

Cover Page



Universiteit Leiden



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Title: Surface-structure dependencies in catalytic reactions

Issue Date: 2015-12-09

Chapter 7

Future prospects

So far, our group has gained valuable knowledge on relevant systems by studying the interaction of molecules with metal surfaces under ultra-high vacuum conditions. Background adsorption of a single type of molecules on flat single crystals is considered a relatively simple type of experiment. The use of supersonic molecular beam techniques and regularly stepped single crystals already increases the complexity of the studied system. We have also studied the interaction of multiple types of molecules (co-adsorption via background) with stepped single crystals. Our UHV apparatus is actually a unique machine than can be used for even more complex measurements, since it has two molecular beams connected to it. In the future, we hope to be able to study the interaction of at least two types of adsorbing molecules via the supersonic molecular beam (SSB) and the effusive beam (EB) on curved single crystals. This chapter provides a short proof-of-principle of the use of the double beam and of the use of curved single crystals.

7.1 Double beam

The UHV machine has been rebuilt in the last few years. More than five years ago, it was a normal and simple surface science machine, capable of adsorbing molecules on surfaces via the background and only equipped with a LEED and QMS for TPD experiments. In the mean time, it was completely remodeled. It now contains a supersonic molecular beam (SSB, as used for the experiments in chapter 3, 4, and 5) and an effusive molecular beam (EB). A schematic top view of the beam

lines is shown in figure 7.1. As described before, the double differentially pumped supersonic molecular beam passes through a set of skimmers and a chopper wheel with a 16% duty cycle. The beam can be modulated by two flags (SSB1 and SSB2) and the slide can separate the entire SSB from the main chamber. The single differentially pumped effusive beam also passes through a set of skimmers. There is one gate (EB1) separating the EB from the main chamber and one flag (EB2) to prevent the beam from impinging onto the crystal directly.

The ratio of molecules in the SSB and EB can easily be adapted by changing the settings of the flow controllers to find an optimal rate for the formation of certain molecules. However, changing the settings will result in different beam conditions, which might also influence the reaction. A different way of changing the flux of the SSB is to keep the chopper wheel in the open position or to modulate the beam so that the incoming flux is reduced to 16%. A detailed analysis of the flux dependencies will provide information on the formation of molecules on stepped Pt. Here, only the proof-of-principle of HD formation from H_2 and D_2 and HOD formation from O_2 and a mixture of H_2 and D_2 is shown.

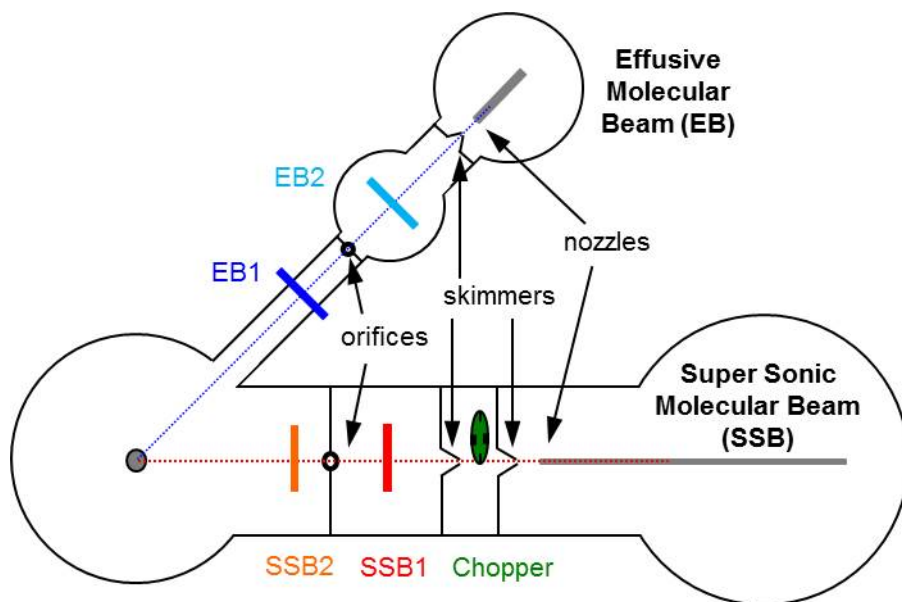


Figure 7.1: Schematic top view of the UHV machine Lion Fish with the SSB and EB lines.

