beam. As the chopper wheel almost spins two times, the spectrum shows both large and small peaks of the wide and narrow slits.

energy of the molecules. Only the small peaks are used for the analysis, as the larges ones are not as well defined. Oxygen is mixed with helium and/or argon to increase or decrease the speed of oxygen. The oxygen molecules and the seed gas molecules do not have the same speed in the beam. This is known as the velocity slip.

A more detailed analysis can be made to estimate the velocity distribution and delay times. For this method, the chopper gating function should be taken into account. The chopper spins fast and has narrow slits, yet there is still a transition before and after complete opening of the slit to the beam. This method is not described in this thesis.
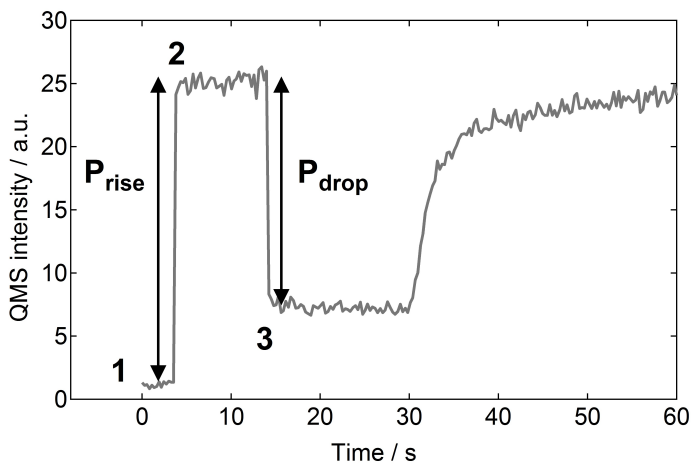
2.2.4   King and Wells

The sticking probability (reaction probability) of O_2 on Pt or Pd single crystals can be determined with the King and Wells technique[8]. Figure 2.3 shows the different steps of a KW experiment. In the first stage, both flags along the supersonic molecular beam are closed, a background pressure of O_2 is measured by the QMS. After 5 seconds, the first flag (in the differentially pumped stage) is opened. The beam enters the main chamber, without impinging onto the sample and the oxygen partial

pressure increases, P_{rise}. The pressure is allowed to stabilize for 10 seconds, before the second flag (in the UHV main chamber) is opened. Oxygen molecules adsorb on the surface, which results in a temporary decrease of the partial pressure, P_{drop}. After a certain time, the partial pressure increases again as the surface coverage increases. The initial sticking probability (S_0) is determined by:

$$S_0 = \frac{P_{drop}}{P_{rise}}$$ (2.3)

Figure 2.3: Determining the sticking probability with the King and Wells technique. The steps are explained in the text.

The reactivity of oxygen on Pd(100) was very high. In order to obtain a good estimate of the real initial sticking probability, an extrapolation method was used as described in the experimental section of chapter 3. The S_0 (first few seconds after opening the second flag) can be plotted against incident energy, surface temperature, or incident angle. The sticking probability changes over time, as the oxygen coverage increases. The complete KW experiment also provides useful information on the adsorption process as function of coverage.