A micro-structured quartz reactor for kinetic and *in situ* spectroscopic studies in heterogeneous catalysis[☆]

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Abstract

A modular micro-structured quartz reactor was developed as a flexible device for controlled catalytic measurements in combination with *in situ* spectroscopic analysis. Depending on the actual reactor configuration, different shaped catalysts can be studied *ex situ* (*e.g.* by microscopy), or via *in situ* optical spectroscopy. The successful application of the reactor is demonstrated on two examples, the temperature-controlled ammonia oxidation over polycrystalline Pt catalyst, and the selective oxidation of propene over a supported molybdenum oxide-based thin film catalyst. The latter thin film catalyst was synthesized by a novel synthetic route using gelatine as wetting agent.
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1. Introduction

Micro-structured reactors are well-established tools for kinetic studies of highly exothermic reactions due to their excellent heat and mass transfer characteristics. Since the defined geometry of the reaction channels assures controlled conditions throughout the reactor, those can be modelled with reasonable effort. Therefore, micro-reactors can be regarded as well-defined model systems for industrial catalytic reactors. Moreover, due to the small characteristic channel dimension, radical chain reactions are suppressed, which enables measurements in the explosive regime of gas mixtures.

Nevertheless, the ability to characterize catalysts during the reaction or thereafter is often limited. One objective of this work was to design a reactor that is suitable to investigate the kinetics of heterogeneously catalyzed reactions, but enables also convenient characterization of the catalyst via *ex situ* and *in situ*

methods, in order to elucidate structure–activity relationships in heterogeneous catalysis.

Particular emphasis was placed on the ability to subsequently analyse the catalyst by surface science methods such as XPS and AFM. However, due to charging effects and surface roughness of industrial powder catalysts a reliable analysis by surface science methods is often impossible. An ideal model system should therefore preserve as much as possible of the structural complexity of an industrial catalysts but at the same time stay accessible to both surface science and bulk analytical techniques. A promising strategy to meet these requirements is to chemically deposit a thin film or nano-particles on an inert, conducting substrate, such as silicon [1]. The deposition of the film is a critical step because it is well known that the exact synthesis conditions of complex oxide catalysts play a decisive role for the final properties of the catalyst.

In the following we will illustrate the concept presenting results of two case studies that have been performed with the new type of micro-structured reactor and also briefly describe a new synthesis approach for the preparation of (*more*) realistic model systems:

- *Case A*. The activity of a wall-coated Pt catalyst in ammonia oxidation was investigated at 420–830 K, evaluating the influence of temperature and time-on-stream on product formation.

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- *Case B. In situ* Raman and catalytic results on the partial oxidation of propene over a complex Mo–V–W–O model catalyst that has been prepared by a new synthetic method starting from aqueous solutions and utilizing gelatine as wetting agent.

2. Reactor concepts

In order to fully use the advantages of micro-structured reaction channels and the defined surface of a flat model catalyst, both had to be manufactured as separate pieces. The concept was to prepare a catalyst on a flat substrate, *e.g.* silicon or quartz, and then fit it in the reactor in a way that it forms a unit with the micro-structured channels. Quartz glass as construction material for the reactor was chosen due to its high-thermal resistance, chemical inertness and optical transparency.

To practically realize the concept, an existing micro-structured quartz reactor [2,3] was modified. The reactor had previously shown to allow temperature-controlled kinetic studies of the highly exothermic ammonia oxidation near atmospheric pressure, applying a 4 μm thick Pt foil as polycrystalline catalyst. A modular design, consisting of a stack of three quartz plates held together by clamps and screws, assures a high versatility of the reactor in terms of catalytic reactions and catalysts to be tested. As only one of the plates – typically the centre one – contains the micro-structures, only part of the reactor needs to be replaced in case that micro-channels or catalyst design/arrangement need to be modified. The micro-structuring was performed in all cases by sandblasting technique [4].

2.1. Micro-structured reactor for the ammonia oxidation on platinum (case A)

Fig. 1 shows photographs of the reactor that was used in case study A. Fig. 1a depicts a bottom view of the cover plate carrying a fresh platinum catalyst and Fig. 1b shows a top view of the centre plate with the micro-structured reaction channels. Fig. 1c contains a photograph of the catalyst after reaction. The same configuration and size has been used before [2,3], except for the modified top plate. In the assembled state, both plates (a and b) are placed on top of each other, so that the catalyst forms the upper wall of the two reaction channels (each 500 μm wide, 300 μm deep) and is thereby exposed to reactants. Sealing is achieved with clamps and screws around the reactor body, avoiding gas leakage up to 1.3 bar. To avoid a bypass of the gas flow at the sides of the catalyst, eight sealing plugs (made from quartz wool) were placed around the sides of the carrier plate in the respective cavities indicated in Fig. 1a.

