

# Chapter 2

## Experimental

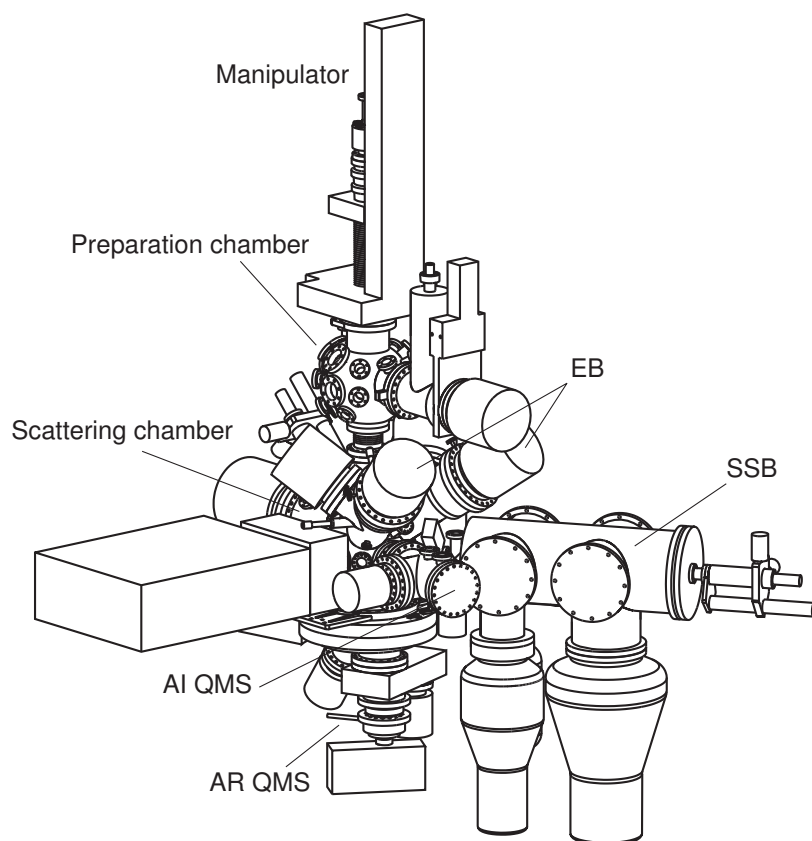
**Abstract** Molecular beam (MB) techniques combined with mass spectrometry provide a large control over the reaction parameters. MBs allow a full control of the flux intensities as well as of the beam direction. Moreover, single scattering of the molecules is insured, so that the number of molecules actually hitting the surface is also under control. Mass spectrometry selectively measures partial pressures of gases. Therefore, the properties of the reactants are controlled by the MBs and the quantity of products is measured by mass spectrometry. As shown in the introduction, size is a crucial parameter for fundamental investigations of catalyst activities. To cover a large range of sizes, three samples are prepared using two different techniques: PVD and EBL. MB, mass spectrometry and the sample preparation methods are reviewed in this chapter.

