FULL PAPERS

Rhenium(VII) Oxide/Aluminum Oxide: More Experimental Evidence for an Oxametallacyclobutane Intermediate and a Pseudo-Wittig Initiation Step in Olefin Metathesis

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Abstract: Reactivity studies of the rhenium(VII) oxide/aluminum oxide olefin metathesis catalyst with various olefins show that initiation does not require an olefin with an allylic C−H bond, and therefore probably takes place *via* a pseudo-Wittig reaction. While it does not react with ethene in the absence of propene, Re_2O_7/Al_2O_3 catalyses the self-metathesis of *Z*-stilbene and its cross-metathesis with ethene.

Additionally, reaction of Re_2O_7/Al_2O_3 with *Z*-2-butene followed by ^{13}C di-labelled ethene shows that it contains only 2% of active sites.
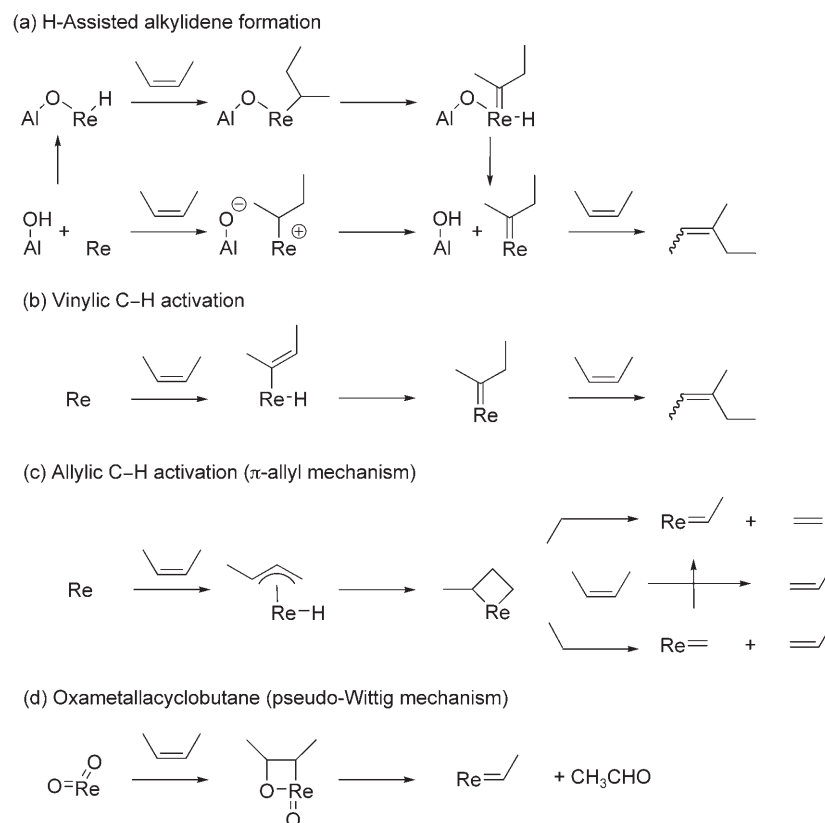
Keywords: initiation; olefin metathesis catalyst; pseudo-Wittig reaction; rhenium(VII) oxide/aluminum oxide