The temperature is measured from the back of the catalyst, *i.e.* by thermocouples located outside the reactor in the indentations as indicated in Fig. 1a. The remaining wall thickness between the thermocouple and the backside of the catalyst carrier was less than 200 μm and assured reliable temperature control. Heat was provided by two ceramic heating elements (SiN) located in the position indicated in Fig. 1b, which were regulated via two Eurotherm controllers. While the central heater controlled the catalyst temperature, the second heater assured that the exit
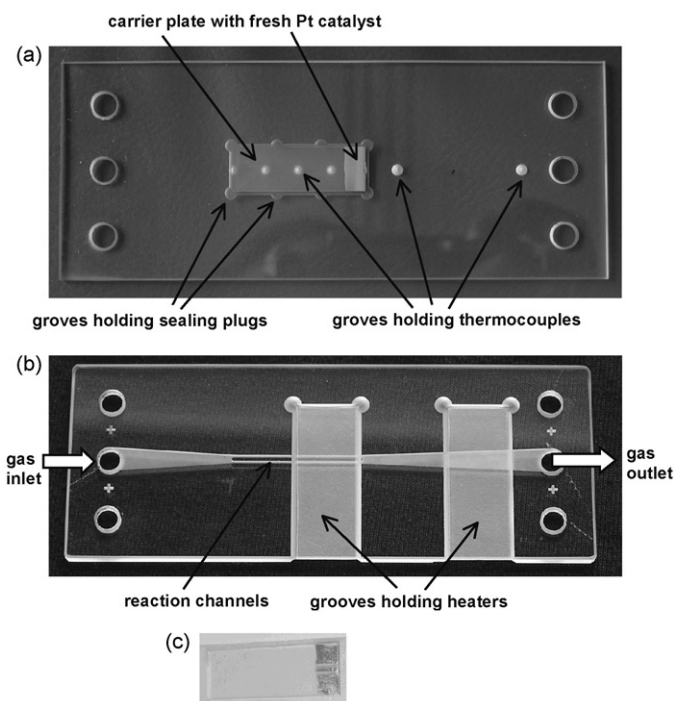

Fig. 1. Photographs of the micro-structured quartz reactor applied to case A. (a) Centre plate featuring gas-channels and compartments for the heaters. (b) Cover plate and catalyst carrier as well as fresh Pt catalyst. (c) Catalyst carrier after reaction.

temperature of the gas remained above 443 K, thus avoiding possible condensation of the reaction products.

2.2. Micro-structured reactor for selective oxidation of propene combined with in situ Raman spectroscopy (case B)

A sketch of the micro-structured quartz reactor used to follow the partial oxidation of propane by *in situ* Raman spectroscopy is shown in Fig. 2. A reactor similar to that applied in case A (Fig. 1) was used, but with the difference that the catalyst carrier is located in a groove inside of one broad reaction channel, *i.e.* in the centre plate, and that temperature control is established via two thermocouples placed inside the gas channels before and after the catalyst.

The base plate, of 100 mm × 142 mm, contains open pockets for the removable heating elements and cut-outs for the gas supply. The centre plate is micro-structured, carrying the catalyst chip in a 10 mm × 10 mm cavity. The silicon substrates were grinded at the sides to fit exactly into the cavity. The remaining gas space over the catalyst forms one channel being 10 mm wide but only 100 μm high, thus preserving the micro-dimensions in one direction. Inside the gas channels axial grooves of 500 μm diameter are embedded that guide the thermocouples. The cover plate is unstructured and has a thickness of 3 mm. Centre- and cover plates are made from Suprasil® quartz to prevent undesirable side-reactions and to allow optical spectroscopy in the ultraviolet region.