### 2.1 Molecular beam apparatus

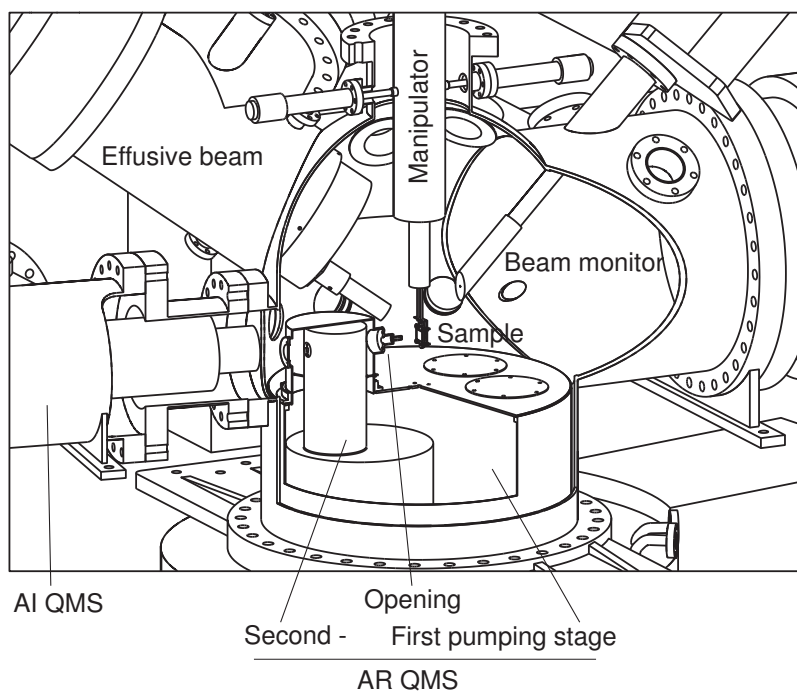
Figure 2.1 gives a schematic representation of the setup. The apparatus is fully reviewed in Refs. [53, 54] and is therefore only briefly presented here. It consists of two ultra-high vacuum (UHV) chambers (base pressure below  $2 \times 10^{-10}$  mbar). The preparation chamber offers all facilities for in-situ sample preparation by physical vapor deposition. The experiments are performed in the scattering chamber, where up to three MBs can be crossed simultaneously at the sample surface. Reactants in the gas phase are detected by means of two quadrupole mass spectrometers (QMSs): one non-line-of-sight angle integrated (AI) QMS, which records background partial pressures; and one line-of-sight differentially-pumped angle resolved (AR) QMS. The machine also allows infrared spectroscopy (see, e.g., [55]) to follow the state of the adsorbates at the sample surface, but this technique is not used here.

#### 2.1.1 Molecular beams

The MB approach is well established in surface science [56–60]. It serves as basis to the experiments presented in the dissertation. A molecular beam is a spatially well defined, directed and collision-free flux of molecules. It encounters single scattering events at the sample surface. This implies that the flux, i.e., number of molecules passing through

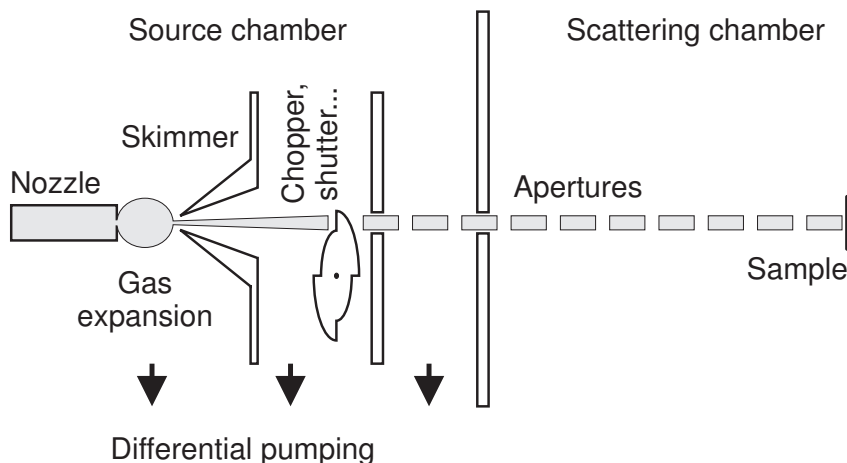


(a) Scheme of the machine, adapted from [53]



(b) Scheme of the scattering chamber, adapted from [53]

**Figure 2.1.** Molecular-beam apparatus.



**Figure 2.2.** Principle of molecular beam generation.

an area during a given time, can be calculated [61]. Internal and kinetic energy of the molecules in the flux are also well defined [56]. Moreover, the area exposed at the sample surface is determined by the apparatus design.

The principle of MB generation is schemed in Figure 2.2. Briefly, the beam is prepared in a first differentially pumped chamber (source). It is generated by a gas expansion from a high-pressure reservoir (nozzle) into vacuum. The centerline of the expansion is selected by a skimmer, whereas the remaining gas is efficiently pumped by several differential pumping stages. After generation, the beam can be temporally modulated by mechanical devices such as shutters or choppers. The pressure difference between the reservoir and vacuum determines the beam energy and flux. And this parameter can be varied during the experiments. The area exposed at the sample surface is determined by the diameter of the nozzle. The background pressure typically generated by MBs is about two orders of magnitude lower than under a direct beam exposure.