Introduction

With the recent developments in homogeneous catalysis, olefin metathesis has become central to the discovery and synthesis of new drugs and materials. Yet, it is still a key reaction in the petrochemical industry, especially because of the high demand for propene, which can be prepared by the cross-metathesis of ethene and butenes.[1] In this area, the process is usually based on the ABB Lummus technology, which relies on WO_3 supported on oxide materials, a catalyst efficient only at high temperatures. Of the various heterogeneous catalysts, $[Re_2O_7/Al_2O_3]$ is the only one working at room temperature and tolerating functional groups (when activated with organotin reagents).[2–4] The mechanism of olefin metathesis is now well-accepted,[5] and, despite years of research, the nature of the active site of Re_2O_7/Al_2O_3 is still unknown, probably because of the low content of active Re (2%), which has precluded a molecular understanding of this phenomenon.[6] In fact, several possible initiation steps have been proposed to explain the formation of the necessary propagating carbene species (Scheme 1):[7] a) H-assisted alkylidene formation,[8] b) C−H activation of a $C(sp^2)$−H bond followed by a σ-vinyl-alkylidene transposition,[9,10] c) C−H activation of an allylic C−H bond followed by the transformation of the π-allyl hydride intermediate into a metallacyclobutane (π-allyl mechanism)[7,11,12] and d) a pseudo-Wittig reaction.[13–17] Note that cases a, b and c require one to start with a reduced Re species.

Noteworthy, the current experimental data do not provide enough information to discriminate the various mechanisms and there are, in fact, contradictory results in the literature, which either favour or disfavour one or the other mechanism.[7,18,19] For example, in 1980 the degenerate metathesis of ethene, observed from a C_2D_4/C_2H_4 mixture, on Re_2O_7/Al_2O_3 was described, thus inferring a pseudo-Wittig pathway.[19] Later, no degenerate metathesis was observed when using a mixture of ^{13}C-di-labelled and unlabelled ethene: the non-reactivity of ethene inferred that it is necessary to have an allylic hydrogen in order to generate the active species.[7] More recent studies have shown that rhenium alkylidene complexes can be generated from the corresponding glycolate through an oxarhenacyclobutane, suggesting that the pseudo-Wittig pathway can indeed be a viable pathway of initiation.[15–17] Here below, a combined reactivity study of various olefins with Re_2O_7/Al_2O_3 shows that this catalyst contains only 2% of active sites, and the propagating alkylidene does not need to be formed through a π-allyl intermediate, so that the pseudo-Wittig reaction is a preferred initiation mechanism.

(a) H-Assisted alkylidene formation

(b) Vinylic C–H activation

(c) Allylic C–H activation (π-allyl mechanism)

(d) Oxametallacyclobutane (pseudo-Wittig mechanism)

Scheme 1.

Results and Discussion

First, we have re-investigated the initiation of Re_2O_7/Al_2O_3 with ethene. No label scrambling occurs upon contacting Re_2O_7/Al_2O_3 with an 1:1 mixture of non- and ^{13}C-di-labelled ethene for 17 h, while propene (590 Torr, 163 equivs.) is transformed into an equilibrated mixture of ethene and 2-butenes in 26 h at 30°C. Noteworthy, after evacuation of this equilibrated mixture, the same catalyst contacted with the 1:1 mixture of non- and ^{13}C-di-labelled ethene gives the statistical mixture of non-, mono- and di-^{13}C-labelled ethene isotopomers (1:2:1). This is consistent with what has been observed previously by Farona et al.,[7] and shows that propene can generate the propagating carbene, while ethene cannot [Eqs. (1) and (2)]!
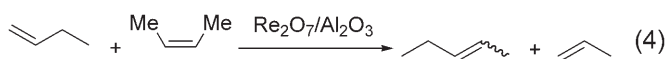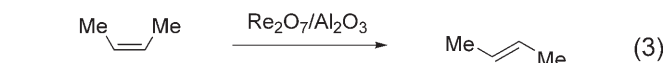
$$= \quad + \quad *= * \quad \xrightarrow{Re_2O_7/Al_2O_3} \quad N.R. \qquad (1)$$
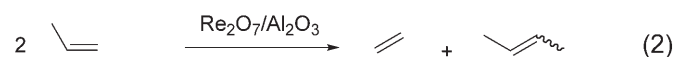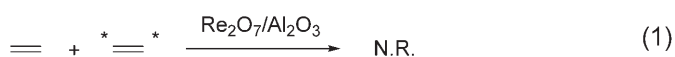
$$2 \quad \diagdown\!\!= \quad \xrightarrow{Re_2O_7/Al_2O_3} \quad \diagup\!\!\diagup \quad + \quad \diagdown\!\!\diagup\!\!\diagdown \qquad (2)$$