We have studied HD formation on Pt(553) at a surface temperature of 500 K, while the crystal points in the direction between the two beams. Figure 7.2 shows the QMS intensities of H₂ (top, 4 ml/min in SSB, no chopping) and D₂ (middle, 0.5 ml/min in EB) and HD (bottom) as a function of time. A sequence of opening and closing the flags of both beams (see figure 7.1) results in changes of the HD, H₂, and D₂ intensities. During the first 30 seconds all flags are closed so that we measure the background pressure of the different molecules. After 30 seconds, SSB1 is opened and the H₂ signal increases as the H₂ molecules enter the main chamber. They do not directly impinge onto the crystal yet. When SSB 2 is opened, the H₂ molecules can impinge onto the crystal. However, as the surface temperature is high, there are no stable chemisorbed hydrogen species on the surface. Therefore, the QMS intensity does not change. After closing SSB2 again, EB2 is opened and D₂ molecules from the EB enter the main chamber but do not directly impinge onto the crystal. EB2 is a gate valve and turning it results in noise in all signals. The D₂ and HD signals increase as expected since HD is partly present in the D₂ bottle and partly forms on other metal surfaces, such as the chamber walls and the filaments. When SSB2 is opened again, the H₂ molecules impinge onto the crystal directly. The H₂ signal slightly decreases, while the HD signal increases, indicating that part of the H₂ reacts on the surface with the background D₂ to form HD. When the EB2 is also opened, both beams impinge onto the crystal directly. The HD and D₂ signals increase significantly, while H₂ decreases. When SSB2 is closed, the HD signal decreases while the other signals increase. The H₂ does not directly impinge onto the crystal anymore. Less H₂ and D₂ react to form HD. Closing SSB1 results in a drop in H₂ and HD. The remainder of these signals results from the D₂ in the EB. The last steps are closing EB2 and EB1 and waiting until the signals stabilize again. Even though HD is already formed without both beams hitting the crystal directly, the Pt(553) crystal does increase the HD formation by a factor of about 2 under these conditions.

A similar type of experiment was performed to study the HOD formation from O₂ and a mixture of H₂ and D₂ on Pt(533) at a surface temperature of 500 K, while the crystal faces the SSB. Figure 7.3 shows O₂ (top, 4 ml/min in SSB, with chopper on), HD (middle, mixture of 4.8 ml/min H₂ and 4.8 ml/min D₂ in EB), and HOD (bottom) as a function of time. The reactants and products show similar behavior to the HD formation (figure 7.2). The O₂ signal shows a small drop when SSB2 is opened, due to dissociative adsorption of oxygen to the surface.