MB sources of two types are commonly distinguished: beams generated from supersonic expansions (SSB) and from effusive sources (EB). One SSB and two EBs are used for the experiments. We refer to the literature [56] for a physical description and concentrate here on the practical applications.

**SSB** Supersonic beams are generated from a high-pressure reservoir, typically in the bar range. The large pressure difference between the reservoir and ambient pressure results in an effective equilibration of the kinetic energies in the beam. Practically, the area exposed at the sample surface remains smaller than the sample itself, so that the flux is well defined there. The beam flux is kept constant and equal to  $5.6 \times 10^{-14} \text{ cm}^{-2} \text{ s}^{-1}$  during the experiments.

**EB** Effusive beams are generated by a lower pressure difference between the reservoir and ambient background. This results in broader velocity distributions. Practically, the pressure in the source is regulated by a baratron and admission of the beam in the chamber is controlled by a valve. This offers several advantages: a reduced gas

consumption, as well as a dynamic control of the pressure in the source, which results in a control of the beam intensities. Beam fluxes from  $1.4$  to  $20 \times 10^{-14} \text{ cm}^{-2} \text{ s}^{-1}$  are used during the experiments. The area exposed at the sample surface is larger than the sample. The surface is here fully exposed to the beam.

### 2.1.2 Mass spectrometry

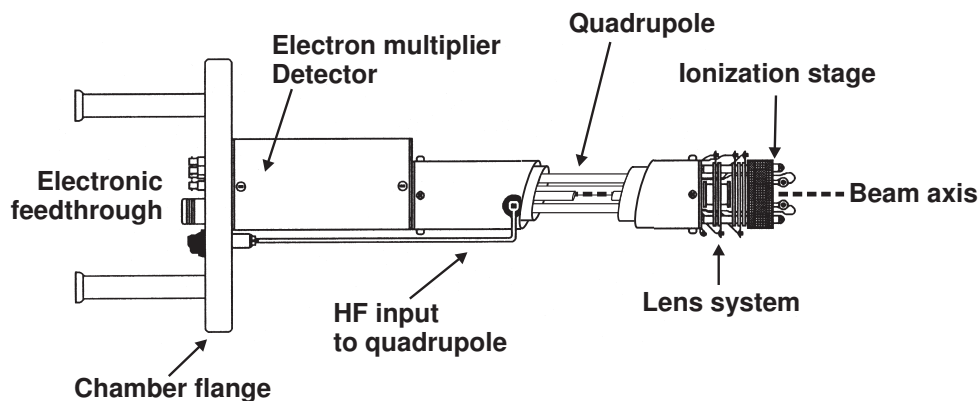
The detection of products in the gas phase is ensured by mass spectrometry. Mass spectrometers are instruments measuring partial pressures, defined as the pressure that would result from the measured gas only in absence of any other species. The sum of every partial pressures is the total pressure. A scheme of a QMS is presented in Figure 2.3. Gas molecules are ionized in the ionization stage. The quadrupole generates electric fields, which separate the ions according to their kinetic energy (function of their molecular mass  $\mathcal{M}$ ) and charge  $z$  by resonance phenomena [63]. Separation occurs along the characteristic ratio  $\mathcal{M}/z$ .

In the apparatus, the partial pressure detection is insured by two QMSs:

