Chapter-3

Experimental

3.1 Instrumentation setup

3.1.1 UHV analysis system

2 ultra high vacuum (UHV) chambers; TDS (1) and PEEM (2), were used in this study. They are connected by a gate valve and the sample could be transferred between them with the help of a magnetic transfer rod. Fig. (3.1) shows a schematic of mainly the TDS (1) and the load lock (reactor) (3) chambers, which were mainly used in this study. The base pressure was below 10^{-10} mbar. The TDS chamber was equipped with a gas inlet manifold, evaporators for iron and potassium, a sputter gun and fully rotatable manipulators with identical sample heating and cooling stations.

The TDS chamber is used for TDS experiments. A Balzers quadruple mass spectrometer (QMS) is mounted horizontally and the sample could be placed in 1 mm in front of a stainless steel tube with a 5 mm diameter, smaller than the sample diameter of 10 mm. This QMS was also used for the thermal programmed oxidation (TPO) experiments.

The TDS chamber (1) contains also a back-view LEED optics and a cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES) measurements, an Ar^+-sputter gun, and an ion gauge. The LEED and AES are used for pre- and post-reaction characterization of the model catalyst structure and chemical surface composition. The PEEM chamber (2) is equipped with an ion scattering spectroscopy (ISS) spectrometer and a photoelectron emission microscope (PEEM).

The load lock chamber (3) was used for high pressure oxidation and treatments. The single crystal flow reactor is located in the load lock chamber (3), was build by Khurs et. al. [62], who has run the first experiments using this system.