Additionally, when Re_2O_7/Al_2O_3 is contacted at 30°C for 45 min with 20 equivs. of Z-2-butene (99.2%) containing E-2-butene (0.66%, 0.13 equiv.), 1-butene (0.12%, 0.024 equiv.) and 2-methylpropene ($<0.01\%$, 1.1×10^{-3} equiv.), the reaction mixture is equilibrated as propene (0.026 equiv.), E-2-butene (11.3 equivs.), Z-2-butene (3.7 equivs.), Z- and E-2-pentene (0.018 equiv., 5:1 ratio); no ethene, 1-butene and 2-methylpropene being detected ($<0.005\%$, $<1 \times 10^{-4}$ equiv.). Beside the isomerization of Z-2-butene into E-2-butene by metathesis [Eq. (3)], initiation by mechanisms (a) and (b) should result in the formation of 3-methyl-2-pentene (Scheme 1), that by mechanism (c) (π-allyl intermediate) in a 2:1 mixture of propene and ethene, and that by mechanism (d) in the formation of acetaldehyde.

First, the formation of 2-pentenes (0.018 equiv.), not expected from 2-butenes even as an initiation product, and propene (0.026 equiv.) results from the cross-metathesis of 2-butenes with the traces amount of 1-butene [Eq. (4)] present in the original mixture (ca. 0.1%, 0.024 equiv.), and not from the initiation step.

Second, the absence of branched higher olefins excludes mechanisms (a) and (b) (Scheme 1 a b). Neither the absence of ethene, nor the presence of pro-

$$Me \diagdown\!\!= \diagup Me \quad \xrightarrow{Re_2O_7/Al_2O_3} \quad Me \diagdown\!\!\diagup\!\!\diagdown Me \qquad (3)$$

$$\diagdown\!\!\diagup \quad + \quad Me \diagdown\!\!= \diagup Me \quad \xrightarrow{Re_2O_7/Al_2O_3} \quad \diagup\!\!\diagdown\!\!\diagup\!\!\diagdown \quad + \quad \diagup\!\!\diagdown \qquad (4)$$

pene speaks for or against mechanisms (c) and (d), respectively. Indeed, mechanism (c) infers the formation of ethene (half the amount of propene, that is, 0.013 equiv.), but its cross-metathesis with 2-butene (20 equivs.) would lead to less than $<10^{-6}$ equiv. of ethene in an equilibrated mixture, which could not have been detected. Similarly, for mechanism (d), the putative ethylidene propagating species can readily be converted into propene (0.026 equiv.) by cross-metathesis with ethene resulting from the metathesis of 1-butene (0.024 equiv.). Thus, these data clearly exclude initiation mechanisms (a) and (b). Nonetheless, both mechanisms (c) and (d) are still consistent with the experimental data (Scheme 1), if propene is not formed exclusively by the cross-metathesis of 1-butene and 2-butenes (*vide infra*).

