In-situ Raman studies of molybdenum oxide based thin film and powder catalysts

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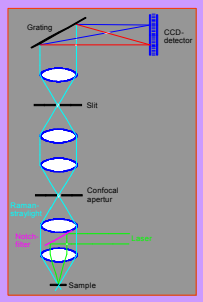
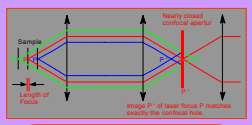
Introduction

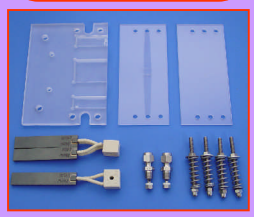
The partial oxidation of light alka(e)nes *e.g.* propa(e)ne to higher valuable chemicals *e.g.* acrolein and/or acrylic acid is technically performed over multi metal oxides (MMO). Although much effort has been made to understand the working mechanism of MMO's, the complexity of such systems has prevented 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 [1]. Our preliminary results are presented here.

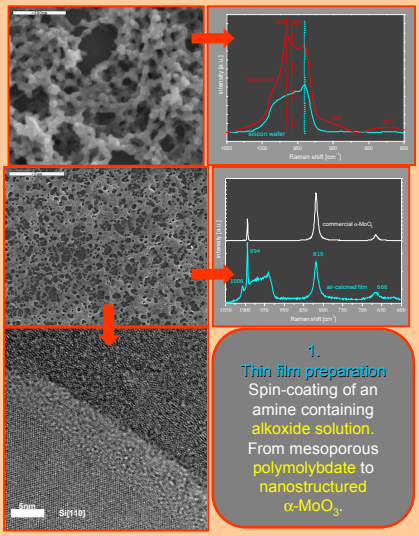




Experimental set-up

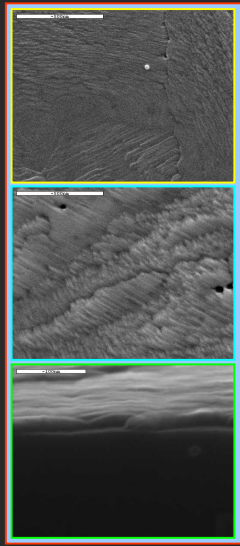
Sketch of the confocal principle used for the *in-situ* Raman experiments (λ = 623 nm). Fotographs of the new micro-reactor.
Feed: Σ1ml/min = [0,1C_3H_6 + 0,2 O_2 + 0,7 He]





1. Thin film preparation

Spin-coating of an amine containing alkoxide solution. From mesoporous polymolybdate to nanostructured α-MoO_3.

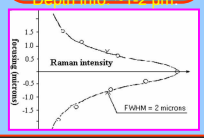


2. Thin film preparation

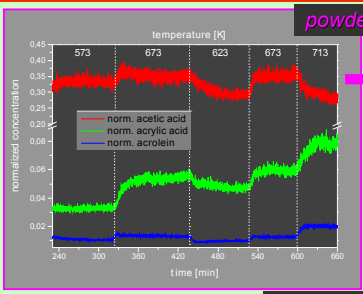
Novel thin film preparation via spin-coating of gelatine composite gels. Film thickness can be adjusted between 10 to 100 nm. Preparation of mixed metal oxides gives the possibility to mimic the aqueous solution chemistry on flat substrates.

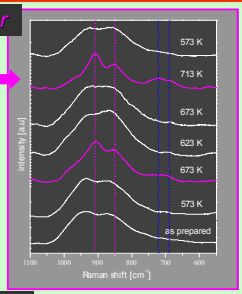
Have in mind...