To perform the *in situ* Raman experiments the whole reactor was placed under a Raman microscope (see experimental part) to collect spectra in the backscattering (180°) geometry (Fig. 2b).
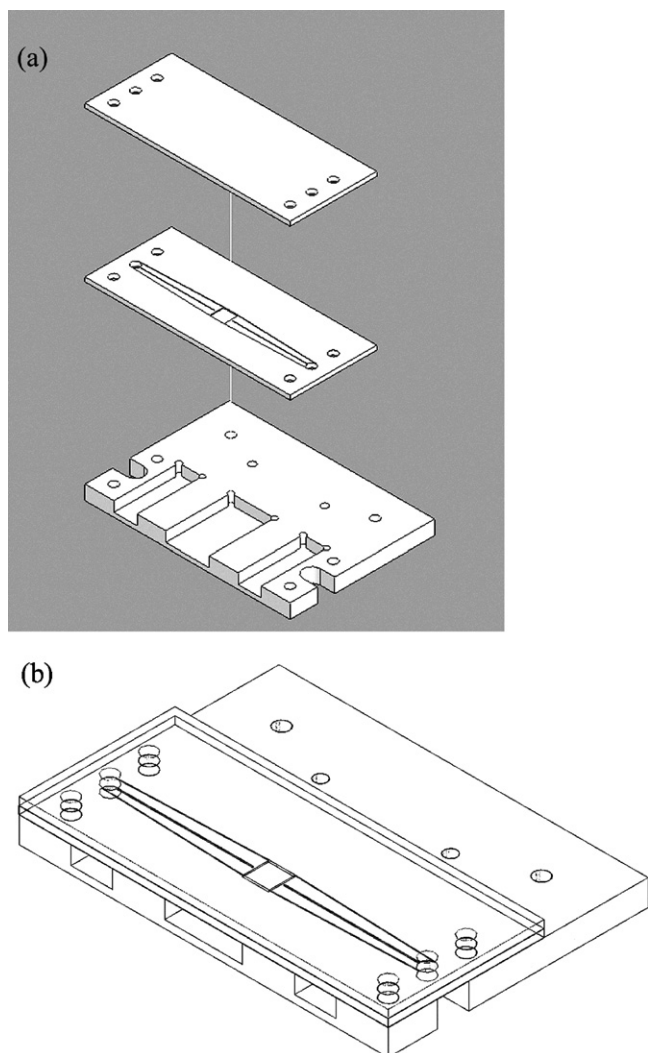
Fig. 2. Sketch of the micro-structured reactor used for the selective oxidation of propene in combination with *in situ* Raman spectroscopy. (a) Exploded view. (b) Assembled reactor, as used for *in situ* Raman microscopy in backscattering mode.

3. Case A: ammonia oxidation on platinum

3.1. Experimental (A)

3.1.1. Catalysts preparation

Ammonia oxidation was studied over a Pt catalyst that was produced by coating a catalyst carrier (30 mm × 10 mm × 1 mm) via sputtering of a Pt target for 2 min in an Ar-ion plasma. The length of the catalyst bed film was adjusted to 5 mm using a stencil. The catalyst carrier was then placed in the micro-structured reactor as indicated in Fig. 1.

3.1.2. Reactivity measurements

The catalytic tests were carried out in continuous flow where a mixture of 3% NH_3 (3.8), 3% O_2 (4.8), 84% Ar (5.0) and 10% Ne (5.0) was dosed to the reactor at a flow rate of 400 ml (STP)/min, corresponding to a contact time of about 1 ms. Back pressure was adjusted to 1.02 bar. Composition of the effluent gas was continuously monitored by QMS (Balzer

Omnistar GSD 300). For quantitative evaluation, all the feed components and reaction products were calibrated with respect to Ne. In catalytic tests of temperature-programmed ammonia oxidation, the temperature was alternately stepwise increased and held constant for 20–40 min at the given temperature level.

3.2. Results and discussion (A)

The composition of the product stream is shown in Fig. 3 *versus* temperature, as well as the consumed amount of oxygen. The continuous increase of oxygen consumption with temperature illustrates that, in contrast to earlier investigation of the reaction on sputtered Pt where ignition occurred [5,6], temperature control of the highly exothermic reaction was established due to sufficient heat removal from the catalyst, providing a basis for kinetic measurements. At the highest temperature, oxygen conversion amounted to about 65%.

As indicated in Fig. 3, all three nitrogen products expected in the investigated pressure range, *i.e.* N_2, N_2O and NO, were formed. Nitrogen was the dominating product at low temperatures, passing through a maximum at around 623 K. Formation of nitric oxide, the desired product in the industrial selective oxidation of ammonia, started at around 623 K and increased continuously with increasing temperature. The side product nitrous oxide was formed throughout the whole temperature range in small amounts, with a maximum selectivity of 8%.

