



Single Crystal Flow Reactor for Studying Reactivities on Metal Oxide Model Catalysts at Atmospheric Pressure to Bridge the Pressure Gap to the Adsorption Properties determined under UHV Conditions

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Abstract

A flow reactor for the investigation of heterogeneous catalytic reactions on single crystalline metal oxide model catalysts has been designed. It is located in a high pressure cell attached to an UHV analysis chamber where the model catalysts can be prepared and characterized by surface science techniques. It can also be run in a batch modus. After sample transfer the high pressure cell can be completely separated from the UHV chamber and it can be used for oxidation treatments and reaction studies at gas pressures up to 1 bar. A new heating system provides direct heating of the sample by laser light up to 1200 K. Product analysis is done by gas chromatography coupled with mass spectrometry, which allows detection in the ppb range. The single crystal flow reactor provides new insight into the atomic scale surface chemistry of metal oxides under real catalysis conditions and bridges the pressure gap for model systems prepared and characterized under UHV conditions. Results on the dehydrogenation of ethylbenzene to styrene over epitaxial potassium-iron oxide films are presented and correlated to thermal desorption measurements on the same films under UHV conditions.

Keywords: single crystal flow reactor, atomic scale surface chemistry, pressure gap, metal oxides, laser heating

1. Introduction

Many important heterogeneous catalytic reactions are performed over metal oxide based catalysts. However, little is known about the reaction mechanisms on an atomic scale. In a first step structure reactivity correlations and the elementary step kinetics are investigated with surface science techniques using single crystalline metal oxide model systems with defined surface structures and compositions[1,2]. In the second step catalytic reactions have to be performed on these model catalysts under conditions similar to the technical catalytic reactions. The adsorption kinetics of reaction educts and products determined in UHV adsorption studies on ordered surfaces that are catalytically active allows to predict the reaction kinetics also under high pressures. Comparison with the experimentally observed kinetics reveals whether the surface chemical properties have changed across the pressure gap. Together with pre- and post reaction UHV surface analysis insight into the atomic scale chemistry on active metal oxide surfaces can be obtained.

Somorjai and coworkers [3,4] started to combine high pressure catalytic reaction studies with UHV surface analytical techniques in the seventies followed by Goodman et al. [5]. The experimental setups consisted of an UHV surface analysis system equipped with a sample isolation cell in it for catalytic studies at high pressures. The high pressure isolation cell was a stainless steel cylinder with a small cavity sealed by a copper gasket. To provide a totally leak-free seal, a pressure of approximately 2000 psi was needed. This was achieved by a small hydraulic press situated on top of the apparatus. The isolation cell and external gas circulation route were operated as a small volume (~100 ml) stirred batch reactor. Goodman's apparatus consisted of two ultrahigh vacuum chambers. One chamber was the UHV

analysis and surface preparation chamber whereas the second chamber was a stirred catalytic reactor of an estimated volume of 500 ml. This reactor could be evacuated from high pressure within a 5-min period.

The theoretical prediction of reaction kinetics at high pressures with the help of kinetic parameters obtained from low pressure UHV single crystal studies was demonstrated by the groups of Ertl [6] and Norskov [7] for iron ammonia synthesis catalysts.

So far, only few attempts to apply this concept to single crystalline metal oxide catalysts have been made. Especially the design of a single crystal flow reactor for reaction studies of ordered metal oxide model catalysts is a new challenge. Bender et al.

[8] recently presented a system for studying heterogeneously catalyzed gas phase reactions on single crystal metal oxide surfaces. The reaction system consisted of a microreactor for single crystal samples mounted into a reactor host. Single crystal microreactor and reactor host were assembled on an UHV chamber. By a magnetic transfer rod, a sample holder could be transferred from the analytical part of the chamber onto a linear motion drive suitable for transferring the sample holder into the reactor host. The true reaction volume was 10-50 μ l. However, no precise thermocouple temperature control was possible with this design.

