zone is speeded up or slowed down, broken into a crescent or spiral parts, etc [4,5].

Figure 5 shows formation of two new reaction zones (by so called wave splitting) from that part of the circular reaction zone that is exposed to the highest negative $\mathbf{E}_{ef}$ ($\alpha \simeq 0$). Comparisons of the shape of the reaction zone with the superimposed dark circles in the first and the last snapshots illustrate changes of the velocity of the reaction zone propagation when an electric field is switched on.

Figure 6 illustrates changes of the reaction mechanism within the reaction zone when an electric field is applied. Circular reaction zone propagating in zero electric field contains intermediate product iodine (dark colour) and converts solution into iodide (white colour behind the dark circle). When an electric field is switched on the migration of ions causes the local changes of the reactant concentrations within the reaction zone. The reaction proceeds with different mechanism and iodine is produced. Dark zone is thus enlarging until the field is switched off again. The production of iodide is then recovered and the growing white zone with iodide separates the propagating reaction zone and the broad, stationary dark zone of iodine.

4. Conclusions

Most of the above described features of electric field effects on the propagating reaction zones in effectively 1D or 2D microreactors can be described by appropriately chosen mathematical models which, depending on the ionic strength of the solution consider or disregard the effects of spatial distribution of charge which can arise due to nonhomogeneous spatial profiles of ionic species in the correspoding reaction-diffusion- migration systems [4-6].

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High-Temperature Micro Catalysis: a New Design for Comparative Reaction Studies in Technical and Model Systems

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We present a system for studying heterogeneously catalytized gas phase reactions on single-crystal surfaces. As a model reaction we studied the high-temperature dehydrogenation of methanol to formaldehyde and furtheron to CO. A new flow microreactor was developed in which a radial gas flow is run over the surface of a single-crystal sample. Residence times can be kept as short as 10^{-3} s opening up the same time scale as in the technical flow reactor.

The apparatus utilizes gas chromatography for gas phase analysis during the reaction. A valve system provides for measurements of residence time distributions and reaction kinetics in technical as well as the new single-crystal flow microreactor. In particular, time-on-stream and formation analysis of the catalyst load is possible. This is of special importance for the combination of the catalytic reaction experiment with the surface scientific *post-mortem* characterization of the sample surface.

Chemical analysis and structural characterization of the sample surface can be carried out by surface scientific tools as there are x-ray induced photoelectron and Auger-electron spectroscopy (XPS/XAES) and low-energy electron diffraction (LEED), respectively. In analogy to the technical catalyst we have prepared thin aluminum oxide films on a nickel-aluminum alloy single-crystal surface. Doping this oxide film with sodium was provided by *in-vacuo* evaporation from an SAES getter source. This system was used as a model system to study the methanol dehydrogenation reaction in the new single-crystal microreactor. The results are compared to those obtained in technical microreactors.

1 Experimental details:

The new modular reaction system consists of a *microreactor* for single-crystal samples mounted into a *reactor host* as part of a rapid sample entry and a *gasflow system for reaction control and product analysis*. Single-crystal microreactor and reactor host are assembled on an ultra-high vacuum chamber which is equipped with facilities for x-ray induced photo- and Auger-electron spectroscopy (XPS/XAES), low-energy electron diffraction (LEED), ion surface scattering (ISS) as well as a quadrupol mass-spectrometer for the detection of thermally desorbing species. By a magnetic transfer rod, a sample holder can be transferred from the analytic part of the chamber onto a linear motion drive suitable for transfering the sample holder into the reactor host. On the linear motion drive, connection of a filament, a thermocouple and a sample ground is provided between sample holder and vacuum feedthroughs. On the sample holder the thermocouple is spot-welded onto the edge of a stainless steel basis plate. The basis plate is screwed onto a ceramic cylinder (Lava Grade A™) which in turn is mounted onto the commercially available sample holder base (Leybold, type PTM/KH 1000). Inside of the ceramic cylinder a tungsten filament is mounted for electron bombardement of the basis plate. On top of the basis plate the single-crystal sample is spot-welded onto four tantalum rods (1mm o.d.) in the centre of a knife edge.

