In situ Raman studies of molybdenum oxide based powder and thin film catalysts during the selective oxidation of light alke(a)nes

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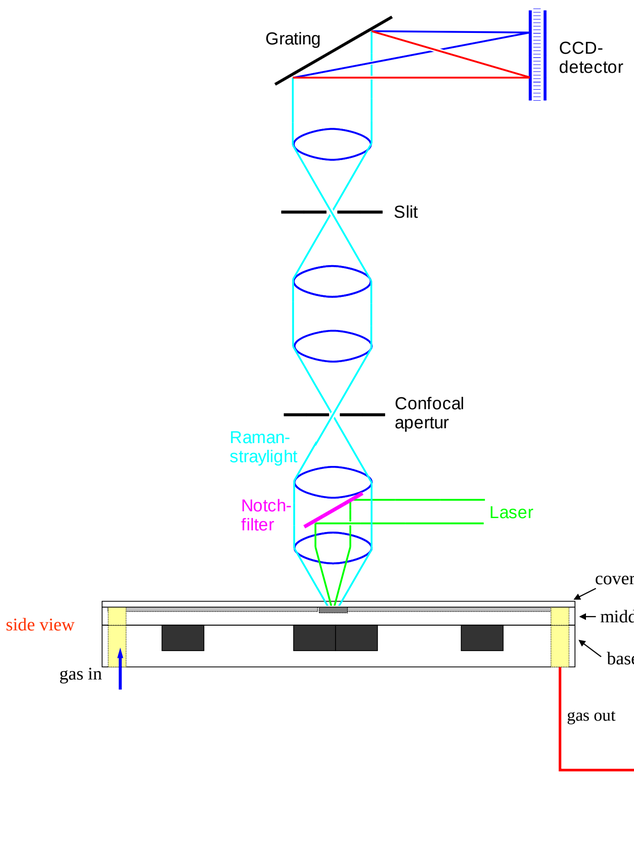
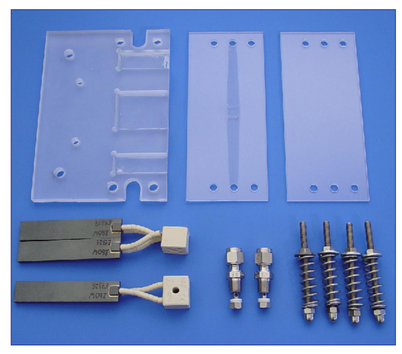
Introduction

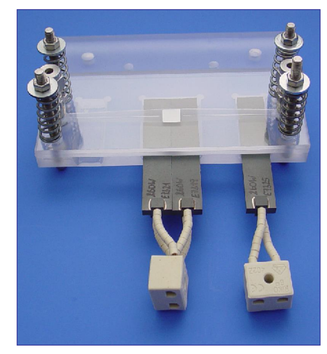
The partial oxidation of light alka(e)nes *e.g.* propa(e)ne to higher valuable chemicals *e.g.* acrolein and/or acrylic acid is technically performed over multi metal oxides (MMO). Although much effort has been made to understand the working mechanism of MMO's, the complexity of such systems has prevented up to now unequivocal proofs for the existing theories. It is obvious that *in situ* analytical methods are indispensable to get such proofs. The main problem is that most of the research on MMO's has only been conducted via bulk analytical techniques (XRD, EXAFS, IR, Raman, *etc.*) because charging effects and surface roughness of real powder catalysts make the reliable analysis by surface science methods impossible. However, a combination of surface sensitive and bulk sensitive methods are necessary to fully characterize and understand such complex systems. Our ultimate goal is therefore to prepare adequate models ranging from pure molybdenum oxides to complex mixed metal oxides which should preserve as much as possible of the chemical and structural complexity of real catalysts but at the same time stay accessible to both surface science and bulk analytic techniques. A promising strategy to meet these requirements is to deposit a thin film or nanoparticles of the metal oxide on an inert, conducting substrate, such as silicon.

The Reactor Concept – Cost Effective – Microkinetics and In Situ



Micro-structured reactors are known as convenient tools for kinetic studies of highly exothermic reactions. Nevertheless, the ability to characterize the catalyst during the reaction or thereafter is limited. A flexible device that overcomes such limitation, a micro-structured quartz reactor, was developed. The reactor consists of a stack of three quartz plates. The middle plate is micro-structured and carries the reaction channels. The catalyst is mounted in the reactor as a thin foil, or a coated carrier plate. Removable heating elements are located in cut-outs of the base plate.