In this work, a new single crystal flow reactor is introduced. Its performance is tested using the dehydrogenation reaction of ethylbenzene to styrene performed over iron oxide based model catalysts. The reactor is located in a high pressure reaction cell attached to an UHV analysis chamber. It is adapted to a sample transfer mechanism that uses sample holders fabricated of sapphire and equipped with thermocouple contacts. This allows to combine thermal desorption measurements in UHV with high pressure reactivity studies. A new heating system provides direct heating of the sample by laser light. The flow reactor can also be run in a batch modus.

2. Instrumentation

2.1 The reactor

Fig. 1a 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. The transfer of the sample from the UHV system (left side) to this reaction cell is performed with a magnetic transfer rod coming from the right. From above, a wobble stick allows to transfer the sample holder 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. The UHV chamber is equipped with facilities for sample preparation, LEED optics with video camera and digital image processing, a quadrupole mass spectrometer with computer control for the detection of thermally desorbing species, an Ar^+ -sputter gun, ion gauge and gas inlet system. For details, see ref. [9].

Fig. 1b 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 holder is the reaction volume (approximately 4 ml). The sample itself is only 0.5 mm away from the reactor cup 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 cup and the gas lines in the reaction cell can be heated resistively to prevent condensation of educt and product molecules. On the left, the feedthroughs for the laser fibers are visible.

A photograph of the whole single crystal flow reactor is shown in Fig. 2. The reactor cup is seen very clearly on the right. From above, the sample can be introduced. In this picture, the sample can be seen at the top of the transfer sledge through which it is moved by the wobble stick. On the left, the feedthroughs for the laser fibers and for the thermocouple are visible. On the sample holder, the thermocouple is spot-welded onto the edge of a Pt(111) single crystal that we use as a substrate for the preparation of epitaxially grown iron oxide model catalyst films.

Fig. 3 shows the reactor without the reactor cup. The sample is illuminated by laser heating from the back.

The reactor cup with gas in- and outlet is mounted onto a CF 64 flange. The reactor with the sample station and the laser and thermocouple feedthroughs is mounted onto a CF 35 flange. The latter is screwed into the sledge of the sample station. As has already been mentioned, a linear motion drive ensures a tight connection of both with a gold gasket between them.

All parts are made of stainless steel. The design of the sample holder is described in detail elsewhere [9].

2.2 The laser heating system

Heating of the sample is performed by two high power fiber-coupled diode lasers (JENOPTIK Laserdiode 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 $^{\circ}$ C is achieved by water cooling. An external power supply is used (Delta Electronics). We use fibers of 1000 μ m in diameter that are polished at the ends.

Fig. 4 shows the sample temperature versus time for full power heating with both lasers at atmospheric pressure without reactor cup. The maximum temperature of the sample is slightly above 1200 K. Up to about 1000 K, the laser heating is very fast.

Using a home made analog PID-controller, defined temperature ramps and hold temperatures are possible so that this new heating system can also be applied for TDS measurements.

2.3 The gas supply system

Fig. 5 shows the gas supply system 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). In order to get a molar ratio of the reaction educts water and ethylbenzene (EB) of 10:1, a flow of 10 ml/min helium passes through liquid ethylbenzene and a flow of 40 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 educt gases without changing the total gas flow. In this case, it is possible to switch off the water and to introduce 40 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. With help of a small membrane pump reduced in pumping speed by a double needle valve the reactor can also be run in a batch modus. All valves and filters are Swagelok products. The membrane pump is from KNF Neuberger GmbH. It has a pumping speed of 5.5 l/min and can be reduced to zero by double needle valves. The head of the pump can be heated to 200 °C in order to prevent condensation of the gases. 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 0.25 μm (5% Phenyl)methylpolysiloxane) and a 250 μl sample loop. A Finnigan ITD 800 ion trap is connected to this gaschromatograph.