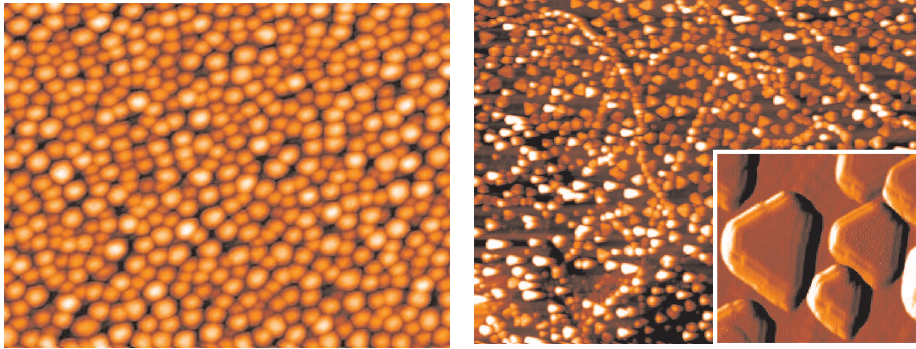
**AI QMS** (ABB Extrel, schemed in Figure 2.3) is non-line-of-sight and far from the sample. The probability of measuring molecules directly emitted by the sample is therefore reduced. This unit allows very accurate mass separations at short dwell times. It is used to detect partial pressures in the ambient background.

**AR QMS** (Hiden, HAL 501/3F-PIC) is located in a differentially pumped housing with a line-of-sight opening of 2 mm diameter. Then, only molecules flying directly from the sample to the AR QMS are detected. This housing is fixed on a rotatable platform, and angles over  $90^\circ$  from the sample surface normal are accessible.

Both instruments may be used in combination.



**Figure 2.3.** Scheme of the AI QMS, adapted from [62].



**Figure 2.4.** STM images of (a) Sample A prepared by PVD, evaporated at  $T = 90$  K and (b) Sample B evaporated at  $T = 300$  K, from [64].

(a) Sample A; STM  $100 \text{ nm} \times 100 \text{ nm}$  (b) Sample B; STM  $300 \text{ nm} \times 300 \text{ nm}$  and inset  $50 \text{ nm} \times 50 \text{ nm}$

## 2.2 Sample preparation

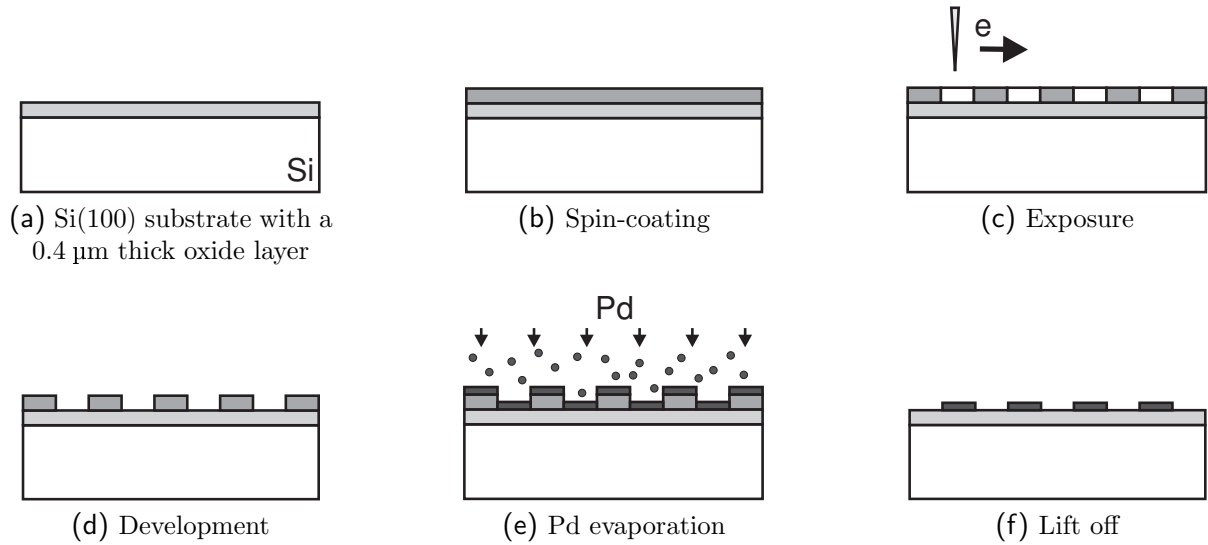
A combination of two different preparation methods, physical vapor deposition (PVD) and electron beam lithography (EBL), allows us to access a range of particle sizes over two orders of magnitude. Both techniques provide a large control over size and shape of the deposited particles. PVD typically allows preparation of particles down to 1–10 nm diameter, whereas EBL allows preparation of particles above 10 nm. Sample A and Sample B are prepared by PVD and consist of Pd/Al<sub>2</sub>O<sub>3</sub>/NiAl(110). Sample C is prepared ex-situ by EBL and consists of Pd/SiO<sub>2</sub>/SiO(100). The substrates differ due to experimental difficulties in the preparations. However, they have equivalent properties as regard to CO oxidation [30, and Refs. therein], i.e., they are flat oxide surfaces, relatively inert, adsorbing weakly the reactants and products and, therefore, their composition plays a minor role in this study.