Figure 1a shows the sample holder in the reaction position inside the reactor host. The basis plate is pushed against a stainless steel fixing plate which is mounted inside the bottom of the host. Sealing of the reactor volume against UHV is provided by two knife edges on the basis plate and the fixing plate, respectively. Between them, a CF16 copper gasket serves for sealing during several reaction runs. This requires reproduction of the sample holder position. Together with reproduction of the sample position in the reaction cell, this is achieved by three pins on the fixing plate driving into corresponding holes in the basis plate during sample transfer.

The fixing plate is screwed together with a ceramic distance ring (Macor™) onto the bottom wall of the reactor host. Sealing at the interfaces between fixing plate, distance ring and host wall, respectively, is provided by two gold wire gaskets (o.d. 0.5mm). Ceramic washers (Macor™) and rings (corundum) provide electrical isolation of the fixing plate from the grounded screws enableing electron bombardement heating of the basis plate in reaction position.

The reaction cell itself consists of two quartz glass pots which are mounted into eachother. (Fig. 1b). During the reaction run the single crystal is positioned into a hole of appropriate size and shape in the centre of the bottom of the outer pot, closing the hole mostly. The gap space between the bottoms of the two glass pots then is the true reaction volume (10-50µl). The gas flow enters this volume through a capillary in the axis of the inner pot. It spreads over the surface and flows into the cooling volume between the cylinder mantles. The outer pot has a tempering jacket to provide cooling to 130°C avoiding product condensation. From the cooling volume the gas flow exits the reactor via a stainless steel capillary (1/16").