Raman spectroscopy, (specially λ = 632 nm) though operated in a confocal mode, is not surface sensitive!!
Depth info: ~1-2 µm



powder

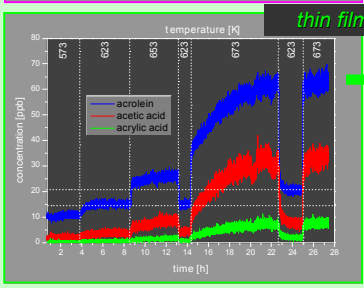


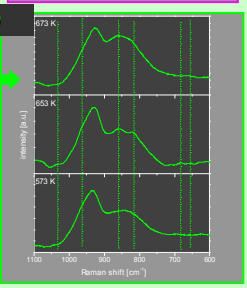


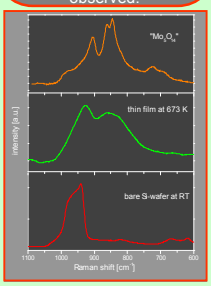
Powder vs. thin film

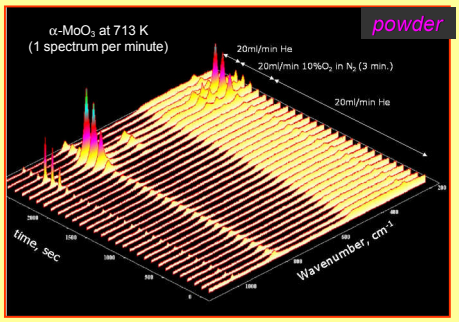
The same sample of a mixed $Mo_{0.68}V_{0.23}W_{0.09}$-oxide precursor [2] was used for powder and thin film preparation. Differences in the selectivities and the structural evolution between powder and thin film catalysts were found. For the bulk sample a reversible structural transformation was observed.

thin film





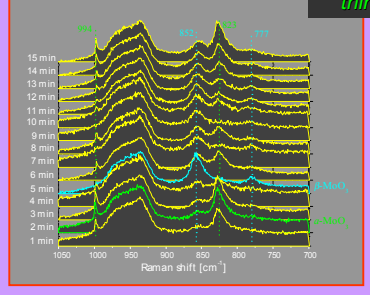




α-MoO_3 - an "oxygen sponge" at elevated temperatures

Between 673 and 723 K some α-MoO_3 samples release and incorporate within seconds oxygen. Raman cross section at λ=632 nm is very sensitive to electronic changes due to a resonance effect. Only small changes in the gas phase chemical potential induce significant changes not only at the surface but also in the bulk oxide. However the redox behaviour of various α-MoO_3 samples differs and strongly depends on their decomposition /formation pathway.

thin film



MoO_3 thin film at 593 K in air – oscillations between α- and β-MoO_3

Decomposition of a polymolybdate film in air is supposed to yield stable α-MoO_3. However an *in-situ* Raman measurement with a high time resolution at 593 K in air revealed that the system is oscillating between α- and β-MoO_3. The temperature seems to coincide with the arrangement/connection among the MoO_6-octahedra *e.g.* corner- vs. edge sharing. The structural transformation from pure corner shared (β-MoO_3) to corner and edge shared octahedra (α-MoO_3) induces the release of oxygen (defects) and will determine to a great extend the nature (*e.g.* crystallinity) of the formed α-MoO_3 (see above).

Conclusions

Thin films of complex oxides have been prepared and showed to be active in the selective oxidation of propene. A novel method for thin film preparation has been developed which allows to mimic the aqueous preparation routine of "real" catalysts. A new micro-reactor concept suitable for powder and thin film *in-situ* optical spectroscopy is presented. For very thin films (<100 nm) it is difficult to get reliable *in-situ* Raman results but the use of a uv-laser could increase the surface sensitivity. The activation of the thin films at high temperatures is accompanied by evaporation of the catalyst. In fact it seems that the activity starts to increase strongly when a certain vapour pressure of the oxide layer is reached. The deposits observed after reaction at the reactor cover are mainly *a*-MoO_3 but a variety of sub-oxides within the Mo_5O_{14}-type were also found. The question weather radical initiated gas phase reaction are involved needs to be investigated.

Literature

[1] J.W. Niemantsverdriet, A.F.P. Engelen, A.M. de Jong, W. Wieldraaijer, G.J. Kramer, Appl. Surf. Sci. **84** (1995) 339.
[2] S. Knobl, G.A. Zenkovets, G.N. Kryukova, O. Ovsitser, D. Niemeyer, R. Schlögl, and G. Mestl, J. Catal. **215** (2003) 177.