After evacuation of the gas phase and treatment under vacuum for 1 h at 10^{-6} Torr, contacting this catalyst with ^{13}C-di-labelled ethene (6.3 equivs.) shows the formation of ^{13}C-labelled propene (0.022 equiv.), un-labelled 2-butenes (0.002 equiv.) and ^{13}C-labelled 1-butene (0.0002 equiv.) (95% mass balance). First, no mono-labelled ethene has been detected [Eq. (5)], which shows that the methylidene species was present only in a small amount (as expected because it would have been generated only from 1-butene). Second, propene is obtained as a mixture of isotopomers: non-labelled ($<1\%$), mono-labelled (66%), di-labelled (18%) and tri-labelled (15%). Mono-labelled propene is probably obtained by cross-metathesis of di-labelled ^{13}C-ethene with the ethylidene propagating species [Eq. (6)], obtained from initiation with Z-2-butene, while di-labelled and tri-labelled propene are possibly formed by the decomposition of the metallacyclobutane intermediate as shown in Eqs. (7)–(9).[20] Third, the presence of unlabelled 2-butenes can result from the decomposition of the stable metallacyclobutane or to remaining physisorbed olefins as olefin adsorbs strongly on alumina (80 kJ mol^{-1}).[21,22] Finally, 1-butene (traces) is formed as a mixture of mono- (76%) and tetra-labelled (24%) isotopomers. The former results from the cross-metathesis of ^{13}C di-labelled ethene with a propylidene propagating species [Eq. (10)], while the latter is probably formed *via* oxidative coupling of two ^{13}C di-labelled ethenes on reduced Re species [Eq. (11)]. Noteworthy, the amounts of propene (*ca.* 0.02 equiv.) and 1-butene (0.0002 equiv.), resulting from the initiating carbene species, show that there are only about 2% of active sites as previously found by various methods.[6] Note also that this is in sharp contrast to what is observed for the well-defined silica-supported Re alkylidene complex, prepared by surface organometallic chemistry, for which initiation is nearly quantitative (0.7 equiv/Re, 70% of active site).[23,24]

Differentiating mechanisms (c) and (d) has been a problem for some years (Scheme 1): data are usually
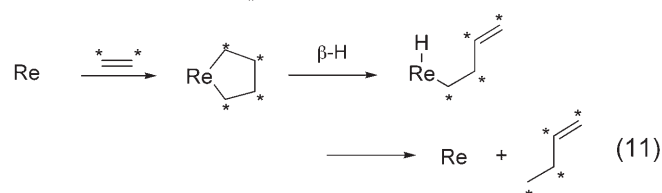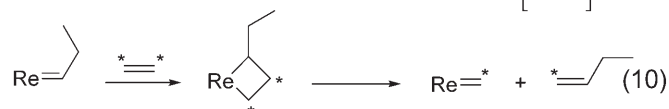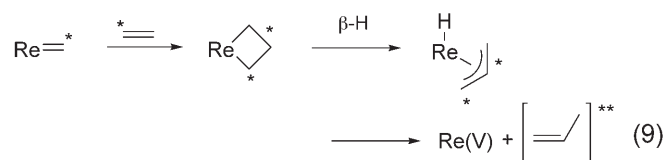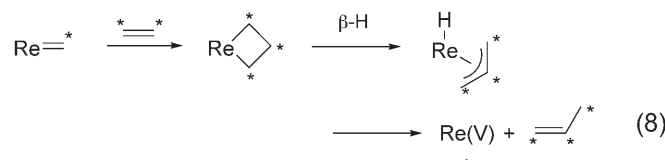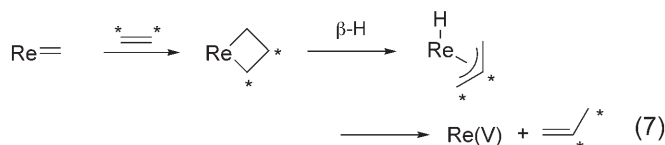
consistent with both mechanisms. Nonetheless, the π-allyl mechanism, requiring an allylic C–H bond, has been preferred because ethene does not initiate the propagating carbene species, while olefins having an α-H, for example, propene and butenes, do. We have therefore investigated the possibility of initiation with an olefin having no α-H, but more reactive than ethene: Z-stilbene.

When contacted with Re_2O_7/Al_2O_3 [Eq. (9)], Z-stilbene is converted into an equilibrated mixture of Z- and E-stilbenes in 72 h at 25 °C [Eq. (12)], while a much slower isomerization occurs on pure alumina pre-treated under the same conditions (Figure 1, i.e., relative initial rates are *ca.* 23), so that isomerization occurs mainly through metathesis.