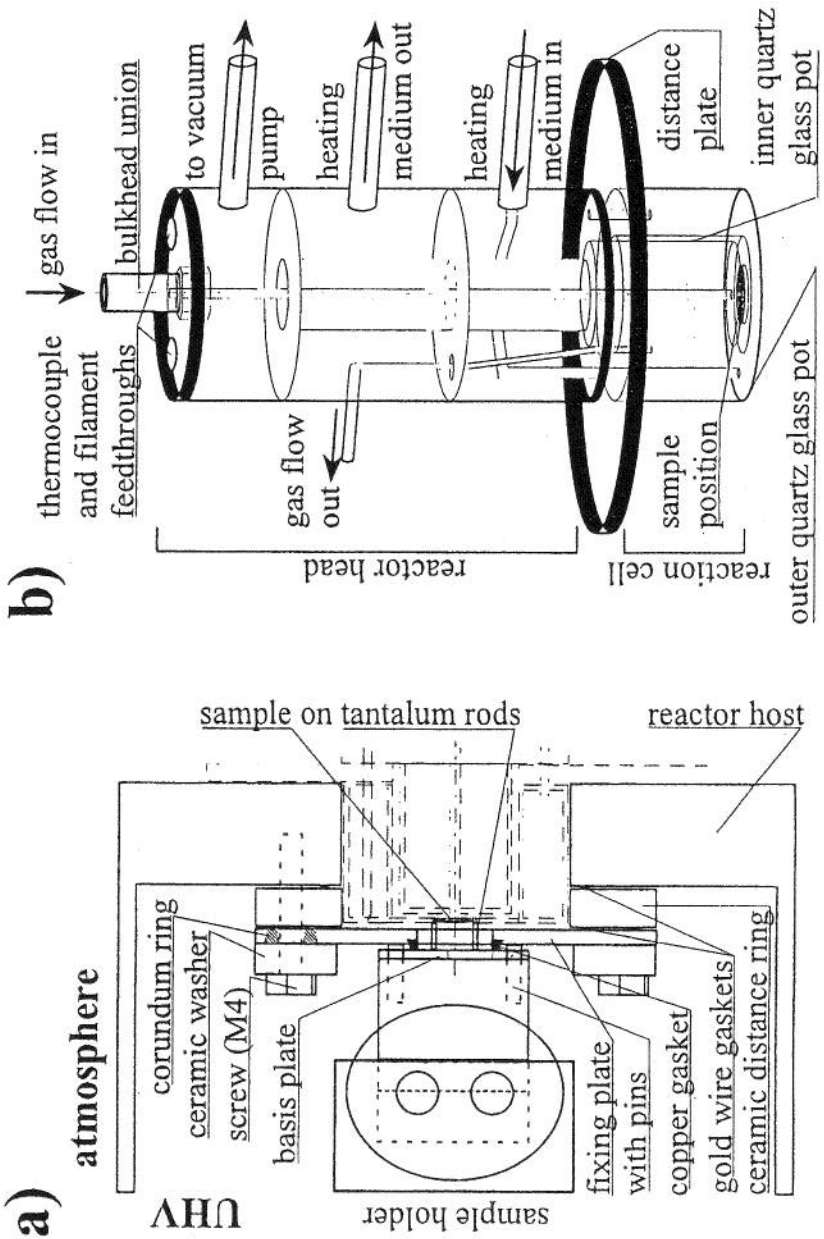

Figure 1: Modular construction of the single-crystal microreactor:
a) Sample holder in reaction position inside the reactor host. Doted lines indicate hidden parts, dashed lines suggest the position of the reaction cell in the wall of the reactor host.
b) Reactor consisting of reaction cell and reactor head, respectively. Inside the reactor head, a filament is wrapped around the central quartz glass capillary over 38 mm length. A Ni/NiCr-thermocouple is attached inside the bottom of the inner glass pot.

The gas flow system for reaction control and product analysis consists of standard gas chromatographic sampling valves (VALCO). A reaction inert gas flow is handled separately from the carrier gas flow to decouple reaction and analysis space velocity conditions. Figure 2 shows a schematic of the gas flow system. The inert reaction gas flow is loaded with the vapour pressure of volatile reactands in a bubble column. Two sample loops are used as starting and destination points of a transient pulse-flow experiment through the microreactor. The first sample loop (SL1) is filled with the loaded gas flow. After closing sample loop (SL1) and bubble column, the clean inert gas flow purges the system. By switching valve V1 it then drives the content of sample loop SL1 as a pulse through the reactor into the second sample loop SL2. By closing valve V3 the pulse is caught in SL2. Via valve V4 it is injected onto the GC. This operation mode serves for measurements of residence time distributions as well as an analysis of catalyst formation processes. Alternatively, a continuous flow of loaded gas can be lead through the reactor allowing for time-on-stream analysis. In both operation modes kinetic data can be obtained varying the residence time by variation of the space velocity through the reactor.

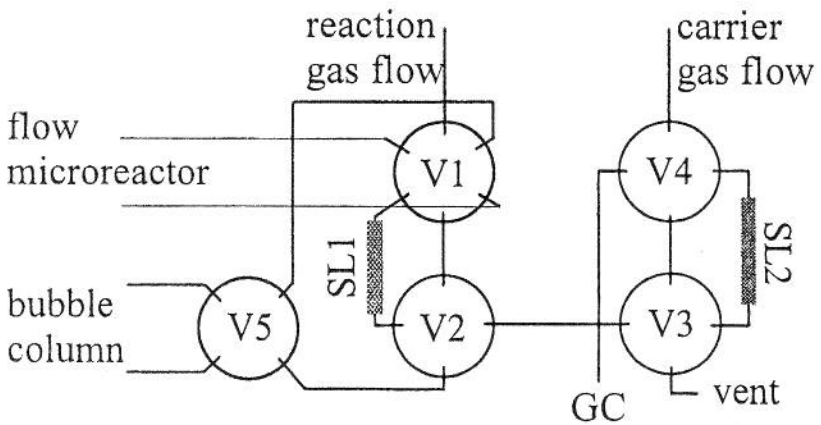

Figure 2: Schematic of the gas flow system:
The commercially available valves (VALCO) are mounted into a heating box on top of a gas chromatograph (Fisons Instruments). The electrical motion drives of the valves are controlled via an auxillary signal interface by the GC measurement software (Fisons ChromCard). This provides synchronous reaction control and GC analysis in the pulsed operation mode.

