

# CH<sub>3</sub>-ReO<sub>3</sub> on $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: Activity, selectivity, active site and deactivation in olefin metathesis

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## Abstract

The active sites (15% of total Re) of CH<sub>3</sub>ReO<sub>3</sub> supported on alumina arise solely from the reaction of the C–H bond of CH<sub>3</sub>ReO<sub>3</sub> with reactive Al<sub>5</sub>–O<sub>5</sub> sites of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface to yield [Al<sub>5</sub>CH<sub>2</sub>ReO<sub>3</sub>], whereas the major species, inactive, corresponds to MeReO<sub>3</sub> chemisorbed through its oxo ligand(s) on Lewis acid sites of alumina. Monitoring the active sites of CH<sub>3</sub>ReO<sub>3</sub> supported on alumina by solid-state NMR spectroscopy shows that no carbenic signals are observed and that the resting states of the catalyst in the metathesis of propene correspond to  $\mu$ -methylene and  $\mu$ -ethylidene species, so that the propagating carbenic species are likely formed only in the presence of olefins. Although this system is highly active in the metathesis of propene, with initial rates similar to some of the best catalysts, it undergoes fast deactivation, which is due to the propene metathesis products, most likely ethene.

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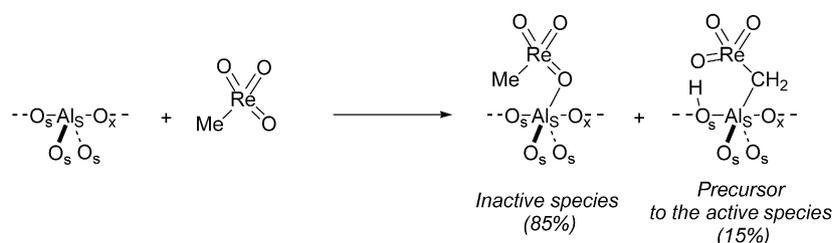
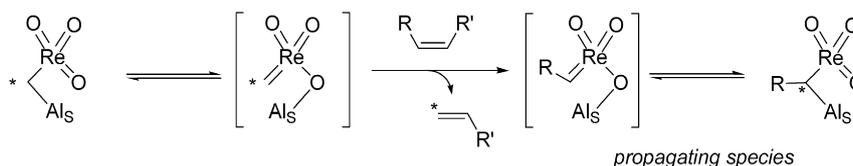
**Keywords:** Heterogeneous catalysis; Olefin metathesis; Methyl trioxorhenium; Alumina; Active site; Flow kinetic; Deactivation

## 1. Introduction

Olefin metathesis (OM) has been a very important industrial process since the discovery of the first heterogeneous OM catalysts [1], and today it is associated with crackers in petrochemical plants to improve the yield of propene through the cross-metathesis of ethene and 2-butenes [2]. Of the various classical heterogeneous OM catalysts, Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> is the only one that works efficiently at room temperature [3,4]. Moreover, this heterogeneous catalyst also can be used to convert oleate esters [5] when activated by organotin agents, which are, however, detrimental to the regeneration process [6]. In contrast, in the early 1990s, Herrmann et al. showed that CH<sub>3</sub>ReO<sub>3</sub> supported on silica–alumina is a highly active metathesis catalyst for functionalized olefins, without the need for an additional co-

catalyst [7]. Activity has been associated with the Lewis acidity of the support [8], and in fact active systems based on CH<sub>3</sub>ReO<sub>3</sub> use Lewis acid-containing supports [8–12]. In all these systems, the structure of the active site(s) and the involvement of the methyl as the source of the carbene have long been a matter of debate. Using spectroscopic (IR, NMR and EXAFS) reactivity and molecular modeling studies, we recently showed that the active sites of CH<sub>3</sub>ReO<sub>3</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-(500) arise from the methyl and corresponds to only a minor surface species, [Al<sub>5</sub>CH<sub>2</sub>ReO<sub>3</sub>], present only as ca. 15% of all Re (Scheme 1) [13]. This species results from the C–H activation of the methyl ligand of CH<sub>3</sub>ReO<sub>3</sub> onto reactive Al<sub>5</sub>–O sites of alumina (where Al<sub>5</sub> denotes surface aluminum sites) [14], thus yielding a  $\mu$ -methylene bridge species [Al<sub>5</sub>CH<sub>2</sub>ReO<sub>3</sub>] that displays a characteristic <sup>13</sup>C NMR signal at 66 ppm [13]. Note that no Re alkylidene has been observed at lower fields (180–400 ppm) [15], and that the  $\mu$ -methylene species is exchanged on contacting <sup>13</sup>C-labeled ethene with CH<sub>3</sub>ReO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-(500), demonstrating that this  $\mu$ -methylene species

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Scheme 1. Grafting of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$ .Scheme 2. Proposed active and inactive sites for the  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$ .

corresponds to the resting state of the catalyst and that the alkylidene species is probably formed in situ in the presence of olefins (Scheme 2).