### 2.2.1 Physical vapor deposition

The main interest of PVD for surface science studies is that it can be accomplished in-situ. It therefore allows preparation of clean samples. PVD is the evaporation of metal onto well-defined substrates, practically oxide surfaces, at submonolayer coverage. It provides a controllable particle size distribution (e.g. [65–70]). Sample A and Sample B are prepared according to a recipe previously published in the literature [71, 72]. Briefly, a NiAl(110)

	Sample A	Sample B	Sample C
Preparation method	PVD @ 90 K	PVD @ 300 K	EBL
Nominal deposition thickness (nm)	0.1	0.4	
Average island diameter (nm)	1.8	5.5	500
Pd atom per island	100	2700	$\gg$
Dispersion	60( $\pm$ 10)%	20( $\pm$ 3)%	1–2%
Coverage of the support	15( $\pm$ 5)%	20( $\pm$ 2)%	9%

**Table 2.1.** Main characteristics of the samples.

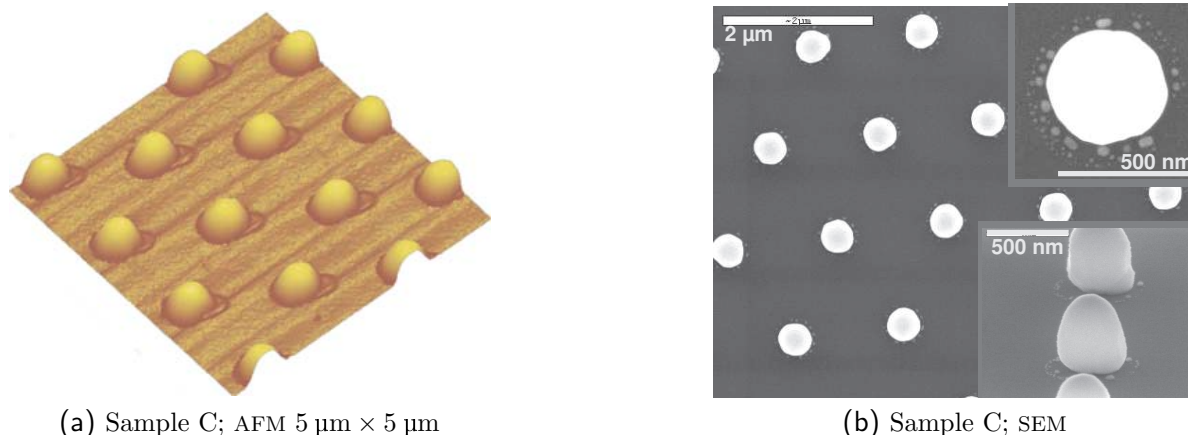


**Figure 2.5.** Sample C prepared by EBL: (a) Cleaning of the Si(100) substrate with a 0.4 μm thick oxide layer; (b) Spin coating of a photoresist layer; (c) exposure to a predesigned pattern with an electron beam; (d) development, i.e. dissolution of the photoresist; (e) Pd evaporation by PVD; (f) lift off, i.e. dissolution of the remaining resist.

single crystal is cleaned by repeated sputtering–annealing cycles. Then, the  $\text{Al}_2\text{O}_3$  thin film is formed by two oxidations at 1150 K during 5 min. The structure and properties of the oxide is known [71–76]. The Pd particle size is controlled by the temperature of the oxide during metal deposition [73]. For Sample A, Pd is evaporated on a surface at  $T = 120$  K (liquid nitrogen temperature). This results in Pd islands of about 1.8 nm diameter. Sample B is evaporated at room temperature, the island diameter is about 5.5 nm, as can be seen in Figure 2.4. Sample A does not exhibit clear faceting, whereas Sample B exhibits mainly (111) and (100) facets [64]. Other properties are recapitulated in Table 2.1.