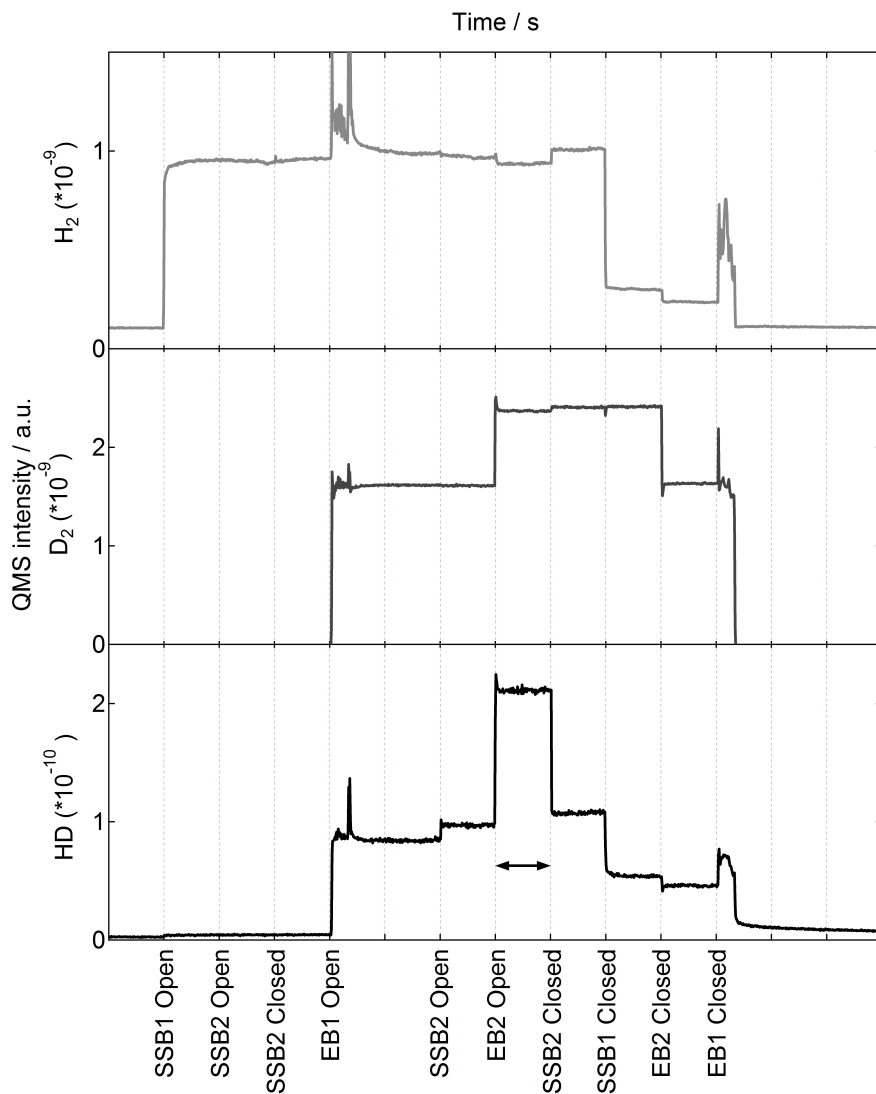


Figure 7.2: QMS intensity of H₂ (top), D₂ (middle), and HD (bottom) during a double beam experiment (4 ml/min H₂ in SSB, no chopper and 0.5 ml/min D₂ in EB) on Pt(553) at a surface temperature of 500 K. The arrow indicates the HD formation on the crystal when all flags are opened.