A comparison of the present results (Fig. 3) to previously reported temperature-controlled experiments over polycrystalline Pt foil under similar conditions [3] reveals strong similarities. Both, the temperature dependence of formation of each product as well as the location of the respective maxima in Fig. 3 resemble those reported for Pt foil. The major difference between the two systems is the fact that the sputtered
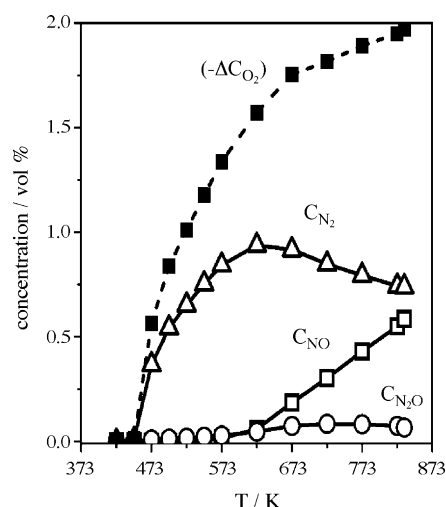

Fig. 3. Composition of the product stream *vs.* temperature in temperature-programmed ammonia oxidation over 5 mm of sputtered Pt showing concentration of products N_2, N_2O and NO (open symbols) and the amount of consumed oxygen (full symbols) (400 ml/min, 3 kPa NH_3, 3 kPa O_2, 84 kPa Ar, 10 kPa Ne) (30 min TOS at each temperature).
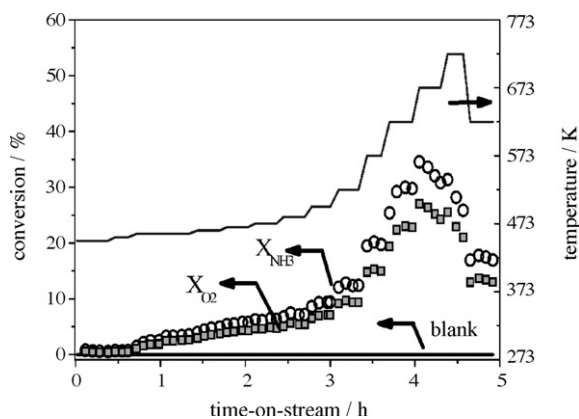
Fig. 4. Conversion and reactor temperature *vs.* TOS in temperature-ramped ammonia oxidation over 1.5 mm of sputtered Pt as well as blank activity (400 ml/min, 3 kPa NH_3, 3 kPa O_2, 84 kPa Ar, 10 kPa Ne) (20–40 min TOS at each temperature).

Pt catalyst produced significantly higher amounts of nitrogen and less nitric oxide than the Pt foil. This deviation in selectivity is rationalised by the fact that single-crystal experiments indicated ammonia oxidation to be a structure–sensitive reaction [7,8] hence catalysts of different morphology such as bulk-like Pt foil and sputter-coated Pt film should perform differently.

The changes in catalytic activity with time-on-stream, observed in a temperature program with higher resolution at temperatures between 453 and 523 K, are illustrated in Fig. 4 with respect to conversion of oxygen, conversion of ammonia and temperature *versus* time-on-stream. The steep temperature steps demonstrate that heating and cooling can be accomplished very fast throughout the full temperature range, giving an excellent temperature control. Moreover, as indicated in the diagram for conversion in the empty reactor (Fig. 4), blank activity of the reactor was negligible for all conditions.

Following oxygen and ammonia conversion over the Pt catalyst *versus* time-on-stream revealed that the catalytic activity changed with time-on-stream (Fig. 4). For temperatures around 473 K a slight activation was seen, whereas at 673 and 723 K catalytic activity rapidly decreased with time. Moreover, the loss of activity was permanent as a comparison on conversion at 623 K after 4 and 5 h (Fig. 4) confirms.

A photograph of the catalyst carrier after removal from the reactor, shown in Fig. 1c, reveals the reason for decreasing activity: the area where the catalyst is exposed to the two micro-structured channels, *i.e.* where the catalyst is exposed to the reaction mixture, significant amounts of Pt were removed from the surface of the carrier. The observation that the catalyst degraded stronger in the front part of the catalyst film (Fig. 1c), *i.e.* at higher reactant concentrations, suggests that the loss of Pt and reactant concentrations are correlated.

However, by extending the range of temperature-controlled measurements, in the highly exothermic ammonia oxidation over supported Pt catalysts, up to 830 K, a basis for kinetic studies under controlled reaction conditions is provided.

