ABSTRACT. Non metathesis active molybdenum oxides supported on TiO₂, SiO₂, Al₂O₃, ZrO₂ and SnO₂ are changed by treating their surfaces with tetramethyltin (SnMe₄) into catalysts for terminal alkene metathesis, which accompany no hydrogen shift and isomerization of the produced alkenes. Making use of the advantage some applications are reviewed and the relative activities of metallacyclobutane (MCB) intermediates are elucidated on MoO₂.₉₂.₃/TiO₂-SnMe₄ with an equimolar mixture of perhydrogenated and perdeuterated alkenes. During treating these supported molybdenum oxides with SnMe₄, methane formed. This fact was interpreted such that α-hydrogen abstraction from methyls occurs (2CH₃ → CH₄ + CH₂) concurrently with picking up hydrogens from surfaces by methyls (CH₃ + H from surface → CH₄) and the CH₂ species thus formed are grafted onto Mo cations. If Mo=CH₂ species predominantly participate in propene metathesis, turnover frequencies are estimated to correspond to more than 0.3 on these supported Mo catalysts. The interaction between MoO₃/SiO₂ and SnMe₄ was studied with X-ray photoelectron spectroscopy.

1. INTRODUCTION

Metal alkylidene and metallacyclobutane intermediates are the most plausible species in alkene metathesis reaction on heterogeneous catalysts[1], although evidence for these species has come from homogeneous metathesis systems[2-4]. If these species are also significant on heterogeneous metathesis catalysts, terminal alkene metathesis is represented as shown in Scheme 1. Metal alkylidene
(M=CH₂) species react with CH₂=CHR to give ethylene and M=CHR through metallacyclobutane (MCB) intermediates (I), M=CHR then reacts with CH₂=CHR to return to M=CH₂ with the formation of RCH=CHR through a MCB intermediate (II). In this reaction sequence, the chain carrying M=CH₂ and M=CHR species participate in the cycle and two molecules of CH₂=CHR are converted into ethylene and internal alkene RCH=CHR.

![Diagram](image)

Scheme 1

If a heterogeneous supported catalyst has an activity to terminal alkene metathesis by the contact with a reactant alkene, the catalyst should have the ability to shift reaction of hydrogens in the alkene as a function of initial alkylidene generation as follows.

*) Initiation (initial alkylidene formation)