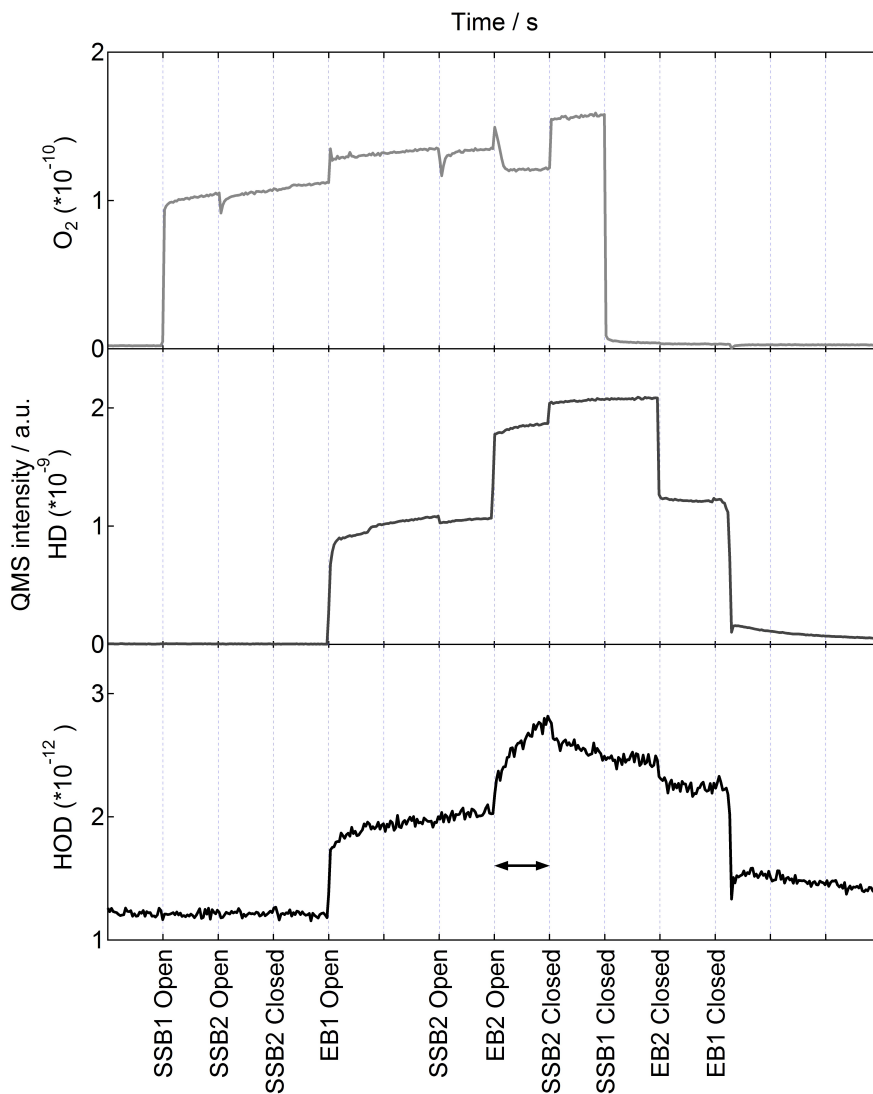


Figure 7.3: QMS intensity of O₂ (top), HD (middle), and HOD (bottom) during a double beam experiment (4 ml/min O₂ in SSB, chopper on, mixture of 4.8 ml/min H₂ and 4.8 ml/min D₂ in EB) on Pt(533) at a surface temperature of 500 K. The arrow indicates HOD formation on the crystal when all flags are opened.

When the surface is saturated, the intensity returns to the normal value (like the normal King and Wells experiments). When EB2 is opened, O₂ shows a small rise before it decreases. The HOD signal slowly increases when all flags are opened.

7.2 Curved single crystals

A single crystal can be cut in any direction to expose a certain surface structure. When it is cut in a cylindrical shape, a large variation of surface structures is exposed. A few years ago, measurements on a cylindrical Ni crystal have been performed with the use of a supersonic molecular beam. With only one crystal, the influence of step type and terrace length can be studied extensively^{154,155}. However, this type of crystal had a few drawbacks. As the crystal was large, it took a long time to heat and cool the sample and it can only be used in one machine. Recently, we started using curved single crystals. They have the size of our regular samples, heat and cool like the other samples, can be used in all of our systems, and still allow us to study a range of surface structures.

A schematic view of a curved crystal is shown in figure 7.4. The curved single crystal in this example contains (111) terraces with the (100) step type on the right side and the (110) step type on the left side. The real crystal exposes surface structures ranging from (111) in the middle to (533) and (553) at the sides. With this crystal, we can study the influence of terrace length from 4 atom wide atoms to 'infinitely long' (111) terraces for both (100) and (110) step type under identical conditions in a short amount of time. The combination of the curved crystals with the double molecular beam will not be easy. When everything works, it will yield valuable and unique new insights in the processes that take place in heterogeneous catalysis.

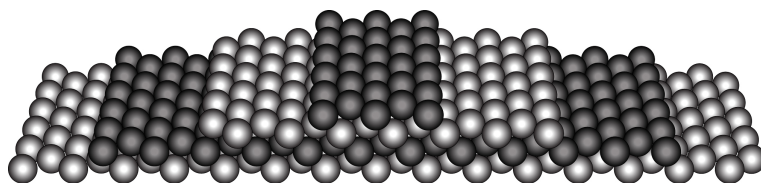


Figure 7.4: Schematic representation of a curved single crystal with (111) terraces and the (100) step type on the right and the (110) step type on the left.