4. Case B: *in situ* Raman on Mo–V–W mixed oxide thin film

4.1. Experimental (B)

4.1.1. Catalyst preparation

Silicon [1 0 0] wafers (p-type doped with boron [15 mΩ × cm] from Silchem) were cut into pieces of 10.0 mm × 10.0 mm × 0.7 mm. The cleaning procedure for the Si-wafers consisted in successive ultrasonic cleaning in chloroform, acetone, ethanol and bi-distilled water. After wet cleaning the Si-wafers were oxidized at 800 °C in air to generate a thin SiO_2 film of about 5 nm thickness. A Mo–V–W mixed oxide powder precursor (relative atom ratio = 0.68:0.23:0.09) has been prepared according to the method described by Knobl et al. [9] via spray drying of mixed solutions of ammonium heptamolybdate (AHM; Merck, p.a.), ammonium metatungstate (AMT; Fluka; purum, >85% WO_3 gravimetric), and vanadyl oxalate of the respective transition metal concentrations. The precursor powder was calcined at 623 K in air (5 K/min) and used as a reference for the catalytic and *in situ* spectroscopic characterization. The pre-calcined powder was pressed into a pellet (8 mg, Ø = 5 mm, 25 bar) and countersunk in a specially prepared silicon wafer, containing a cavity of the precise pellet size. The thin film catalyst was then prepared via a gelatin–polyoxometalate composite gel by dissolving the spray dried Mo–V–W–O powder (1 wt%) in a gelatin (1 wt%) containing aqueous solution at 60 °C. The pH of the resulting sols was ~6.5. The obtained sol was subsequently filtered through a micro-filter (pore diameter = 0.2 µm) and cooled down to 37 °C before spin coating at 5000 rpm on the silicon substrate. The as prepared thin films were dried over night at 37 °C and then pre-calcined for 3 h at 573 K in static air (2 K/min).

4.1.2. Raman spectroscopy

A Labram system from Yobin Yvon equipped with a confocal microscope (Olympus) and a He/Ne laser (15 mW) was used for the Raman investigation. All spectra were recorded in backscattering mode. The parameters used for spectra acquisition on the thin films were: 50× long distance objective (NA = 0.75, Olympus), slit 500 µm, confocal hole 200 µm, integration time 300 s with 3 averages. Filters were used to reduce the laser power at the sample to ~1 mW (measured by power meter).

4.1.3. Reactivity measurements

The educt gas compositions and flows were controlled by mass flow controllers (Bronkhorst). Propene (Messer, 99.95%) and oxygen (Westfalen, 99.999%) were used as reactants and He (Westfalen, 99.999%) as an inert diluent. The total flow of reactants was 1 ml/min consisting of 10 vol.% propene and 20 vol.% O_2 balanced by He.

Part of the gas outlet from the micro-structured reactor was fed into a proton-transfer-reaction mass spectrometer (PTR-MS, Ionicon Analytik) used for reaction product analysis. This system is based on the principle of chemical ionization using H_3O^+ as the proton donor combined with the swarm technique of the

flow tube type. It is especially suitable for a qualitative and quantitative product analysis at ppb level [10,11]. The PTR-MS was used because activity measurements over the thin film were challenging and impossible to measure with an ordinary quadrupole mass spectrometer. In order to be able to directly compare the results of different measurements, the amount of propene fed into the PTR-MS was adjusted to 7 ppm before reaction.

4.2. Results and discussion (B)

4.2.1. Preparation of the mixed Mo–V–W–O model thin film catalyst

Industrially used mixed oxide catalysts are usually prepared via co-precipitation or spray drying of aqueous solution and/or by wet impregnation. It is now generally accepted that the exact preparation steps during the synthesis of complex oxide catalysts play a decisive role for the final properties of the catalyst. In the experimental part and in Ref. [9] a description of the precursor powder synthesis by spray drying the aqueous metal containing solutions is made. However, the high surface tension and low vapor pressure of water inhibits the use of aqueous solutions for the preparation of dense and closed thin films. Inspired by the fabrication of photographic paper we have prepared smooth mixed oxide films by dissolving/suspending the spray dried precursor powder in a gelatin gel. Only few reports dealing with the interaction between gelatin and inorganic material have been found in the literature. Apart from the photographic process most work has been conducted in the field of biomineralization [12,13]. Recently Coradin et al. reported on the synthesis of silica-gelatin nano-composite material [14]. To the best of our knowledge no investigations on the use of gelatin for the preparation of inorganic oxide thin films have been reported so far. It should be mentioned that the usage of gelatin requires strict control of synthesis conditions. As a biopolymer gelatin is very sensitive to changes in temperature and pH. Only few degrees above blood temperature the three-dimensional ordered helical structure of gelatin in aqueous solutions transforms into randomly oriented coils, inducing drastic changes in the rheological properties [15].