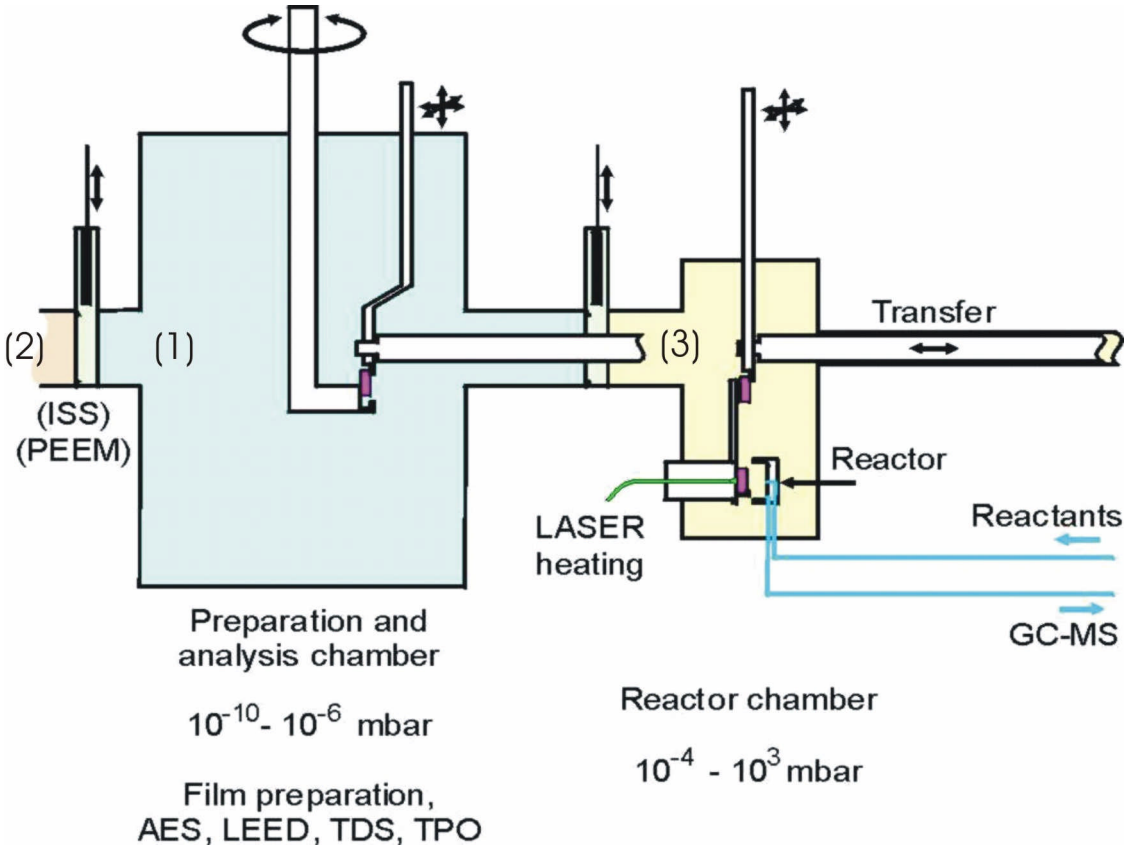


Fig. (3.1). Experimental setup, schematic, consisting of the preparation and analysis chamber (TDS) (1), PEEM (2) working at ultrahigh vacuum and the reactor chamber(3), working at pressures up to 1 bar. The sample on its support (Fig.(3.2)) is moved by a magnetically coupled transfer rod. The transfer between the rod and the manipulator or the reactor is accomplished by wobble sticks.

3.1.2 Sample transfer and heating

Fig. (3.2b) shows a front view photograph of the manipulator head with the sample heating-cooling station and the sample on its support, pushed half-way into the sample quiver [18]. Fig. (3.2a) is a schematic side view in the transfer position with the transfer rod and wobble stick. The magnetic rod is connected to the manipulator by the indicated centering bores which provide mechanical stability during transfer. Using the wobble stick, the sample support can be pulled to the transfer rod, where it is held by spring

clamps, or it can be pushed from the transfer rod into the sample quiver on the manipulator. Afterwards, the wobble stick and the transfer rod are retracted. Due to the mechanical connection between manipulator and transfer rod the transfer is safe and a sample loss is not possible.

a) ***b)***

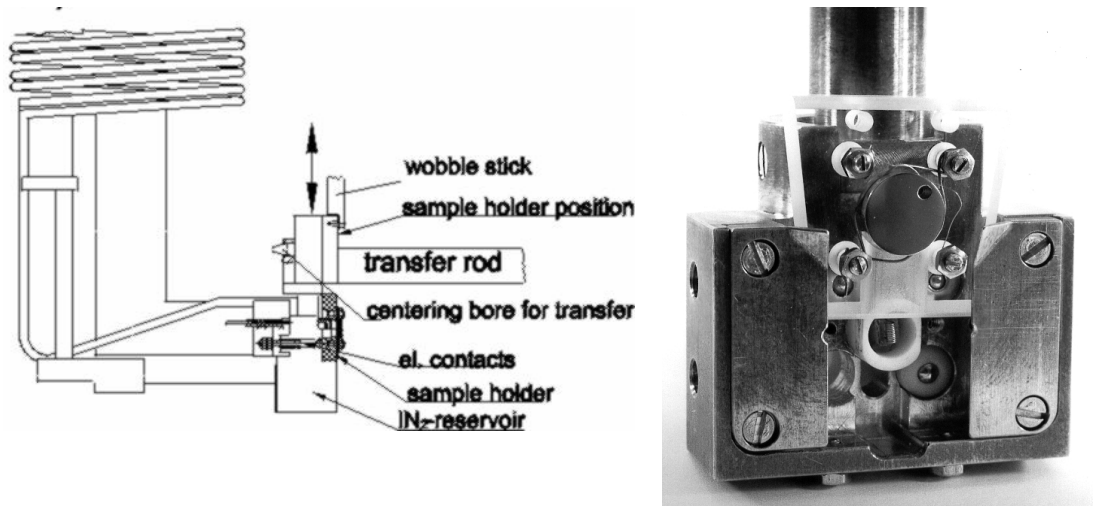


Fig. (3.2): a) Schematic side view of the magnetic transfer rod, the wobble stick, and the heating-cooling station in the transfer position. b) Front view photograph of the sample heating-cooling station on the manipulator.