3 Results

3.2 TDS measurements

In the upper part of Fig. 6 TD spectra for increasing amounts of EB adsorbed onto the potassium doped iron oxide model catalyst film $\text{KFe}_x\text{O}_y(111)$ prepared as described elsewhere [10] are shown. At low exposures a desorption signal labeled γ with a maximum at about 265 K appears. With increasing exposure it shifts slightly to lower temperatures (260 K) until it saturates at about 1 L. We attribute this signal to desorption of chemisorbed EB species. Then a physisorption signal β appears at 230 K, which shifts to 206 K with increasing exposure. Finally, the condensed EB multilayer signal α evolves at 155 K. The ST spectra shown below look very similar to those of EB. There is no difference in the desorption temperatures and saturation coverages of the chemisorbed γ signals of EB and ST. The physisorbed ST species β start to desorb at 238 K, about 20 K higher than the physisorbed EB β signal, followed by the desorption of condensed ST multilayers α . An exposure of 1 L of EB or ST at a gas temperature of 300 K corresponds to 1.96×10^{14} molecules cm^{-2} impinging onto the surface. The van-der-Waals area of EB and ST molecules lying flat on the surface is approximately 50 \AA^2 , so that 1 ML defined as a densely packed layer corresponds to $N = 2 \times 10^{14}$ molecules cm^{-2} . Condensation occurs at 150 K for these molecules and we assume a sticking probability near unity for the adsorption temperature of 100 K. This can be used to calibrate desorption intensities into coverages. We find that the saturation exposure of 1L for the chemisorbed species corresponds to about 1 ML (2×10^{14} molecules cm^{-2}). The chemisorption sites for EB and ST thus do not represent a minority species like defect sites. With the Langmuir isotherm we can extrapolate the relative EB and ST surface coverages to the technical styrene synthesis reaction conditions, for details see ref. [10]. It turns out that under reaction conditions the occupation of the physisorbed β states (and the condensed α states) is less than 1% whereas the occupation of the chemisorbed γ species is much higher (around 20%). Therefore, we consider the chemisorbed species alone to be important under reaction conditions.

3.2 Reactor experiments

A reactor experiment with the new single crystal flow reactor is presented in Fig. 7. An ordered $\text{KFe}_x\text{O}_y(111)$ as investigated with TDS was prepared in the UHV system and transferred into the reactor. With a total He pressure of 1 bar and assuming saturation of the helium carrier gas flows with ethylbenzene and water, 6.7×10^{-6} mol/min of EB and 6.7×10^{-5} mol/min of water enter into the reactor. With a reactor volume of about 4 ml and a total gas flow of 50 ml/min a residence time of about 5 s can be estimated. Gas leaving the reactor is injected into the GC-column every three minutes via sample loop. The reaction temperature was 873 K. First, only the ethylbenzene peak and no detectable styrene production was observed. But after an activation period of two hours under reaction conditions styrene could be detected as shown in the upper part of Fig. 7. Styrene production could then be observed in many other reaction experiments performed with the same sample. From each point of a gaschromatogram, a MS can be obtained. In the lower part of Fig. 7, a MS from one of the small peaks indicated with an arrow is shown. The mass 104 clearly shows that this second small peak is styrene. An average styrene yield of 3.5% with respect to the amount of ethylbenzene introduced was determined.

4. Discussion

A single crystal flow reactor for studying reactions on model catalyst samples with a surface area of only 1 cm^2 was build and successfully operated for the ethylbenzene dehydrogenation on a potassium promoted iron oxide film with

single crystal quality even though the yields are very small. In comparison to rates of the technical reaction, the rate observed on the KFe_xO_y film here is about one order of magnitude higher. This is probably due to the fact that in our experiment the flow of educt molecules per catalyst surface area is 10^4 times higher if compared to technical reactors. There are 2×10^{14} molecules per cm^2 chemisorbed on the film under investigation as determined by TDS. This number is supposed to be equal to the number of active site density as these chemisorbed sites can potentially be occupied under reaction conditions and an interaction of a certain strength of educt to substrate is necessary for dehydrogenation. As we have a surface area of about 1 cm^2 , 2×10^{14} active sites can be assumed. This enables us to calculate the turn over frequency (TOF) to be 12 s^{-1} .