Moreover, when the reaction mixture was further contacted with ethene (13 equivs., 450 Torr), styrene (4 equivs.) was formed, probably through the cross-metathesis of stilbene and ethene [Eq. (13)], two olefins having no allylic-H (note that no styrene is formed when stilbene and ethene are contacted with alumina under the same reaction conditions). While
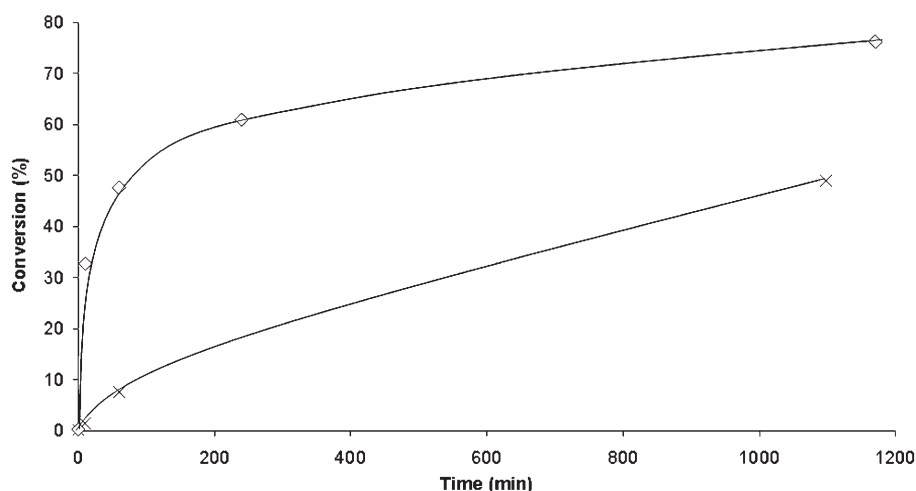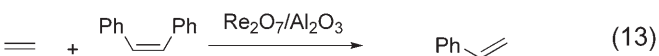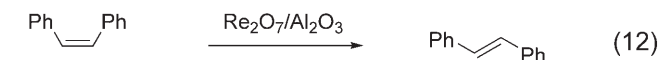
Figure 1. Comparison of the reactivity of *Z*-stilbene with Re_2O_7/Al_2O_3 and γ-Al_2O_3.

no aldehyde resulting from the pseudo-Wittig reaction could be detected (note that aldehyde reacts with alumina),[25] these data show that allylic C–H bonds are not necessary to generate the propagating species as required by the π-allyl mechanism (c), and that the pseudo-Wittig reaction is the only consistent initiation step (Scheme 1 d).

$$Ph \diagdown\diagup Ph \xrightarrow{Re_2O_7/Al_2O_3} Ph \diagdown\diagup Ph \qquad (12)$$

$$ {=\!=} \; + \; Ph \diagdown\diagup Ph \xrightarrow{Re_2O_7/Al_2O_3} Ph \diagdown\!\!\diagup \qquad (13)$$

Conclusions

In summary, we have shown that the initiation of Re_2O_7/Al_2O_3 does not require, *per se*, an olefin with allylic C–H bonds, and therefore the formation of the necessary carbene species probably involves a pseudo-Wittig reaction. Yet, this catalyst does not indeed catalyse the degenerate metathesis of ethene, probably because of its lesser reactivity. Finally, titration of the carbene propagating species shows that there are indeed only 2% of active sites per total Re, which makes the understanding of the nature of the active species of heterogeneous catalysts difficult.[4] We are currently investigating what the exact nature of the active sites is in order to develop well-defined heterogeneous catalysts through a molecular approach.[26]

Experimental Section

General Procedure

All experiments were carried out under dry and oxygen-free argon using either standard Schlenk or glove-box techniques

for the organometallic synthesis and catalytic tests. For the syntheses and the treatments of the surface species, reactions were carried out using high vacuum lines (1.34 Pa) and glove-box techniques. Gas phase analysis was performed on a Hewlett Packard 5890 series II gas chromatography (GC) apparatus equipped with a flame ionisation detector (FID) and a KCl/Al_2O_3 column (50 m × 0.32 mm). Liquid phase analysis was performed on a Hewlett Packard 6890 series II GC apparatus equipped with an FID detector and an HP5 column (30 m × 0.32 mm). Products were identified by GC/ MS (HP G1800 A) equipped with a KCl/Al_2O_3 or an HP5 column. Elemental analyses were performed at the University of Bourgogne, Dijon (H, C and N) and at the SCA in Solaize (Re).