A great advantage of the gelatin method is the ability to use the original spray dried powder catalyst for the thin film preparation, thereby avoiding deviations from the original synthesis steps. Hence, the resulting thin film can be compared directly with the (*real*) powder catalyst. In our case the synthesis conditions (see experimental part) were chosen to obtain a smooth thin film of ∼25 nm thickness (Fig. 5).

4.2.2. Selective oxidation of propene

Before starting the catalytic tests, several blind tests were carried out, which proved the reactor system containing an uncoated silicon wafer to be inactive for propene oxidation below 723 K. Reactions were therefore performed at different temperatures, but never higher than 713 K. Additional temperature limitations were imposed due to the low sublimation temperature of the thin films, starting at ∼673 K. Fig. 6 shows the four main partial oxidation products, acetaldehyde, acrolein, acetic acid and acrylic acid, when propene is oxidized over the thin film.
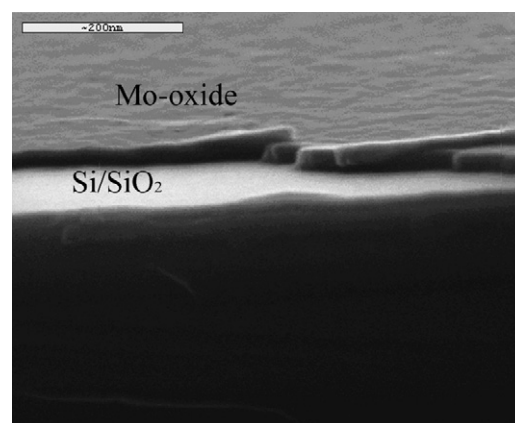

Fig. 5. Cross-sectional scanning electron micrograph of the thin film catalyst. On top lies the smooth ∼25 nm thick molybdenum oxide film, on a surface oxidized silicon wafer.

An activation period during the partial oxidation of acrolein to acrylic acid related to the formation of an active crystalline phase, has been reported for the industrial-type Mo–V–W oxide catalyst [16] and was also found by Knobl et al. [9]. In order to detect a possible activation of the film during time-on-stream, the temperature was decreased two times back to 623 K after having been up to 653 and 673 K. Activation was observed for all partial oxidation products but was especially large in the case of acrylic acid (Fig. 6). After 7 h time-on-stream at 673 K the mass signal intensity for acrylic acid at 623 K has been increased significantly compared to its initial value and compared to the relative increase for the other products at the same temperature. The activation is further supported by the observation that yields are restored directly when increasing the temperature back to 673 K.
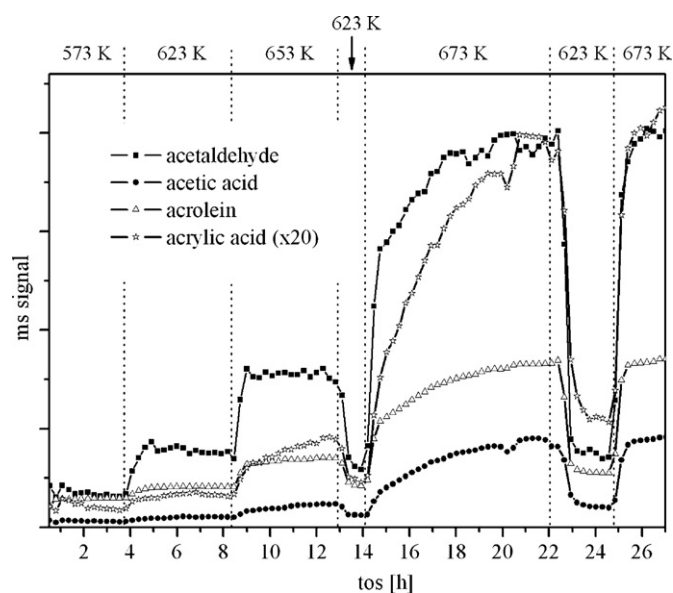

Fig. 6. Mass spectrometric signals during the reaction of the thin film at different temperatures; 20-fold magnification of ms signal for acrylic acid, emphasizing on the activation of the thin film.