### 2.2.2 Electron beam lithography

The fabrication of particles by EBL has recently been used successfully in surface science and catalysis (e.g. [78–82]). The advantage of the method as compared to PVD is that it provides ultimate control over structural parameters such as particle size, shape and separation. It is a serial technique in which an electron beam is rastered across the surface of an electron-sensitive polymeric film (resist), creating a computer-generated pattern. A schematic diagram of the EBL procedure is shown in Figure 2.5. A 0.4 μm thick thermal oxide layer is grown on a Si(100) substrate. The Pd towers are fabricated with a double layer resist system, consisting of a bottom layer of PMGI-SF7 (polyimide) and top layer of 1:2 diluted ZEP520 in anisole. The pattern is exposed with a dose of  $160 \mu\text{C cm}^{-2}$  in an EBL system (JEOL JBX9300FS). After dissolving the exposed polymer, a 500 nm thick film of Pd (99.95% purity, K.A. Rasmussen, AB) is vapor deposited at  $3 \times 10^{-6}$  mbar at a flux of  $0.8 \text{ nm s}^{-1}$  in an electron-beam-deposition system (AVAC HVC-600). The remaining



**Figure 2.6.** AFM and SEM images of Sample C, from [77]. See text for details.

resist is lifted off in Shipley 1165 (N-methyl-2-pyrrolidone) leaving the Pd towers in the prescribed pattern. After resist removal, the sample is cleaned for 1 h at 770 K in 5%  $\text{O}_2$  in Ar, followed by 1 h at 820 K in 2%  $\text{H}_2$  in Ar at a flow rate of  $500\ \text{mL min}^{-1}$  in a flow reactor, and cooled in Ar. This procedure removes about 70% of the contaminants according to X-ray photoemission spectroscopy (XPS) [77].

Sample C was fabricated at the Chalmers University of Technology by Grant and Kasemo and transported to the FHI, where the MB experiments are performed. The sample is further cleaned in the MB UHV apparatus by exposure to  $4 \times 10^{-4}$  mbar  $\text{O}_2$  from a gas doser for 2 h at a sample temperature of 650 K and subsequent oxygen removal by CO exposure. Finally, the cleanliness of the Pd particles is verified by CO titration. For this purpose, the sample is exposed to a MB of  $\text{O}_2$  ( $3 \times 10^{14}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , 30 s) at room temperature, followed by a titration at 440 K with a MB of CO ( $2.9 \times 10^{14}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , 30 s). The amount of  $\text{CO}_2$  produced is compared to the value expected on the basis of the Pd surface area calculated from the structural parameters of the sample and the oxygen saturation coverage [48,83].

The particles fabricated by EBL consist of 450 nm high Pd towers with 500 nm diameter. The particles are arranged in a hexagonal array with 1500 nm particle separation (center to center) covering a  $1\ \text{cm}^2$  area. The morphology of the particles is investigated by scattering electron microscopy (SEM) and atomic force microscopy (AFM) prior and by SEM after the experiments (Figure 2.6) to verify that no major changes occurred, as reported in, e.g., Ref. [78] under more drastic conditions.

A close inspection reveals a ring of small Pd islands surrounding every Pd tower. This effect is likely due to reshaping of the polycrystalline particles toward the Wulff shape in the annealing and cleaning sequences during which the small aggregates may split off the central particle. Similar effects were observed previously for Pt model catalysts prepared by EBL [78,79,84]. From Figure 2.6b, the surface ratio of primary EBL particles to split off particles is estimated about 5. CO oxidation should therefore be dominated by the primary particles under all conditions. In particular, CO oxidation shows a weak structure dependence, so that no enhanced activity of smaller particles is expected. Concerning AR

experiments, small particles only give rise to an additional symmetric contribution to the CO<sub>2</sub> signal (see Chapter 4). It should therefore not critically affect the results discussed in this dissertation.