2 Results and discussion:

Initially, results were obtained from technical flow microreactors. Corundum capillaries with 1mm i.d. and a filament heating zone of 38 mm length were used as wall reactors. Temperature measurement was carried out by a thermocouple close to the filament. Maximum formaldehyde yields of 12 to 16%, comparable to the results from technical flow-tube reactors, were observed at 1000 - 1050 K, about 150 K below the technical results. The lower temperature is due to a smaller tube diameter, providing a higher rate of heat transfer into a smaller amount of reactands. This indicates a major objective using technical microreactors in catalytic studies. With the size of the system, heats of reaction and amounts of reactands scale down more rapidly than the corresponding rates of heat and mass transfer, respectively. Especially, in catalytic reactions mass transfer towards and from the catalyst surface is often rate limiting rather than the surface reaction itself. One purpose of catalytic microreactors is the prevention of transport limitation in kinetic measurements. In particular, the present reaction of methanol to formaldehyde is endothermic. Hence, the influence of the heat transfer rate can be reduced considerably using a flow microreactor in this case. Figure 3 shows kinetic data of the blind reaction obtained by variation of the residence time in the corundum capillary. Fitting kinetic time laws to the product spectrum yields two rate constants for a simple reaction sequence A → B → C and it is easily suggested that activation energies can be obtained from temperature dependent measurements of these rate constants then.

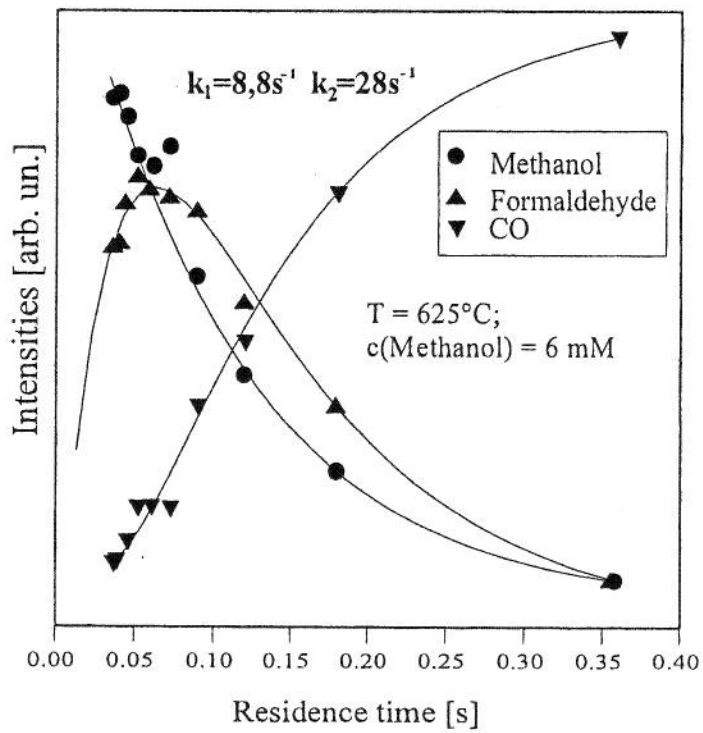

Figure 3: Kinetic measurement of the blind reaction in the corundum capillary
The full lines indicate the fit to kinetic time laws of a reaction sequence A → B → C.

Following the blindreaction we also studied catalytic conversion of methanol to formaldehyde in the technical flow microreactor. Zaza et al [1] report on formaldehyde synthesis from methanol over sodium carbonate on an active carbon support in a fixed bed reactor. Resembling these experiments, we prepared a sodium coating in the corundum capillary by heating a Na_2CO_3-filling to temperatures above 1000°C and removing most of the carbonate filling mechanically, thereafter. Operating this microreactor continuously (Fig. 4a) we observed about 55% formaldehyde yield at 850-900 K i.e. 150 K lower than for the maximum yield in the blind reaction. In contrast to this, the pulsed operation mode led to a maximum yield of 30 % formaldehyde only (Fig. 4b). The difference between stationary and transient operation mode may be understood by a glance at the mechanism principle of the catalyzed reaction. The methanol conversion takes place in the gas phase and is supported probably by sodium atoms which are thermally emitted from the solid at the reaction temperature [2]. The difference between stationary and transient runs of this reaction may then be due to different kinetic couplings between the thermal emission of sodium atoms and the net gas phase reaction in both cases.