5. Summary and Outlook

A new single crystal flow reactor has been designed. It allows reaction studies on iron oxide based single crystal model catalyst samples with a surface area of only 1 cm^2 .

The reactor is located in a high pressure reaction cell that is attached to an UHV analysis chamber where the model catalysts are prepared and characterized. The reaction cell is completely separated from the UHV chamber and can be used for oxidation treatments and reaction studies at a total pressure up to 1 bar. Heating of the sample is performed by a new laser heating system which minimises heating of other parts of the assembly.

First experiments show that the small styrene yields to be expected on our model systems can be detected by GC/MS for a potassium promoted iron oxide based model catalyst film. Together with TDS measurements performed under UHV conditions, the turn over frequency for this reaction could be determined. This reactor can bridge the pressure gap for the model systems prepared and characterized under UHV conditions. Comparative studies with iron oxide films of different stoichiometries in single crystal quality are underway in order to compare differences in TDS performed under UHV conditions on the various films to differences in reactivity performed at atmospheric pressure in the single crystal flow reactor on the same films.

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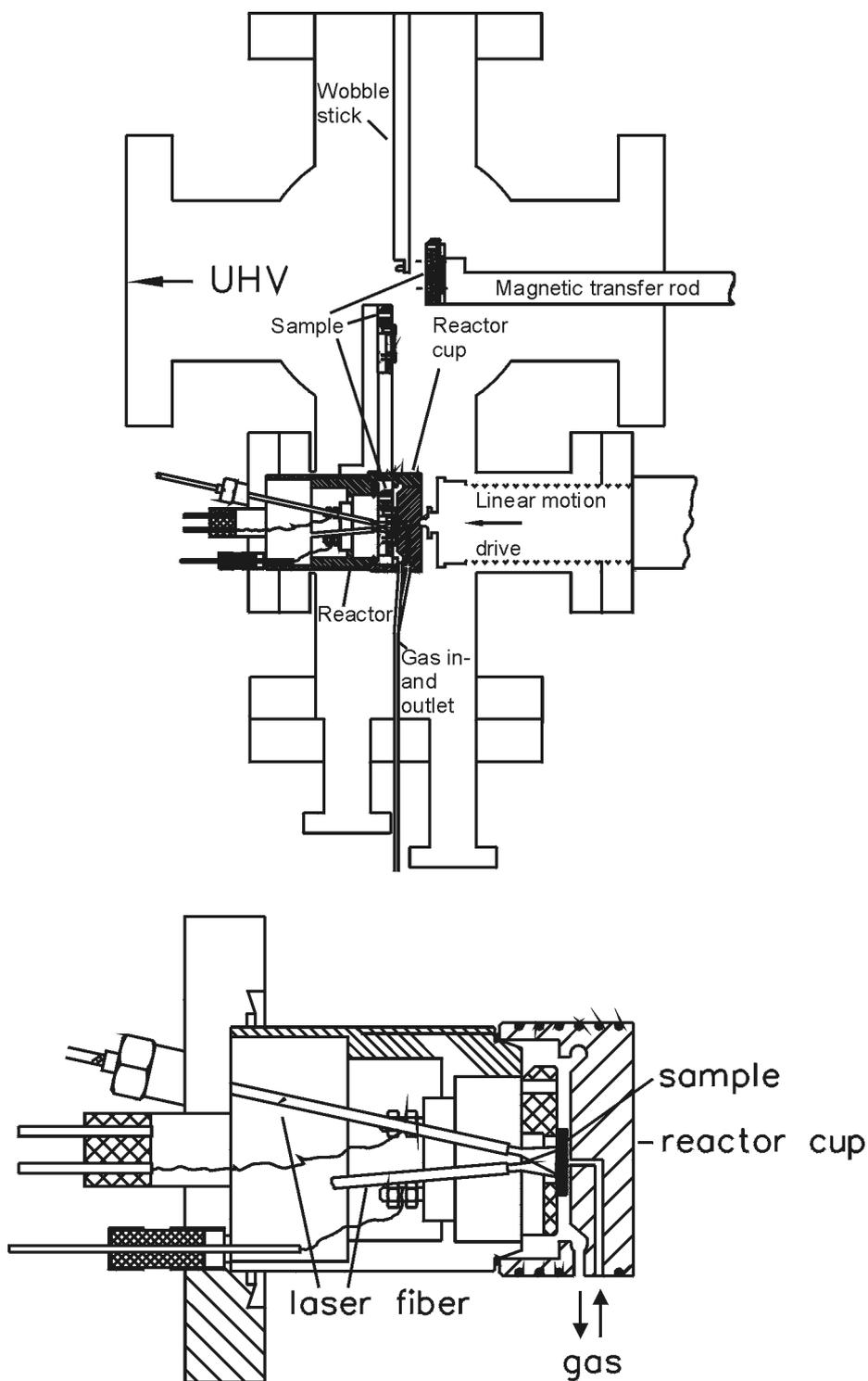