The sample support is fabricated from a sapphire single crystal. Sapphire was chosen because it has a high thermal conductivity below room temperature allowing fast liquid nitrogen cooling, whereas its thermal conductivity is low at elevated temperatures thus lifting the thermal contact during annealing. Sapphire is mechanically stable and generates no trouble during sample transfer. It is chemically inert, which makes it suitable for prolonged oxidation treatments at elevated pressures and catalytic

experiments in reactive atmospheres. Heating from 100 to 1300 K with 5 K/s does not damage the sapphire sample support if it was annealed at 2100 K before. In the front view photograph (Fig. (3.2b)) of the sample heating-cooling station the sample holder with a mounted platinum sample can be seen. Behind the sample, the sapphire support has a 8 mm diameter hole, so that electron beam heating from behind is possible when the sample holder is placed into its final position on the manipulator. The filament of the electron beam heater is placed within a ceramic tube and can be seen in Fig. (3.2b). Sample temperatures up to 1500 K are reached with this heater. Four holes around the sample are used for screws that provide electrical contact with spring bolts on the manipulator station. Two screws provide electrical contact to a thermocouple spot-welded to the side of the sample. Two screws are used to fix the sample either by Pt clamps or by tungsten wires. The manipulator head contains a liquid nitrogen reservoir made from copper for sample cooling down to 100 K.

3.1.3 High pressure reaction cell

The high pressure cell (a side-view schematic with the reactor inside is shown in Fig. (3.3) consist of a 63 mm diameter double cross which is separated from the main chambers by a 63 mm gate valve. The sample is transferred in the same way from the magnetic rods into the sample stations of the high pressure cell as described in the previous section. The sample station is similar to that on the manipulator but since electron beam heating is not possible at high pressures oxidation and reactivity measurements conditions, a laser heating system with 100 W power (explained in more

detail in Fig. 3.4) is used for oxidation treatments in oxygen pressures up to 1000 mbar [19].

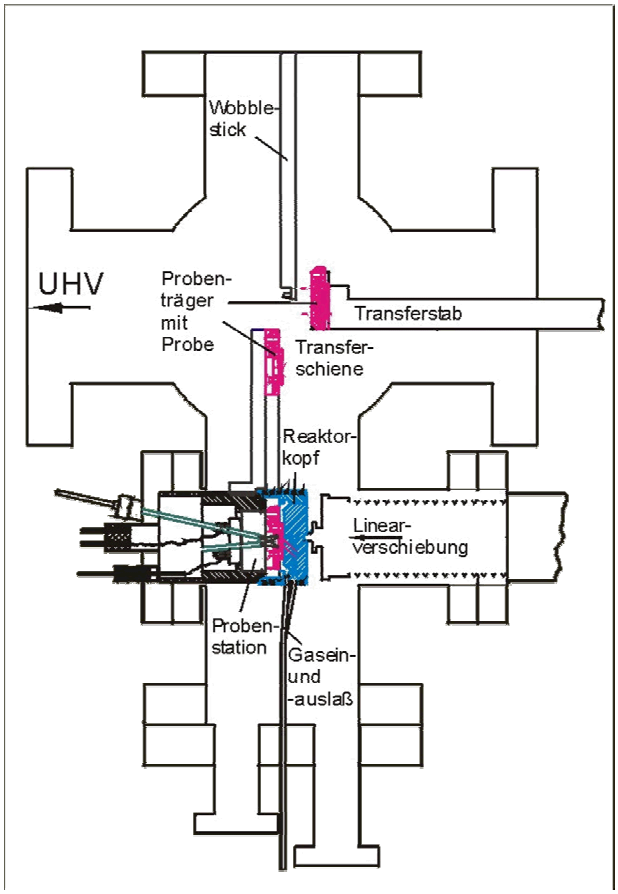


Fig. (3.3). A side view of the high pressure reaction cell with the flow reactor located inside. The sample is transferred from UHV chamber using magnetic transfer line. With the help of wobbelstick the sample is transferred and placed inside the reactor down in the chamber.

3.1.4 The reactor

Fig. (3.3), displays a side view of the high pressure reaction cell with the flow reactor located inside. The reaction cell can be pumped down to 10^{-8} mbar to allow sample transfer from the UHV analysis chamber. From above, a wobble stick allows transferring the sample support from the magnetic transfer rod into the reactor below. For this purpose, the reactor cup has to be opened. It can be closed with a linear motion drive.

The high pressure reaction cell is separated from the UHV chamber by a 64 mm gate valve. After transfer, the reaction cell can be vented with nitrogen or helium.