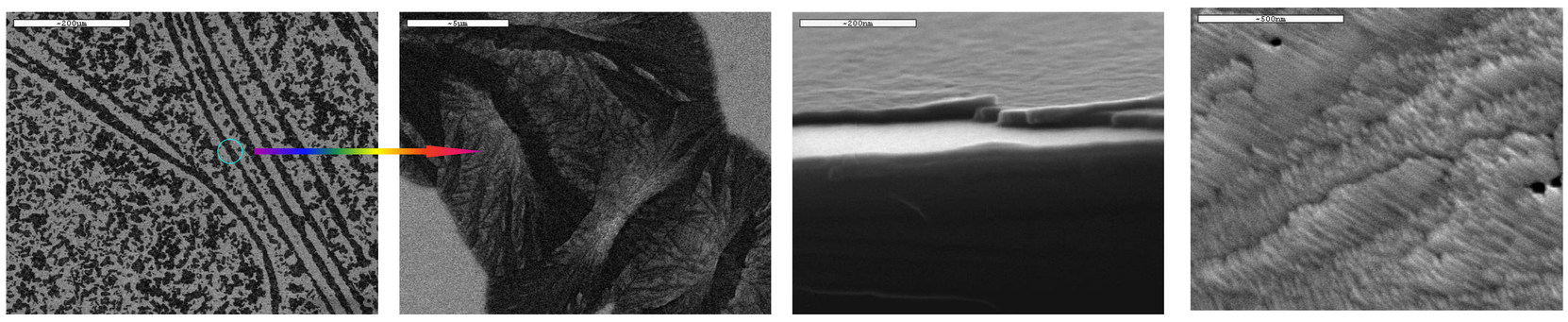


Temperature control is achieved via thermocouples integrated into the reactor wall, or located in the gas supply channels. A thin top plate made of Suprasil® quartz leaves the catalyst surface exposed, and makes it accessible for optical spectroscopy. A Labram system from Yobin Yvon® equipped with a confocal microscope and a HeNe (15mW) laser was used for the Raman investigation.

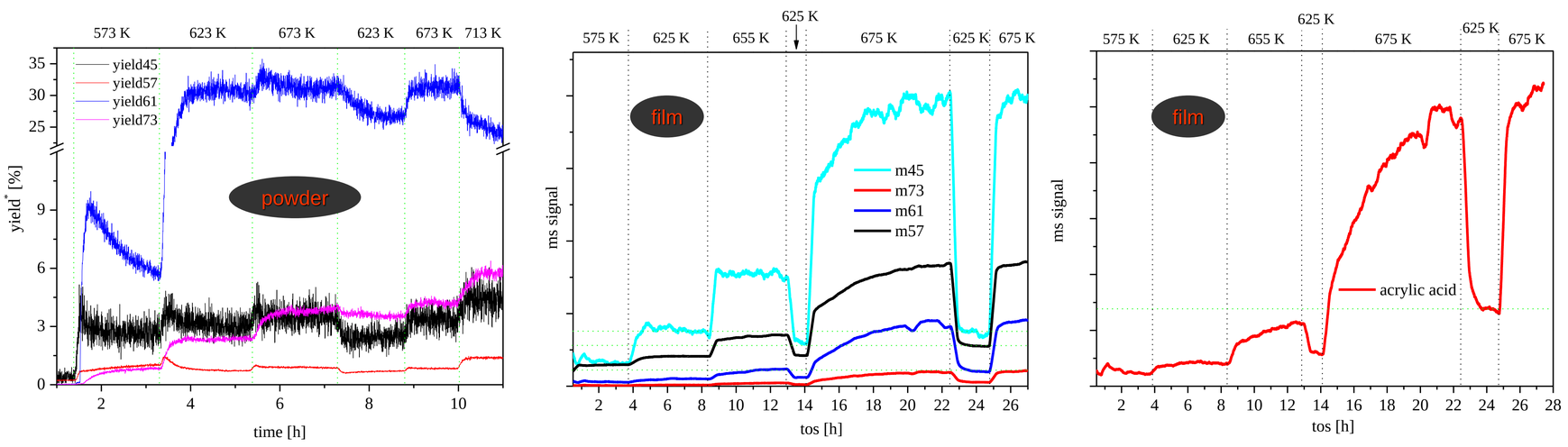
For gas analysis a PTRMS was used, because the conversion over the thin films was very low and not measurable with a normal quad mass spectrometer. The drawback of this analytic technique is that the products of total oxidation (CO_x) could not be detected and thus we were not able to give any total quantitative information. Anyhow, several valuable conclusions can be drawn from the obtained data (*see below*).

The Synthesis Strategy – Complex Catalysts on Flat Substrates – Bridging The Materials Gap

We have dissolved different inorganic precursors, like polyoxometalates, in gelatin and subsequently spin coated these solutions on silicon substrates. We were able to adjust the thickness of the films in a range from a few nanometers to several microns by increasing the concentration of gelatin in the gel. Further we could modify the surface morphology of the films by increasing the ratio of gelatin to inorganic component.