Fig. 1: a) Side view of the high pressure reaction cell with the single crystal flow reactor mounted. A wobble stick allows to transfer the sample from the magnetic transfer rod into the reactor below. b) Single crystal flow reactor. A linear motion drive from the right (not shown here) ensures a tight connection between the reactor and the reactor cup using a gold gasket. The gas flow enters the reaction volume through a capillary and spreads over the surface. On the left, the feedthroughs for the laser fibers are visible.

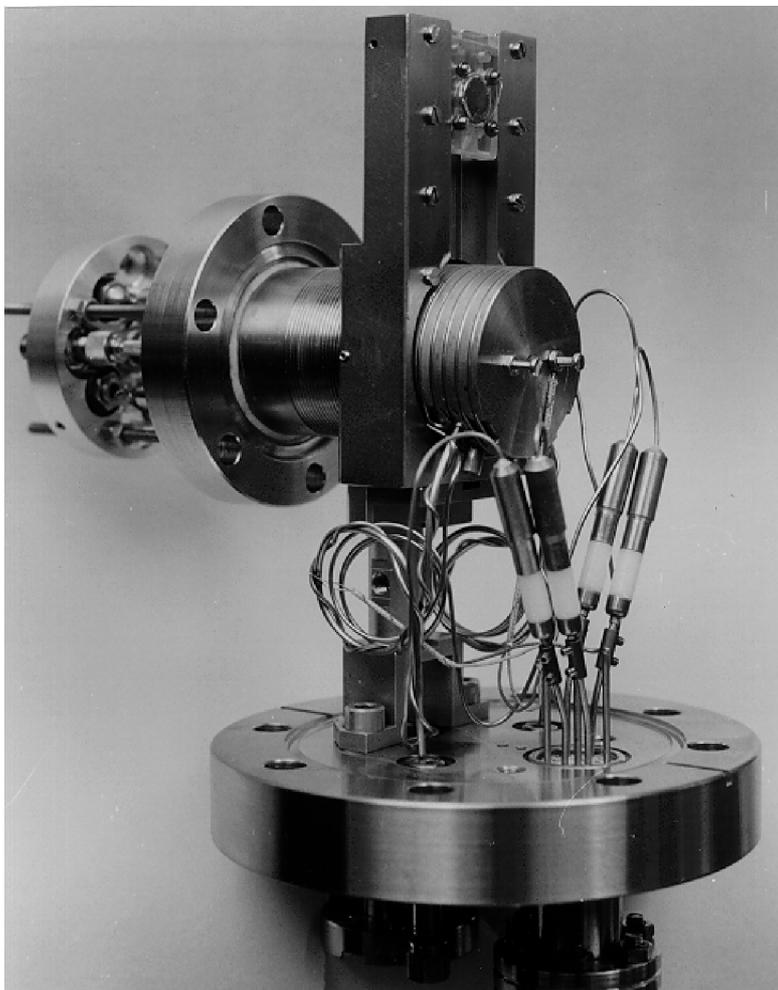


Fig. 2: Photograph of the single crystal flow reactor. On the right, the reactor cup can be seen. From above, the sample can be introduced. The feedthroughs for the laser fibers as well as for the thermocouple are visible on the left.