Preparation and Activation of Re_2O_7/Al_2O_3

Re_2O_7/Al_2O_3 was activated under a flow of oxygen (20 mL min^{-1}) for 24 h at 500 °C (7.6 %wt Re).

Reaction of a 1:1 Mixture of Non-labelled and ^{13}C-Di-labeled C_2H_4 on Re_2O_7/Al_2O_3

Re_2O_7/Al_2O_3 (52 mg, 21 μmol of Re) was introduced under Ar in a 20.4-mL batch reactor. After evacuation of Ar, a mixture of ethene (107 Torr, 5.5 equivs.) and ^{13}C-di-labelled ethene (106 Torr, 5.5 equivs.) was added. After 17 h, the isotopomer distribution in the gas phase was unchanged according to GC/MS analysis (1:1 mixture of unlabelled and di-labelled ethene).

Reaction of Propene on Re_2O_7/Al_2O_3 Previously Treated with a Mixture of Non-labelled and ^{13}C-Di-labelled C_2H_4

Using the reaction mixture above, the mixture of ethenes was removed by trapping gases into another Schlenck tube using liquid nitrogen and then replaced by propene (287 Torr, 14.8 equivs.). The reaction was monitored by GC, which showed the conversion of propene into its metathesis products (26 h).

Reaction of a 1:1 Mixture of Non-labelled and ^{13}C-Di-labeled C_2H_4 on Re_2O_7/Al_2O_3 Previously Treated with Propene

Using the reaction mixture above, propene was evacuated for 1 h under vacuum, and a mixture of ethene and ^{13}C-di-labelled ethene was introduced into the reactor. After 1 h, the gas phase was analysed by GC and GC/MS, which showed that a statistical mixture of unlabelled, mono-labelled and di-labelled ethane was formed.

Reaction of Z-2-Butene on Re_2O_7/Al_2O_3 Followed by Contact with ^{13}C-Di-labelled C_2H_4

Re_2O_7/Al_2O_3 (52 mg, 21 µmol of Re) was introduced under Ar in a 22-mL batch reactor. After evacuation of the gas phase, Z-2-butene (360 Torr, 20 equivs.) was added. After 1 h, the gas phase was analysed by GC and GC/MS and then evacuated from the reactor under high dynamic vacuum for 1 h at 25 °C before being replaced by ^{13}C-di-labelled ethylene (114 Torr, 6.3 equivs.). After 30 min, the gas phase was analysed by GC and GC/MS.

Reaction of Z-Stilbene on Re_2O_7/Al_2O_3 Followed by Contact with C_2H_4

In a 22-mL batch reactor was introduced 100 mg of Re_2O_7/Al_2O_3 (40 µmol of Re) and 3 mL of a 7.5×10^{-2} M solution of Z-stilbene in cyclohexane (224 µmol). The reaction monitored by GC and GC/MS showed the isomerization of Z-into E-stilbene. After 72 h, ethene (450 Torr, 13 equivs.) was added at 25 °C, and the reaction was monitored by GC and GC/MS: TOF $= 7.3 \times 10^{-5}$ mol stilbene/(g cata·min) after 10 min.

Reaction of Z-Stilbene on Al_2O_3

In a 22-mL batch reactor was introduced 100 mg of γ-alumina$_{(500)}$ and 3 mL of a 7.5×10^{-2} M solution of Z-stilbene in cyclohexane (224 µmol). The reaction was monitored by GC and GC/MS: TOF $= 3.2 . 10^{-6}$ mol stilbene/(g alumina·min) after 10 min.

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