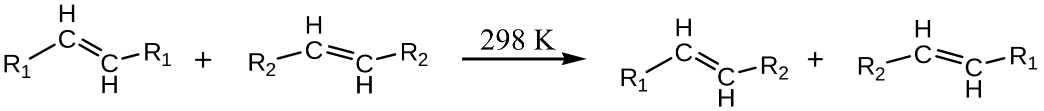
1. Introduction and Motivation

Allyl (C_nH_{n+2}) complexes of transition metals play an important role as catalysts in a variety of reactions, among them the alkene or propene metathesis[1] catalysed by $Mo(C_3H_5)_4$ at 273 and 298 K. Depending on the nature of the support, the molybdenum tetraallyl system catalyses other reactions as well, ranging from ammonia synthesis to polymerisation of butadiene, polymerisation of cycloolefins[2], etc. The catalytic activity of some selected systems based on $(C_3H_5)_4Mo$ are summarised in the table below:

Table 1.1[1] Some $Mo(C_3H_5)_4$ based catalysts

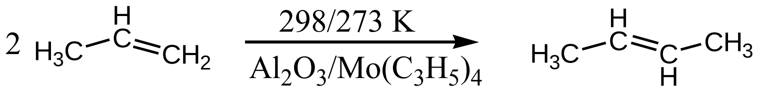
Catalyst system	**Catalytic activity**
$(C_3H_5)_4Mo$	-polymerisation of cycloolefins by ring opening mechanism
$(C_3H_5)_4Mo/Cl_2$	-polymerisation of butadiene
$(C_3H_5)_4Mo/HBr$	-disproportionation of propylene
$(C_3H_5)_4Mo/C_3H_5X$	-polymerisation of butadiene to a syndiotactic polymer with 97% to 99% 1,2 links.
$(C_3H_5)_4Mo/TiCl_3$	-polymerisation of propylene to isotactic polymer.
$(C_3H_5)_4Mo/SiO_2$ or Al_2O_3	On SiO_2: -disproportionation of propene at -60 to 200 °C to ethylene and butene. -disproportionation of hex-1-ene to C_2, C_6 and C_{10} olefins. On Al_2O_3: -propene methathesis at 273 K to ethylene, but-2-ene and but-1-ene. -transalkylation at 273 K to but-1-ene and i-butene. -methathesis of propylene at 273 K and a C_3H_6 pressure of 21 Torr.

Metathesis is simply the dismutative rearrangement of alkylidene units between two alkene moities[3,4], e.g.:



(1.1)

It is widely used in the chemical industry to upgrade alkenes when excess feedstocks of unsuitable chain length exist. For example, excess propylene supplies can be converted to ethylene and more valuable n-butenes.



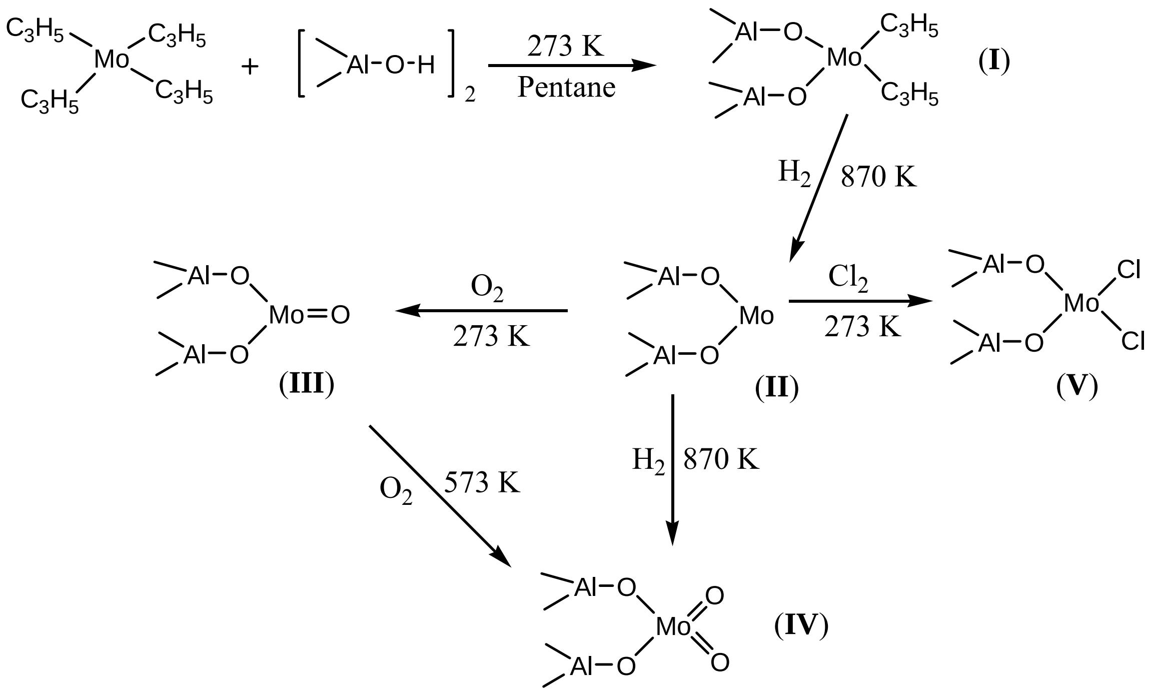
$$2\ H_3C-\overset{H}{C}=CH_2 \xrightarrow[Al_2O_3/Mo(C_3H_5)_4]{298/273\ K} H_3C-\overset{H}{C}=\underset{H}{C}-CH_3 \qquad (1.2)$$