Here we present a detailed kinetic study of the propene metathesis in a flow reactor (effect of time on stream and space time velocities) and an investigation of the active sites and their life cycle by titration studies and by solid-state NMR spectroscopy.

## 2. Experimental

### 2.1. General procedure

All gases were purified on R-3/11 provided by BASF and MS 4 Å before use. Gas-phase analysis was performed on a Hewlett–Packard 5890 series II gas chromatograph equipped with a flame ionization detector and a  $\text{KCl}/\text{Al}_2\text{O}_3$  on fused silica column (50 m  $\times$  0.32 mm).

#### 2.1.1. Solid-state NMR spectroscopy

All solid-state NMR spectra were recorded under MAS ( $\nu_R = 10$  kHz) on a Bruker Avance 500 spectrometer equipped with a standard 4-mm double-bearing probe head (125.73 MHz for  $^{13}\text{C}$ ). The freshly prepared samples were introduced in the 4-mm zirconia rotor in a glove box and tightly closed. Compressed air was used for both bearing and driving the rotors. Chemical shifts are reported in ppm downfield from  $\text{Si}(\text{CH}_3)_4$  ( $\pm 0.1$  and 1 ppm for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, respectively). The typical cross-polarization sequence was used for the  $^{13}\text{C}$  CP MAS NMR spectra:  $90^\circ$  proton pulse, cross-polarization step to carbon spins, and detection of the carbon magnetization under proton decoupling TPPM-15 [16]. For the CP step, a ramp radio frequency (rf) field centered at  $\nu^{\text{CP}} = 60$  kHz was applied on protons, whereas the carbon rf field was matched to obtain the optimal signal. The contact time for CP was set to 2 ms. An exponential line broadening of 80 Hz was applied before Fourier transform. All other details are given in the figure captions.

### 2.2. Preparation of $\gamma\text{-Al}_2\text{O}_3(500)$

$\gamma\text{-Al}_2\text{O}_3$  from Degussa was calcined at  $500^\circ\text{C}$  in dry air for 18 h and then treated at  $500^\circ\text{C}$  under vacuum (0.13 mPa) for 18 h to give  $\gamma\text{-Al}_2\text{O}_3(500)$  (105  $\text{m}^2/\text{g}$ ).

### 2.3. Reaction of $\gamma\text{-Al}_2\text{O}_3(500)$ with $\text{CH}_3\text{ReO}_3$

$\gamma\text{-Al}_2\text{O}_3(500)$  (1 g) was contacted, while stirring, with 100 mg of  $\text{CH}_3\text{ReO}_3$  at  $25^\circ\text{C}$ . After 3 h, removal of the excess of molecular complex was performed by reverse sublimation, and the resulting solid was then treated under vacuum (0.13 mPa) for 3 h. Elemental analysis: Re 3.8 wt%.

### 2.4. Metathesis of propene catalyzed by $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$

$\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$  (50 mg, 10.2  $\mu\text{mol}$  of Re) was introduced under Ar in a 195-mL batch reactor. After evacuation of Ar, 533 Torr of propene (547 equiv) was added. During the reaction at  $25^\circ\text{C}$ , aliquots were expended in a small volume, brought to atmospheric pressure, and analyzed by gas chromatography (GC).

### 2.5. Metathesis of ethyl oleate catalyzed by $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$

Into a 22-mL batch reactor was introduced 104 mg of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$  (21.4  $\mu\text{mol}$  of Re) and 2.8 mL of a 0.8 M solution of ethyl oleate in pentane (2.24 mmol). During the reaction at  $25^\circ\text{C}$ , aliquots (1 to 2 drops) were taken, diluted in pure solvent (0.2 mL), and analyzed by GC.

### 2.6. Reaction of $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$ with Z 2-butene followed by contact with $^{13}\text{C}$ di-labeled ethene (titration of active sites)

$\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$  (98 mg, 20  $\mu\text{mol}$  of Re) was introduced under Ar in a 22-mL batch reactor. After evacuation of the gas phase, Z 2-butene (44 Torr, 2.6 equiv) was added. After

30 min, the gas phase was analyzed by GC and GC/MS and then evacuated under high dynamic vacuum for 1 h at 25 °C before being replaced by  $^{13}\text{C}$ -di-labeled ethene (20 Torr, 1.2 equiv). After 30 min, the gas phase was analyzed by GC and GC/MS.