4.2.3. In situ Raman spectroscopy

Measuring *in situ* Raman spectra of the thin film catalyst was challenging because of the very weak Raman signal originating from the active catalyst coating and the high background from the Raman signals of the underlying silicon wafer (Fig. 7). The silicon phonon band at $520\,cm^{-1}$ is the most intense feature in the spectra even after coating the wafer. This is primarily due to the He/Ne laser ($\lambda = 633\,nm$) used for the Raman experiments, which penetrates through the catalyst coating deeply into the silicon wafer (by using the 488 or 514 nm lines of an Ar-ion laser, which was not available in this study, the signal from the silicon wafer should be considerably reduced). A further difficulty emerged at higher temperatures due to the broadening of the silicon band at $941\,cm^{-1}$ caused by symmetry forbidden phonons (Fig. 7) [17,18]. It was therefore difficult to determine exactly the positions of bands in this spectral area, which is typical for metal–oxygen double bonds. As a result, the comparison between the *in situ* Raman spectra of the powder catalyst and thin film catalyst was not straightforward. As already mentioned in the reactivity part (see above) the thin film started to sublime at ~673 K and if the temperature was hold long enough, deposits of sub-micrometer, fine needle-type crystals have been observed at the inner side of the cover plate. The Raman spectra of these crystals resemble almost exactly the band positions of the "fingerprint" Raman spectrum of the nano-crystalline Mo_5O_{14} type mixed oxide catalyst published by Mestl [19]. The spectrum of the sublimed crystals was therefore taken as a reference spectrum for the crystalline tetragonal Mo_5O_{14} structure [20]. In Fig. 8 selected *in situ* Raman spectra of the thin film (b–d) and the powder pellet (e) are shown together with the spectra of the uncoated silicon (a) wafer and of the reference (sublimed) Mo_5O_{14} (f) sample. It is obvious, that the structure of the thin film is chang-
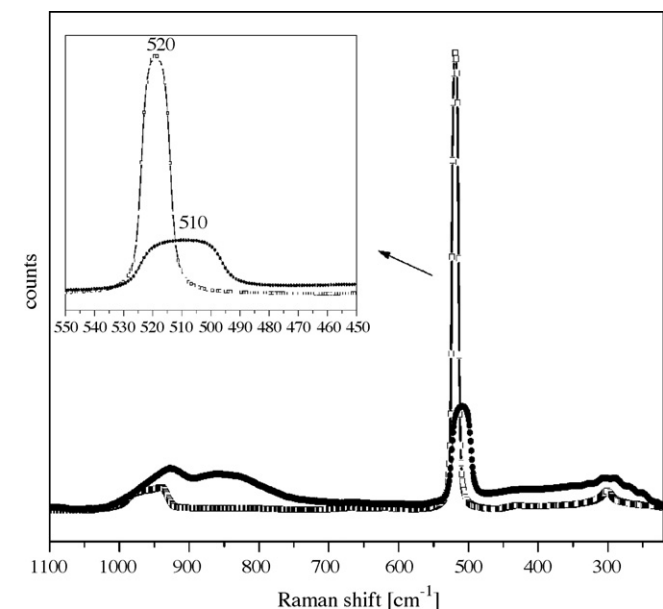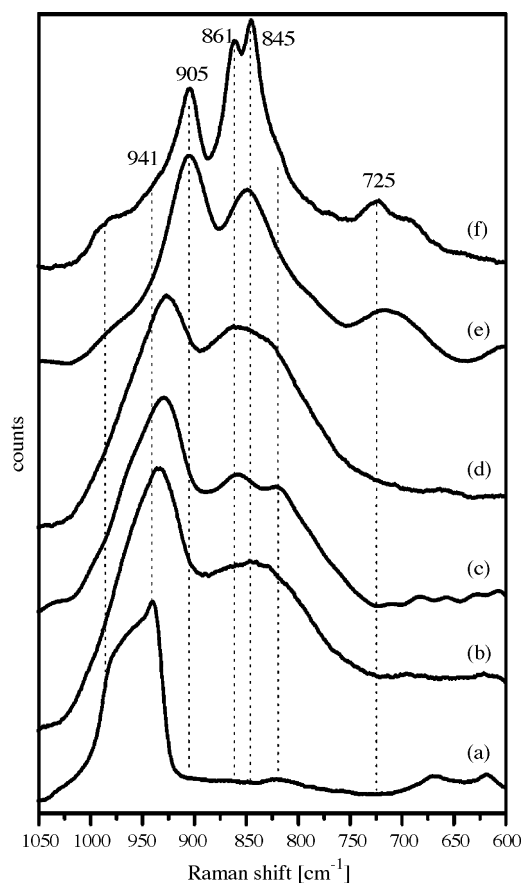