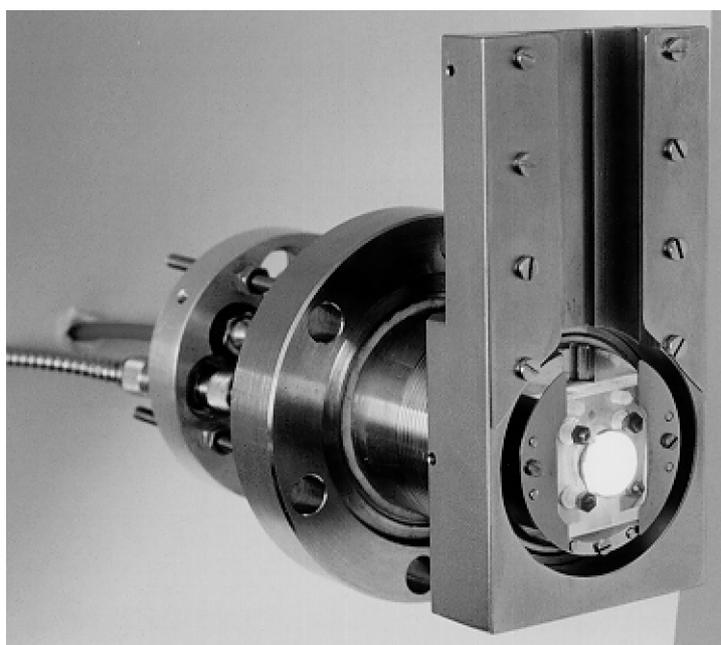


Fig. 3: Reactor without reactor cup. The sample is glowing by laser heating from the back.

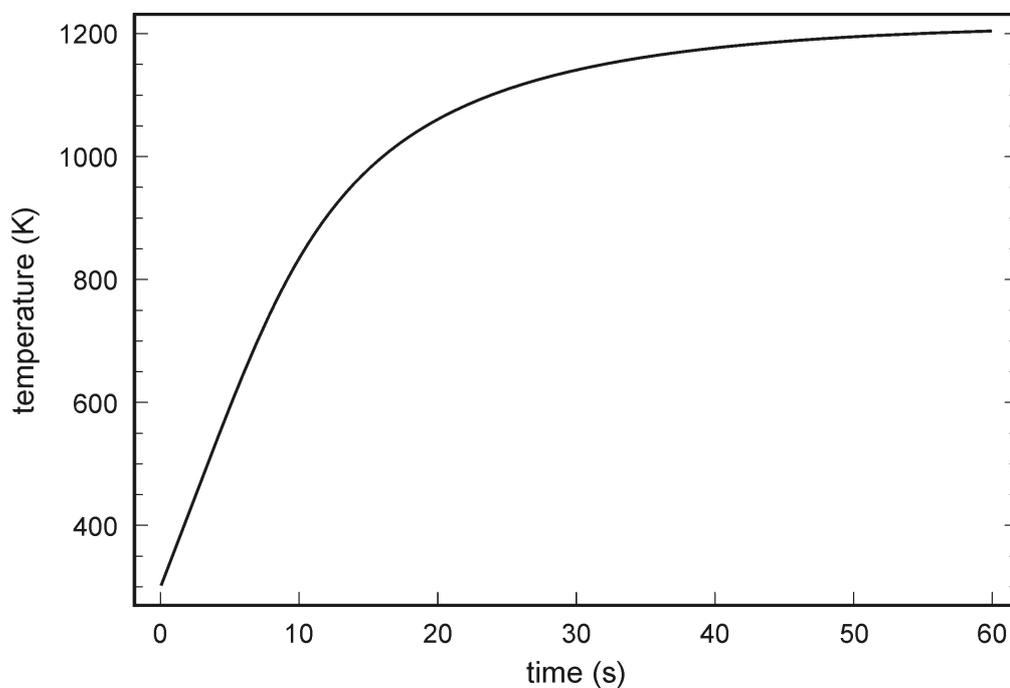


Fig. 4: Sample temperature versus time for full power heating with two lasers. The maximum temperature of the sample is slightly above 1200 K.