Fig. (3.4) shows the reactor in more detail. The linear motion drive coming from the right (not shown here) ensures a tight connection of the reactor and the reactor cup with a gold gasket between them. The space between reactor cup and sample support is the reaction volume of the reactor (approximately 4 ml), Since the continuous gas flow prevents back streaming, the effective reactor volume is only that between the sample and cap. The sample itself is only ~1 mm away from the reactor cap with the gas inlet. The gas flow enters this volume through a capillary of 0.2 mm in diameter and spreads onto the center of the sample surface. Gas outlet goes to the sides of the reactor cup. The reactor cap and the gas lines in the reaction cell can be heated resistively to prevent condensation of educts and product molecules. On the left, the feedthroughs for the laser fibers are visible. The outer parts are made of stainless steel. The design of the sample holder was described in detail in 3.1.2 [19].

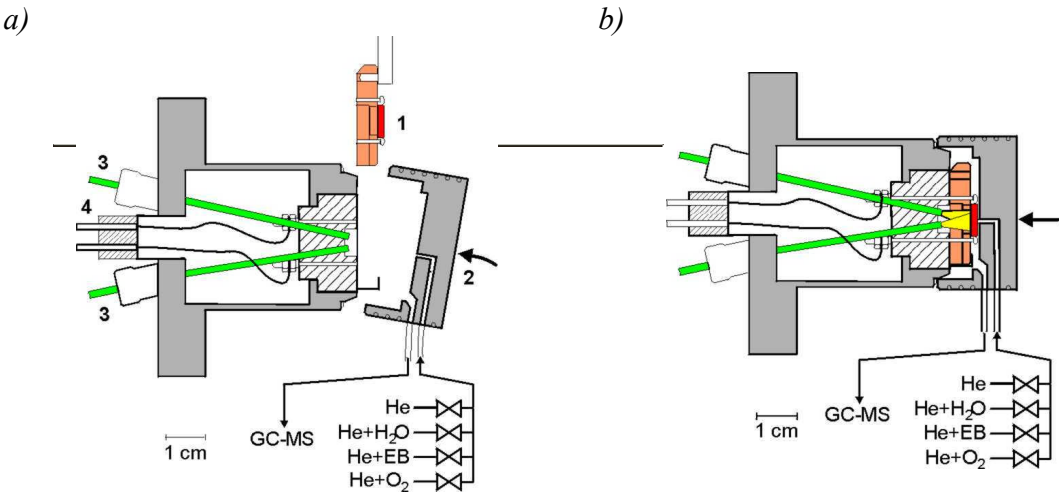


Figure (3.4). Stagnation point micro-flow reactor for model catalysis at high pressure. 1: sample on sapphire support; 2: reactor cap; 3: fibber rods for coupling in laser irradiation; 4: thermocouple feedthroughs. (a) during insertion of the sample on a wobble stick, reactor cap withdrawn. (b) reactor cap closed, gas admission and analysis lines schematically shown.

3.1.5 The laser heating system

Heating of the sample is performed by two high power fiber-coupled diode lasers (JENOPTIK Laser diode GmbH) with a total optical output power of 100 W. In this way, the spot size (4 mm in diameter) is well defined on the back of the sample which guarantees that the sample is the warmest place in the reactor.

The lasers have a wavelength of 809 nm, the operating current for 50 W each is 40 A. A working temperature of 25 °C is achieved by water cooling. An external power supply is used (Delta Electronics). We use fibers of 1000 µm in diameter that are polished at the ends. Using a home made analog PID-controller, defined temperature ramps and hold temperatures are possible.

3.1.6 The gas supply system

Fig. (3.5) shows the gas supply system for the investigation of the St synthesis reaction carried out over iron oxide based catalysts in the presence of steam. All tubes are 1/16 inch in diameter. Helium (5.0) is used as carrier gas. The helium passes a 0.5 µm filter located directly in front of mass flow controllers (Bronkhorst). In order to get a molar ratio of the reaction educts water and ethylbenzene (EB) of 10:1, a flow of 5 ml/min helium passes through liquid ethylbenzene and a flow of 20 ml/min helium through liquid water both held constant at 30 °C. In order to achieve equilibrium, two reservoirs are passed sequentially. Small drops are separated by the empty reservoirs. The additional helium gas line (40 ml/min) as well as the outlet valves allow fast switching between educts gases without changing the total gas flow. In this case, it is possible to

switch off the water and instead introduce 20 ml/min of helium together with the ethylbenzene instead to study the role of the water in this reaction.