The physicochemical interest in this reaction stems not only from the interesting reaction mechanism, but also from the potential use of the products in polymerisation and oxidation reactions[5]. As crude oil is becoming a very important factor that influences economic trends in global markets, the recycling of petroleum products is of increasing importance.

This work focuses on the synthesis and characterisation of the metathesis catalyst $Mo(C_3H_5)_4$ based on an Al_2O_3 support. The first stage involves the preparation and characterisation of planar thin alumina films from appropriate metal single crystal surfaces. It is embedded in a larger project aiming at the preparation of a model catalyst supported on a well defined planar Al_2O_3 support. Thin films were prepared in ultra high vacuum and have been characterised using Auger electron spectroscopy (AES), X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), low energy electron diffraction (LEED) and low energy ion scattering (LEIS) techniques.

The various active catalysts based on the $Al_2O_3/Mo(C_3H_5)_4$ system and which have already been investigated for real systems under various reaction conditions are presented in the series of chemical reactions below[6]:

All five species show different metathesis activities. The fixed catalyst (I) is known to be active for propene metathesis without any activation. Activation involves annealing in hydrogen to higher temperatures. Catalyst (III) was found to have a high activity in propene metathesis at 273 K. The catalysts with a dioxo-Mo^{6+} structure (IV) and Mo^{2+} (II) were almost inactive. Whilst (III) seems to have a higher activity, (I) has a higher selectivity[6].



Aluminium oxide has found wide spread application as a catalyst support material with γ-Al_2O_3 usually being the catalytically most suitable form of the oxide[7,8]. In order to disentangle the complicated mechanistic processes on such catalysts in detail, we decided to perform our studies under ultra-high vacuum (UHV) conditions and with single-crystal substrates. Due to its conductivity, a metal single-crystal substrate covered with a thin alumina film is more advantageous than a bulk alumina single crystal sample, which cannot routinely be investigated and characterised with the common electron spectroscopies due to charging effects. One could use an Al single crystal and grow, by appropriate oxygen exposure, an oxide layer on top. However, thickness (and morphology) of such a prepared film is difficult to control. In the literature, thin epitaxial films of alumina have almost entirely been prepared by selective oxidation of Al atoms present in a binary Al-Me single-crystal alloy, Me being, for example, nickel[9,10,11]. Nevertheless, the structure of these films, at least until recently, was not precisely determined, as it is characterised by a complicated structure. In our work, we take a different approach, viz., using a Cr(110) single crystal as a substrate on top of which chromia is formed by oxidation, which in turn serves as an appropriate substrate and template for the growth of alumina.

The second phase entails the synthesis and structural elucidation of the organometallic complex and the last and final phase concentrates on the combination of the phases (support and catalyst) in UHV, followed by a thorough structural investigation. The pure complex itself was investigated by NMR, XAFS and ICP-MS, whilst the $Al_2O_3/Mo(C_3H_5)_4$ system was investigated using XPS, UPS, TID and MS. By preparing a model system that combines a well-defined substrate with a $Mo(C_3H_5)_4$ deposition method used for practical catalysts, we have thus taken the first step towards bridging of the “gap” that exists between real and model catalysis.

The following work is composed of five sections. Sections I deals with a brief introduction and highlights some important properties of the Al_2O_3/Mo(allyl) system, while section II gives a brief theoretical treatise on all spectroscopic methods used in this work as well as some description of the UHV and other systems on which all investigations were carried out. In section III, the results will be presented, with brief descriptions of experimental procedures. Section IV deals with the discussion of important results with reference to existing literature and the final section (V) gives a brief resume of the whole work.