Fig. 8. Comparison of *in situ* Raman spectra of the thin film at different temperatures together with an uncoated silicon wafer, the *in situ* reference spectrum of the powder pellet at 673 K and the *ex situ* reference spectrum of the Mo_5O_{14} type structure from the sublimed crystals (see text). (a) Uncoated silicon wafer; (b, c and d) *in situ* Raman spectra of the thin film at 573, 653 and 673 K, respectively; (e) reference *in situ* spectrum of the powder pellet at 673 K; (f) *ex situ* reference spectrum of Mo_5O_{14} type structure.

ing with temperature and time-on-stream and finally at 673 K converting to a structure that gives Raman bands in the same frequency range as observed for Mo_5O_{14}. The *in situ* Raman spectrum of the powder pellet at 673 K (Fig. 8e), though much less resolved clearly corresponds to the spectrum observed for the Mo_5O_{14} reference (Fig. 8f). The relative intensities of the bands centred at 905 and $850\,cm^{-1}$ have shown to be temperature dependent (not shown). The obvious differences between the *in situ* Raman spectra of the thin film and the *in situ* spectrum of the powder pellet are believed to be due to the lower degree of long-range order in the thin film as compared to the powder pellet. However, the structural motifs and type of chemical connectivities, giving rise to localized modes, seem to be similar in both cases.

Besides the negative interference of the silicon Raman bands in the fingerprint region of the Mo_5O_{14} structure, the most intense silicon band at $520\,cm^{-1}$ has been identified as very useful for accurate temperature measurements during an *in situ* experiment. Hart et al. [17] found that both the half-width and the frequency shift of the silicon phonon band behave linearly over a broad temperature range. Thus, the position of the band at 298 K is $520\,cm^{-1}$, whereas at 673 K it should be shifted to $510\,cm^{-1}$.

Fig. 7. The Raman spectrum of an uncoated silicon wafer at room temperature (open squares) together with the *in situ* spectrum of a ~25 nm thick Mo–V–W oxide coating at 673 K (filled circles). The inset highlights the frequency shift of the silicon phonon band with temperature.

This is exactly what was found experimentally (Fig. 7, inset) and confirms nicely the excellent temperature control achieved in the micro-reactor.

5. Conclusions

An earlier proposed modular micro-structured reactor was modified to study catalyst films coated on flat substrates instead of metallic thin-foils. The concept was successfully applied to the ammonia oxidation on sputtered Pt. By preparing more sophisticated model catalysts on the exchangeable carrier plate with variable particle size, shape and oxidation state of Pt, it will be possible to elucidate the influence of the catalysts morphology on reaction kinetics and time-on-stream behaviour, and to evaluate the reaction-induced changes of the catalyst with different *ex situ* and *in situ* characterization techniques.

Furthermore, one reactor was successfully interfaced with a confocal Raman microscope that acquired spectra of high quality under reaction conditions, while catalytic activity was followed in parallel. In the presented special case the coincidence of the silicon bands and the fingerprint bands of the Mo_5O_{14} type structure complicate the analysis of the Raman spectra. However, by applying *in situ* Raman spectroscopy, the structural dynamics of the system have been revealed, which will be discussed in detail elsewhere.

Temperature readings from thermocouples inside the reactor were successfully validated against the know temperature-shift of Raman bands of silicon. Since the reactor was made from a transparent material, flow conditions over the catalyst were not altered by the characterization. In addition, the modular design of the catalyst carrier also enabled *ex situ* characterization of the catalyst (*e.g.* microscopy) without any additional effort of sample preparation.

A new method for the preparation of complex oxide thin films is presented. Raman spectroscopic and reactivity measurements proved the film to serve as a realistic model system for mixed oxide catalysts used in partial oxidation reactions. The preparation of gelatin–inorganic composite gels represents a facile method for the synthesis of well-defined mixed oxide thin films and can easily be extended to other systems as for example the deposition of previously prepared nano-particles.

The presented concept of a modular micro-structured reactor was established as a valuable tool to investigate structure–activity relationships in heterogeneous catalysis supported by *in situ* Raman spectroscopy. Moreover, the presented device is not limited to the application of Raman spectroscopy, and a combination with other spectroscopic methods using visible light, such as UV–vis, is suggested.

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