The educts then pass a 0.5 µm filter before entering the reactor. A reactor bypass allows detection of the educts before reaction. All valves and filters are Swagelck products. All tubes, valves and filters located behind the ethylbenzene and water reservoirs are heated to prevent condensation.

Analysis is done by a GC/MS system. We use a Varian 3400 gaschromatograph with a VA 5 MS 30 m column (I.D. 0.25 mm, film 0.25µm (5% Phenyl)-methylpolysiloxane) and a 250 µl sample loop. A Finnigan ITD 800 ion trap is connected to this gas chromatograph.

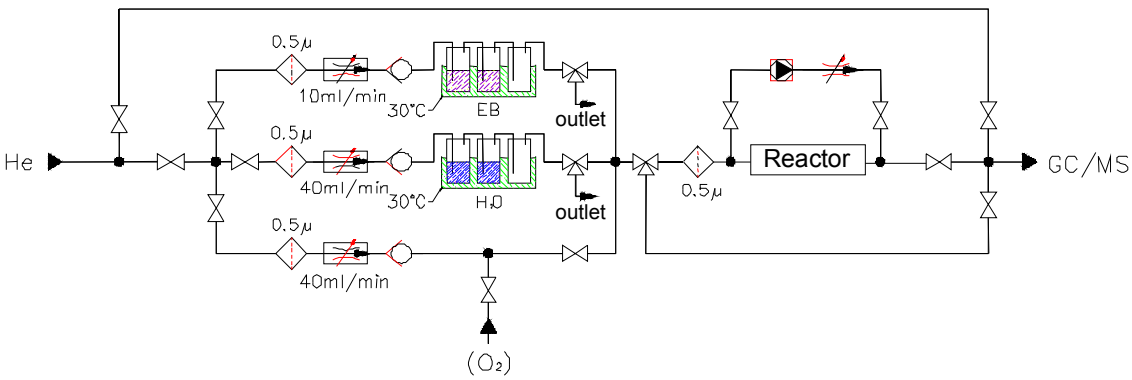


Fig. (3.5). The gas supply system used for the investigation of the styrene synthesis reaction carried out over iron oxide based catalysts in the presence of steam. All tubes are 1/16 inch in diameter. Helium (5.0) is used as carrier gas. The helium passes a 0.5 µm filter located directly in front of mass flow controllers (Bronkhorst).

3.2 Spectroscopic and microscopic characterization methods

3.2.1 LEED, TPO and AES

The LEED measurements were performed using OMICRON optics at *T*=320 K. The diffraction patterns were recorded with a CCD camera from the LEED screen and stored via computer. AES measurements were done using an OMICRON spectrometer with a CMA as detector. The range was chosen from 100-800 eV were the characteristic peaks of K, C, O and Fe appear, the intensity of the peak ratios of O, C, K with respect to the Fe peak (i.e. $\mathbf{I_C/I_{Fe}}$, ..etc.), were used for comparing the thin films compositions before and after reaction. For TPO experiments the heating rate was always 5 K/s, the maximum temperature 1000 K and the O_2 pressure 1×10^{-6}mbar. This has the advantage of partial removal of coke, partial reordering of the surface and no reoxidation of the substrate [79].

3.3 Preparation of epitaxial iron oxide films

Single crystalline iron oxide films were grown epitaxially on Pt(111) substrates. The Pt(111) surface was cleaned by cycles of argon ion bombardment (1 keV), annealing to 1300 K and by oxidation-annealing cycles until it exhibited a sharp LEED pattern and show no contamination signals in AES. The iron oxide films were prepared by iron deposition at room temperature and subsequent oxidation for at least 5 min at temperatures between 870 and 1000 K in 10^{-6} mbar oxygen partial pressure as shown in Fig. (3.6). In this way 1-2 monolayer thick FeO(111) films and 100 200 Å Fe_3O_4(111) multilayer films can be prepared. α-Fe_2O_3(0001) films were obtained by oxidizing Fe_3O_4 films in oxygen pressures between 10^{-4} and 1 mbar in the separate high pressure cell. After this oxidation, the samples were cooled down to room temperature in the high

pressure oxygen atmosphere, then the oxygen was pumped off and the sample was transferred back into the analysis chamber [59].

