

# Synthesis and Characterisation of Planar Model Catalysts for Olefin Metathesis

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by

Karifala Dumbuya  
from Kukuna, Sierra Leone

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1<sup>st</sup> Referee: Prof. Dr. Klaus Christmann

2<sup>nd</sup> Referee: Prof. Dr. Hans-Heinrich Limbach

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*This work is dedicated to my dear Son Karif Babadee Dumbuya*

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## 5. Summary and outlook

The preparation and structural elucidation of the metathesis catalyst  $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$  have been carried out. Thin epitaxial films of  $\text{Al}_2\text{O}_3$  have been prepared and characterised with the help of a wide range of electron as well as photon spectroscopic methods. The metal complex was also synthesised and characterised with the aid of magnetic resonance and inductively coupled mass spectroscopies. Lastly, the catalyst system was studied and preliminary catalysis tests were performed. The most important results we obtained are summarised in the few paragraphs below:

- The combined XPS, LEED, AES and LEIS measurements show that controlled growth of  $\text{Al}_2\text{O}_3$  on a  $\text{Cr}_2\text{O}_3(0001)$  substrate could lead to epitaxial growth of planar and well ordered films of the former on the latter.
- Evaporation of Al with the substrate maintained 300 K does lead to the formation of an ultra thin oxide film, a process that tends to destroy the underlying oxide structure due to reaction between Al and substrate oxygen atoms. Further deposition of Al and annealing in oxygen to higher temperatures (up to 923 K) does not improve the situation. AES results show that metallic Al predominates the films and epitaxial growth is difficult to achieve.
- Co-deposition on the other hand at 825 K and  $5 \times 10^{-7}$  mbar oxygen led to the epitaxial growth of thin (up to 30 Å) films of  $\text{Al}_2\text{O}_3$  as shown by LEED, AES, XPS and LEIS. Furthermore, the results show that there is no mixing between the two oxides with increasing  $\text{Al}_2\text{O}_3$  coverage and that there is a layer-by-layer (Frank-van-der-Merwe) growth of the deposited film under these conditions. LEIS results convincingly exclude the presence of Cr in the uppermost atomic layers at a coverage of about 13 Å. CO adsorption results also show that the films may be O-terminated due to their complete inertness towards CO (9 and 25 L) in vacuum.
- XAFS and NMR results have shown a perfect agreement in that the allyl groups are bound to the Mo atom in the form of a symmetric  $\pi$ -system, whilst ICP-MS results reveal that the complex was very clean. A co-ordination number of 3.6 and Mo-C

distance of 2.35 Å are acceptable values and compare well with values found in the literature for similar compounds. A small modification of the synthesis procedure (0 °C instead of -20 °C; eqn. 3.1) helped to increase the yield from 28% to 33%.

- Our newly developed transfer system proved to be a simple but very efficient way of combining UHV and wet chemistry. With the aid of this system, a successful transfer of the complex on the thin alumina was accomplished as revealed by evidence from XPS, UPS, TID and MS. As far as we know, this is the first time such a reaction was undertaken and successfully executed. This combination is not only useful for such purposes; it could also be of immense use to synthetic organic chemists who are very much dependent on NMR. Very useful qualitative elemental (see the XP spectra of the Grignard reagent, fig. 3.25) analysis is possible with this system.
- Thermally induced desorption results indicate that up to 798 K, the active complex is still present in a hydrocarbon form on the surface and does not seem to have undergone any observable changes in its structural and chemical integrity in this temperature range studied as revealed by XPS and UPS. The major fragments H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>5</sub><sup>+</sup>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub> were similar to those observed for the real catalyst system in the same temperature range and therefore agree remarkably well with the literature.
- Dosing 3500 L propene at 300 K in the environment of the active complex hints at selective catalysis with butene and butane, i.e., C<sub>4</sub>-units being the main products. No definite conclusions can be drawn at this point, as these experiments need to be reproduced. Control reactions without the allyl complex under similar conditions would be necessary.

This work has paved the way for future work on the Mo(C<sub>3</sub>H<sub>5</sub>)<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> system based on model catalysis. Initial catalytic testing on the active catalyst has shown promising activity. However, these results are only in their infancy, as further control tests using pure recipient

and pure support under similar conditions need to be carried out in order to relate the observed metathesis activity to the active complex species prepared.

Lastly but not least, XAFS experiments need to be carried out on the active complex species so as to shed some light on the bonding scenario between Mo and the allyl units on the one hand and the alumina support on the other. In-situ XAFS monitoring of the catalysis is also necessary. Temperature programmed desorption (TPD) measurements are necessary for a thorough look at the energetics of the desorption process. Also, angle resolved photoemission (XPS, UPS) investigations on the active complex would be very useful.

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