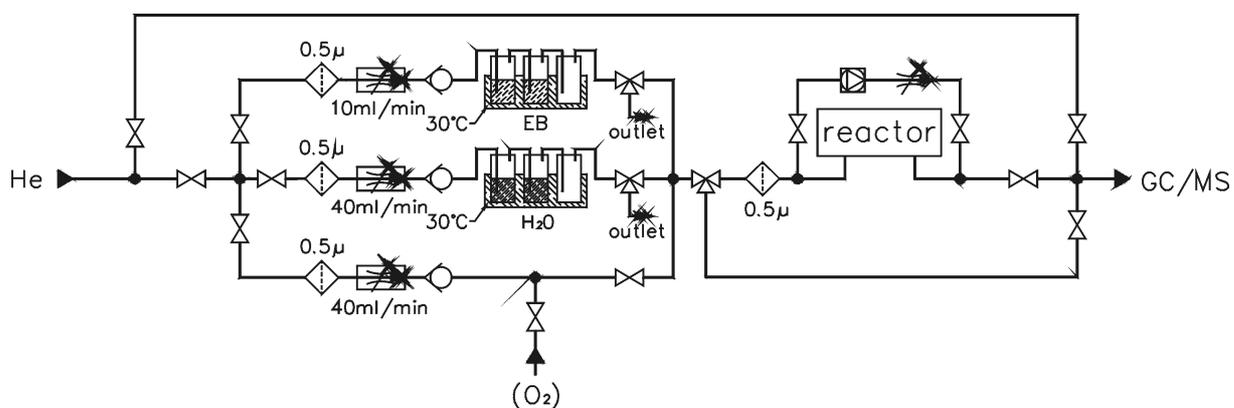


Fig. 5: Gas supply system for the single crystal flow reactor. All tubes are 1/16 inch in diameter. Helium 5.0 is the carrier gas.