Promoted iron oxide thin films (KFe_xO_y) are prepared by deposition of potassium from a getter source (SAES) on the Fe_3O_4 (111) or Fe_2O_3(0001) iron oxide thin films at room temperature and subsequent annealing up to 950 K in vacuum or in 1x 10^{-6} mbar oxygen . In some preparations we used repeated deposition-annealing or (deposition-oxidation) cycles in order to get a high potassium coverage. Potassium coverage was monitred by AES. The LEED pattern of the promoted catalyst depends on the amount of potassium content as has been investigated [59,88].

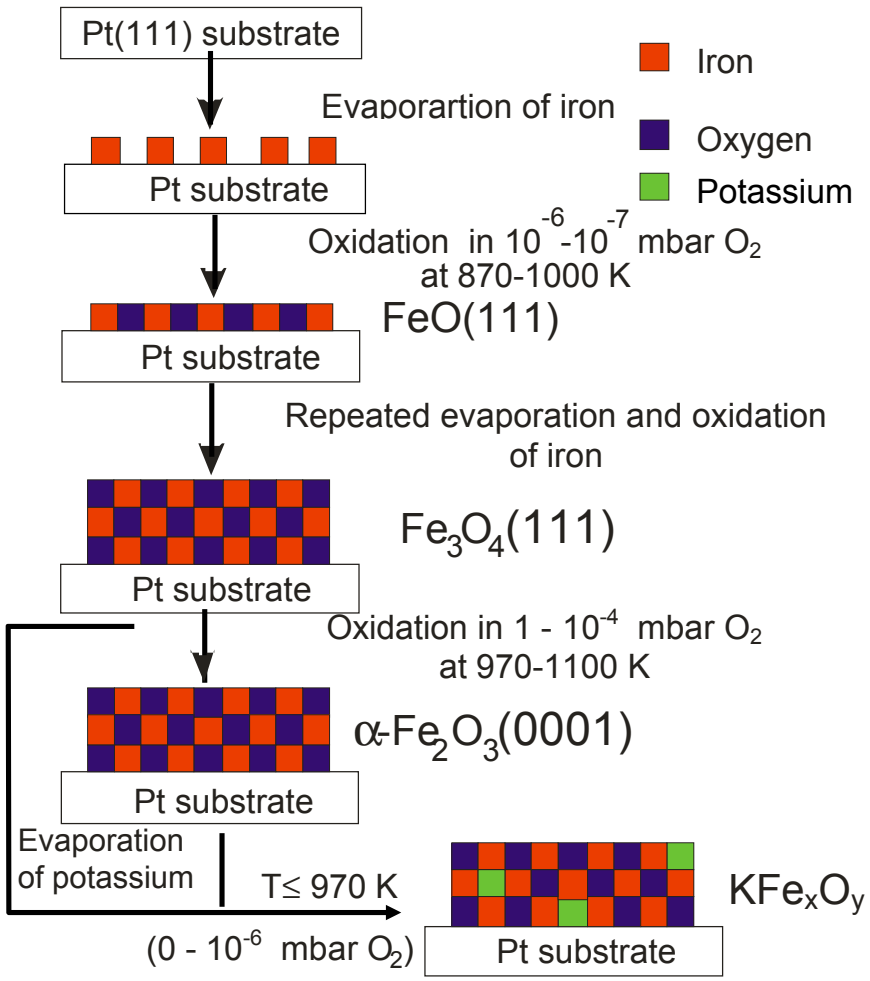


Fig. (3.6). Schematic representation of the preparation of epitaxial iron oxide films Fe_xO_y and KFe_xO_y on Pt(111), accomplished by repeated cycles of iron deposition and subsequent oxidation.