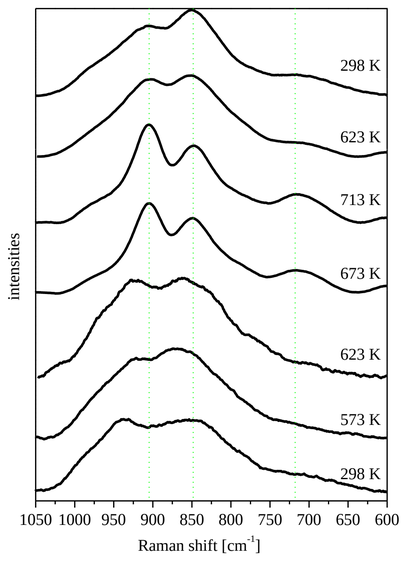
Selective Oxidation of Propene on Thin Films and Powder Pellets

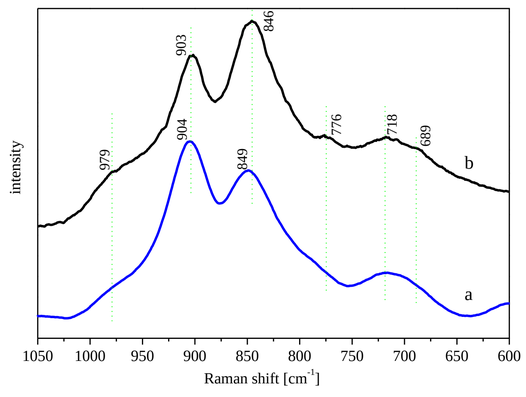


The films convert propene to different partial oxidation products (acetic acid, acrylic acid, acetaldehyde, acrolein) and can be regarded as active catalysts. The films show the typical activation behavior that is observed for this kind of catalysts, which can be seen by comparing the time necessary to achieve maximum ms signal after the two short cooling steps at 625 K. Even more important is that during this activation process the activity towards the desired product, acrylic acid, is clearly increasing much faster than for all other products, which is equivalent to an increasing selectivity.

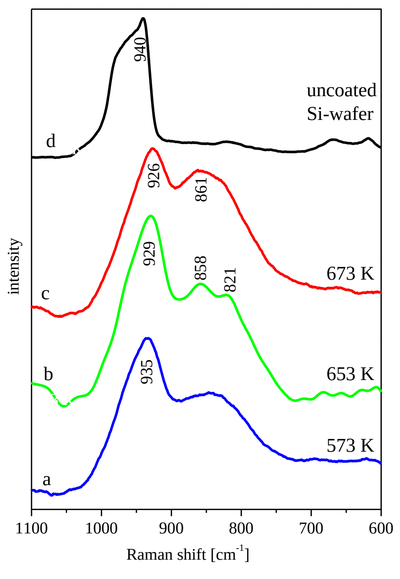
In Situ Confocal Raman Microscopy

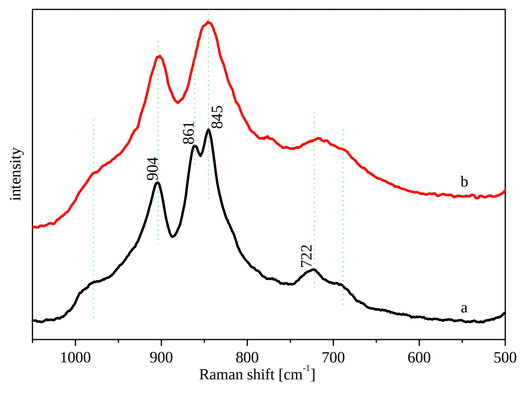
In situ Raman spectra of the powder pellet catalyst at different temperatures are displayed. The series of spectra reveal why in situ techniques are necessary in determining the active catalytic species: the Raman spectra before and after catalysis are obviously different from the spectrum observed for the working catalyst. The presence of α-MoO_3 in the catalyst can be excluded as the Raman spectrum of α-MoO_3 shows a resonance effect when interacted with the 632 nm of a He/Ne laser used in our experiments.





Fingerprint Raman spectrum of nanocrystalline Mo_5O_{14}-type mixed oxide catalyst[1] (black) together with the in situ spectrum of our powder catalyst at 713 K (blue).





Sublimed crystals during reaction (black) seem to be the crystalline counterpart to the nanocrystalline industrial Mo-V-W mixed oxide (red).

Conclusions:

We have presented a method for the preparation of thin films, which have been used as a realistic model system for the mixed oxide catalysts used in partial oxidation reactions. A new type of micro-reactor has been tested successfully in the partial oxidation of propene at elevated temperatures and has shown to be suited for the application of in situ Raman spectroscopy. However, the reactor could be used for other optical spectroscopies as for example uv-vis spectroscopy. The obtained results together with the observation of the increasing activity when the catalyst is close to sublime let us believe that the active surface of mixed metal oxide catalysts used in selective oxidation reactions is actually a very dynamic one and probably not comparable to a stiff crystal structure. This would further imply that all the structural data which can be obtained from the catalyst surface must be seen as a snapshot of a dynamic structural process.

[1] G. Mestl, *J. Raman Spectrosc.* **33** (2002) 333.