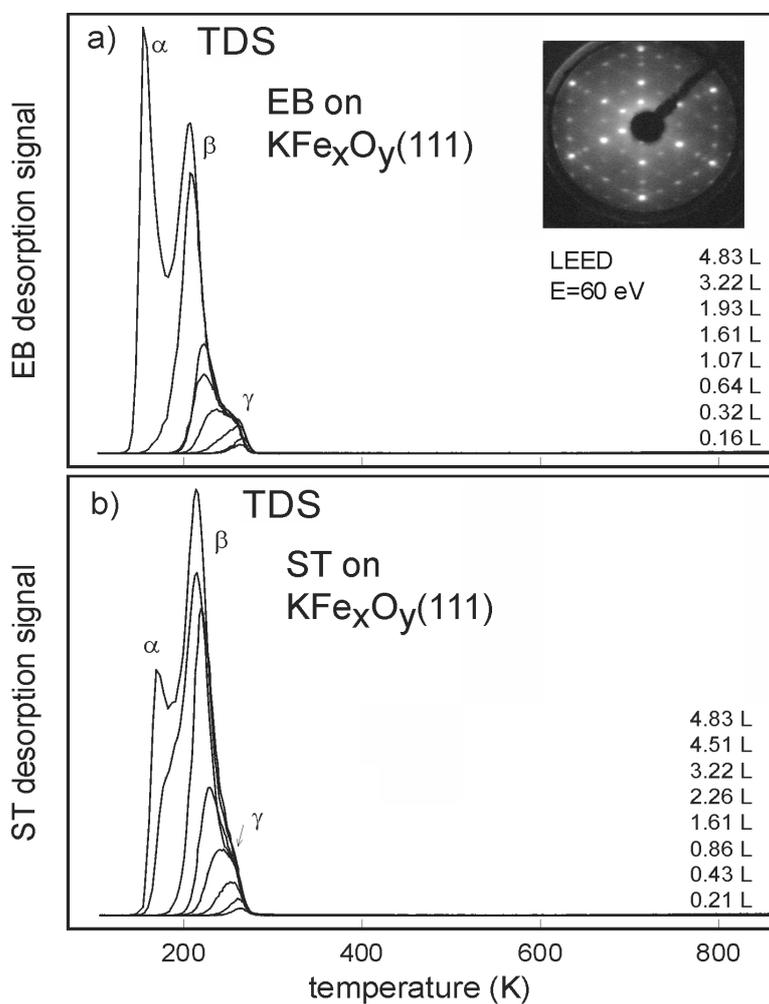


Fig.6: Thermal desorption traces of ethylbenzene (a) and styrene (b) adsorbed onto the $\text{KFe}_x\text{O}_y(111)$ surface. The exposures are indicated in Langmuir units. The insert in (a) shows the LEED pattern of the clean surface.

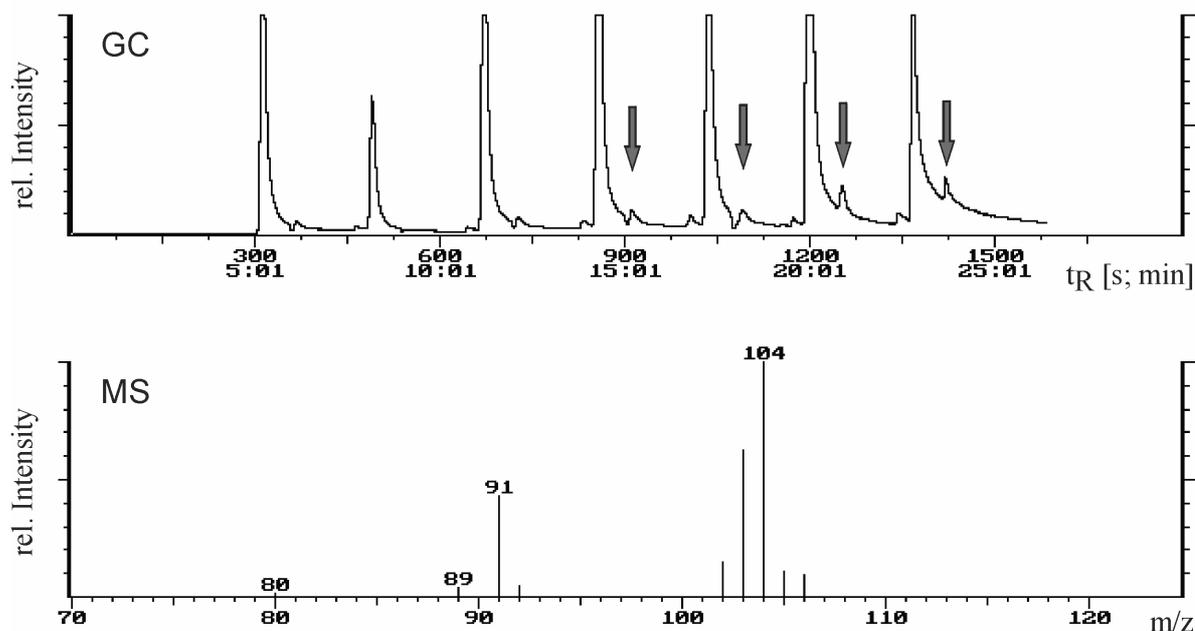


Fig. 7: Reactor experiment over an ordered potassium promoted epitaxial iron oxide film. The gas leaving the reactor is injected into the column every three minutes via sample loop. Initially, only the ethylbenzene peak and no detectable styrene production was observed. After an activation period of two hours under reaction conditions, styrene could be detected. Styrene production could be observed in many other experiments performed with the same sample after the activation procedure. In the lower part of Fig. 7, a MS from one of the small peaks indicated with an arrow is shown. The mass 104 shows that this second small peak really is styrene.