3.4 Pressed Unpromoted Fe_2O_3 powder samples.

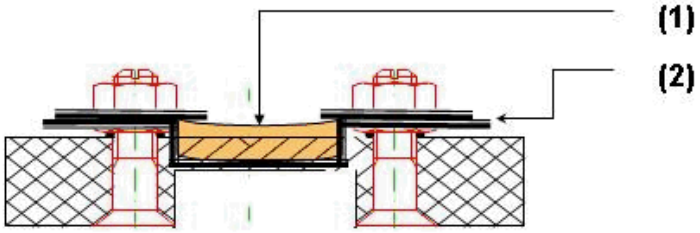
3.4.1 Preparation of the pressed pellets

Polycrystalline catalyst samples with the same outer dimensions as the Pt(111) substrates for the model catalysts, were prepared from ordinary hematite powder, purity > 99% and the alkali metal content below the detection limit. The main idea was to obtain catalyst samples with sufficient mechanical stability and a well ordered geometry while maintaining the high purity of the material. Dry pressed powder pellets were prepared by drying them for 24 hours at ambient conditions, followed by a three step calcination procedure (3 hours at 100^{o}C, then 2 hours at 300^{o}C, and finally 2 hours at either 600, 700 or 800^{o}C). The samples were prepared by A. Schüle from the ICVT institute in technical university of Stuttgart [84].

The pellet weight was about 100 mg. Sample clamps from pure platinum sheets with 0.2 mm in thickness were designed for holding and heating these pressed powder samples on the sapphire sample support. A thermocouple was spot-welded on the platinum sample clams for temperature measurements. A picture of the sample (1) and the sample clamps (2) on the sapphire support is seen in the Fig.(3.7a and b).

The homogeneity of heating these pellets with this designed sample clamps was tested using the reactor head and the laser as a source for heating at air for visual inspection. The sample was heated with the laser from the back and the temperature of the sample was also measured using an external thermometer, the temperatures measured were compared and did not show a considerable difference. Fig(3.7c) shows the sample heated up to 890 K (the temperature distribution was homogenous from the visual inspection as seen in the picture).

a) b)



c)

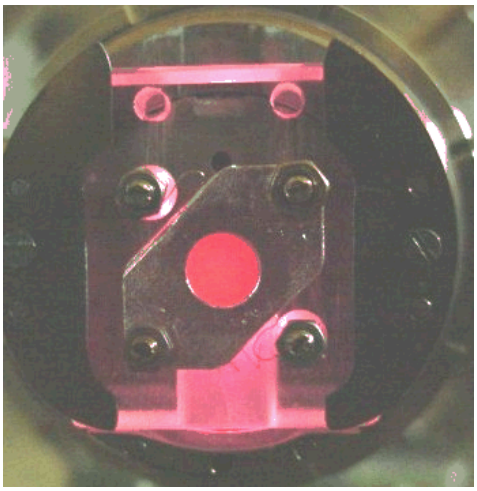


Fig. (3.7). a) The pressed (Fe_2O_3) powder samples in form of pellets. b) A side view of the pressed pellet (1) mounted on a sapphire sample support with the help of Pt clamps (2) designed for this purpose, the thermocouple is mounted on the Pt clamps. c) A heating homogeneity test in air at 890K, for the sample using the laser source.

3.5.2 Characterization of the powder samples (BET, XRD and SEM-EDX)

Since hematite (Fe_2O_3) is known as an insulator, characterization of the pressed sample with surface science techniques like AES was not possible due to charging . Ex-situ characterization methods like X-ray diffraction (XRD) for characterization of the phase of the iron oxide before and after reaction and Scanning electron microscopy (SEM) and Energy-Dispersive X-ray analysis (EDX) were used for determining the

overall morphology, microstructure, composition and particle size of the fresh sample and used ones after reaction. A simple test we have used for testing the reduction of the Fe_2O_3 to Fe_3O_4 is by using a permanent magnet to differentiate between the Fe_3O_4 which is magnetic and Fe_2O_3 which is not.

The surface area of the pressed powder samples (2.8 m^2/g) was measured using a single point BET measurements, Nitrogen was used as the adsorbent gas.