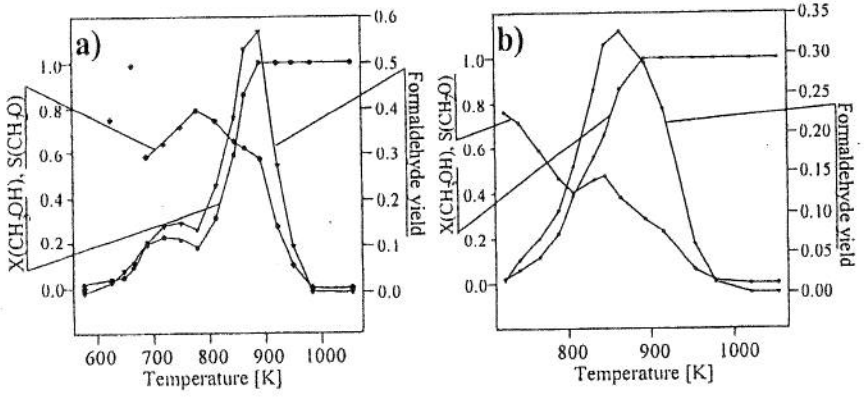

Figure 4: Temperature dependent methanol conversion over Na_2CO_3:
a) Continuous flow operation mode.
b) Pulsed flow operation mode.
Methanol concentration = 7mM; residence time = 360ms.

Approximate residence time distributions of the single-crystal microreactor are shown in Fig. 5a. The intensity distributions were obtained in delay-time experiments with nitrogen pulses passing through the reactor in a continuous flow of helium gas. The residence time distributions indicate a by-pass flow parallel to a flow through an ideal continuously stirred tank reactor resulting from the cooling volume (≈ 3ml). For the reaction volume itself this causes a distortion of the radial gas flow into one with a preferential flow direction resulting in a broadening of residence times in the reaction zone above the sample surface.

First temperature dependent methanol conversion data (Fig. 5b) was obtained from the single-crystal reactor, thereafter. A thick, disordered and oxidized aluminum film was deposited on a NiAl(110) single-crystal substrate surface. XP spectra taken before and after the reaction run revealed only a slight carbon contamination by the reaction. XAE spectra showed an increase of the oxide film thickness on the aluminum film. The formaldehyde yield of 11% indicates an uncatalyzed blind reaction. The corresponding temperature, however, is 350 K lower than in the corundum capillary experiments mentioned above. As the substrate was not actively heated, the conversion is probably achieved in the quartz entrance capillary already and the reaction volume acts as a cooling volume only. Hence, further experiments have to invoke active substrate heating.

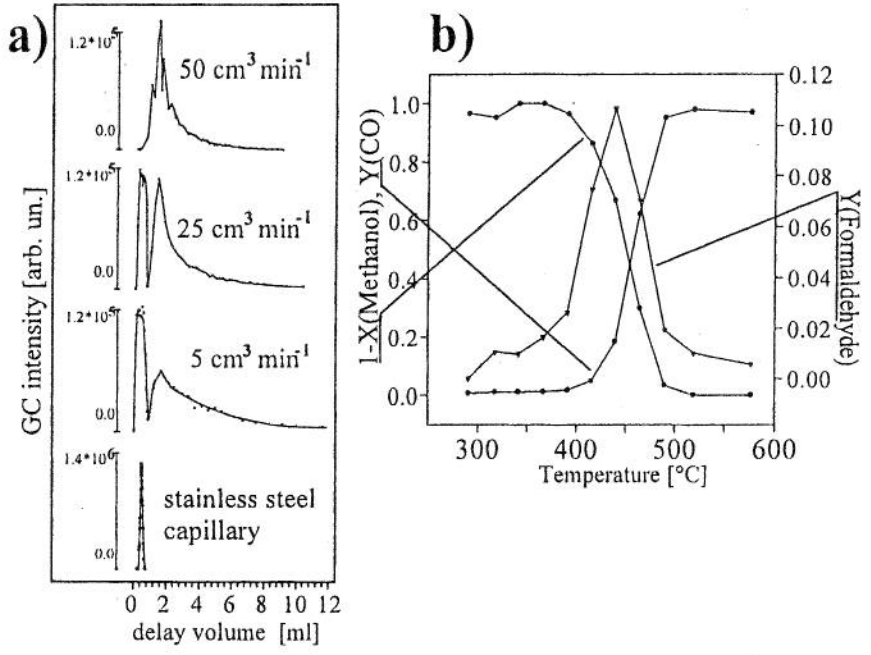

Figure 5: First experiments in the single-crystal microreactor:
a) Residence time distributions of the single-crystal microreactor:
b) Temperature dependent reaction data over a thick aluminum oxide film grown on an aluminum metal film on a NiAl(110) single crystal.

3 Literature:

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