3.5.3 Cleaning of the pressed powder samples.

The pressed powder samples were cleaned in the high pressure cell by heating them up to 1000 K in 1 mbar oxygen pressure for 30 minutes which corresponds to the oxidation treatment of the unpromoted model catalyst. The fresh samples without cleaning, show a very low activity (< 1% conversion) when used in the micro-flow reactor. During the reaction experiments the samples were heated in the presence of only water and oxygen in the feed for a bout 20 minutes before the EB was admitted and the experiment continued. The effect of sample cleaning on the particle size and shape was studied by characterizing the sample after the cleaning procedure with SEM and EDX.

3.4 Reaction experiments

A flow reactor designed for investigating the heterogeneous catalytic reactions on the model catalysts was used which was described in detail (in section 3.1.4). The space between the reactor cup and the sample holder is the dead volume. The gas flows and enters this volume through a capillary and spreads onto the center of the sample surface. Gas outlet goes to the sides of the reactor cup. A laser source was used for heating the

sample from the back, up to reaction temperature. This heating period takes a bout 25 min is crucial, it was optimized to make sure that that changes to the catalyst during this period are minimized.

All the reactions were done under the same standard reaction conditions of a (25 ml/min) total flow rate, atmospheric pressure and 870 K reaction temperature. The feed composition (EB: water : oxygen molar ratios shown inTable 3.1) where varied for performing different reaction experiments. In case of reactions on the Fe_3O_4 no oxygen was introduced in the feed during the heating period, in case of reactions without water 20 ml/min of He alone were introduced to keep the same total flow. In case of promoted catalysts the sample was heated up to the reaction temperature in presence of 20ml/min He alone and then the mixture of EB and H_2O in He was introduced.

Table 3.1. Partial pressures and molar ratios of reactive gases in the gas feed for the used standard reaction conditions. The rest to the working pressure of 1 bar is He. The standard reaction temperature is 870 K, the standard total flow 25 ml min^{-1}.

Reaction conditions	p (mbar)	Molar ratios
Normal	p(EB)=3.3 p(H_2O)=33	EB : H_2O 1 : 10
Reductive	p(EB)=3.3	--
Oxidative	p(EB)=3.3 p(H_2O)=33 p(O_2)=1.7	EB : H_2O : O_2 1 : 10 : 0.5

The standard reaction experiment consists of the following steps:

1. Sample preparation in UHV, pre-reaction characterization by LEED and AES
2. Sample transfer under vacuum into the reactor
3. Preheating the reactor cap to 400 K and out-gassing in vacuum
4. Backfilling the reactor chamber with N_2 (p=1 bar)

5. Sample heating during flow of He, if wanted with admixture of H_2O and/or O_2,
6. After reaching the T_{reac}: H_2O and/or O_2 are stopped (if wanted), EB is admitted, GC-MS is started,
7. Reactivity measurement,
8. Stop of EB, H_2O, O_2,
9. Cooling in He to T<500 K,
10. Evacuation and back-transfer to UHV,
11. Post-reaction characterization by AES, LEED; if necessary removal of coke by TPO cycle(s), followed by AES and LEED [82,83].

The primarily measured quantities are GC peak areas. Under typical reaction conditions, the sum of the peak areas of all aromatics (EB, St and traces of toluene, benzene) is ~95% of the EB peak area without reaction (e.g. at low temperature). The missing ~5% go thus into products which we cannot detect like C_xH_y, CO, CO_2, H_2. The highest observed conversions were ~10% so that the EB peak area corresponds in all cases to more than about 85% of the admitted EB. In view of the uncertainties of the EB-flux and the sample area which enter the determination of an absolute rate, we neglect the missing 15% and refer the conversion yield *y* in % to the main EB peak area as measured. The conversion rates presented below are then calculated from the yield according to

$$r\ (\mathrm{cm^{-2}\ s^{-1}}) = [F \times y(\%) \times 10^2] / A = 6.54 \times 10^{14}\, y(\%),$$

with the EB-flux $F = 3.27 \times 10^{16}$ molecules s^{-1} and the model catalyst area A=0.5 cm^2. Rates are always given in St molecules cm^{-2} s^{-1}.