### 2.7. Reactivity of $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$ with $^{13}\text{C}$ mono-labeled propene for 15 min followed by contact with $^{13}\text{C}$ di-labeled ethene and unlabeled ethane

Into a 22-mL batch reactor was introduced, under Ar,  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  (262 mg, 53.6  $\mu\text{mol}$  of Re). After evacuation of Ar, 22 Torr of  $^{13}\text{C}$  mono-labeled propene (0.48 equiv) was added. After 15 min, the gas phase was analyzed by GC and GC/MS, and then evacuated from the reactor under high dynamic vacuum for 1 h at 25 °C. Part of the used catalyst (86 mg) was used to prepare the NMR sample and the remaining part of the solid (176 mg, 36  $\mu\text{mol}$  of Re) was contacted with unlabeled ethylene (33 Torr, 1.08 equiv). After 15 h, the gas phase was analyzed by GC and GC/MS, and the powder was analyzed by solid-state NMR spectroscopy. The same procedure was used for contact with  $^{13}\text{C}$  di-labeled ethene.

### 2.8. Metathesis of propene in a flow reactor catalyzed by $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$

For each reaction, the flow rates were controlled by a mass-flow controller (Brooks); they were in the range of 6–500 mL/min. The catalyst was first loaded in the reaction chamber in a glove box (31 mg, 6.3  $\mu\text{mol}$  of Re). The isolated reaction chamber was then connected with the reactor system, the propene pressure was set to 1 bar, and the flow rate was set to 34.5 mL/min. After the tubes were flushed with propene (purified on R-3/11 from BASF and MS 4 Å) for 2 h, the reaction chamber valve was opened ( $t = 0$ ), and the temperature was set to 30 °C. The outlet flow was analyzed by online GC.

### 2.9. Simulation of deactivation

Deactivation was modeled by numerical simulation of the conversion of propene as a function time ( $A$ ) based on  $A_0$  (the initial conversion of propene, which is proportional to the number of active sites  $\{A \propto [\text{cat}]$  in Eqs. (1)–(3) at  $t = 0$  min),  $k$  (the rate constant of deactivation), and  $[=]$ , the concentration of ethene measured in the feed (/mol):

$$-\frac{\Delta A}{\Delta t} = k[A], \quad (1)$$

$$-\frac{\Delta A}{\Delta t} = k[A][=]_{\text{measured}}, \quad (2)$$

$$-\frac{\Delta A}{\Delta t} = [A] \times (k[=]_{\text{measured}} + k'). \quad (3)$$

### 2.10. Metathesis of ethene followed by that of propene in a flow reactor catalyzed by $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$

After  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  (60 mg, 12  $\mu\text{mol}$  of Re) was loaded in the reactor in a glove box, the reactor was connected to the

ethene line, the pressure was set to 1 bar, and the tubes were flushed for 2 h before the inlet valve was opened. The temperature was set to 30 °C, and the flow rate was set to 5 mL/min. After 1188 min, the ethene valve was closed and the propene valve was opened. The propene pressure was set to 1 bar, the temperature to 30 °C, and the flow rate to 77 mL/min. The reaction was monitored by online GC.

### 2.11. Metathesis of Z 2-butene followed by that of propene in a flow reactor catalyzed by $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$

After  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  (58 mg, 1.18  $\mu\text{mol}$  of Re) was loaded into the reactor in a glove box, the reactor was connected to the Z 2-butene line, the pressure was set to 1 bar, and the tubes were flushed for 2 h before the inlet valve was opened. The temperature was set to 30 °C; the flow rate, to 5 mL/min. After 1188 min, the ethene valve was closed and the propene valve was opened. The propene pressure was set to 1 bar, the temperature to 30 °C, and the flow rate to 77 mL/min. The reaction was monitored by online GC.

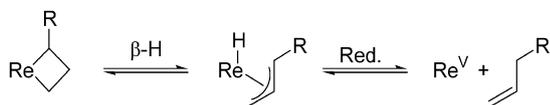
## 3. Results and discussion

### 3.1. Preliminary tests of olefin metathesis activity of $\text{CH}_3\text{ReO}_3$ supported on $\gamma\text{-Al}_2\text{O}_3$ ( $_{(500)}$ ) $\{\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$ ( $_{(500)}$ )}

At room temperature, the  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  ( $_{(500)}$ ) system rapidly transformed 550 equiv of propene into a thermodynamic mixture of ethene and 2-butene, completing 190 turnovers (TON) in less than an hour, which is  $\sim 100$  times faster compared with  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ . Moreover, at room temperature,  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  ( $_{(500)}$ ) also equilibrates 100 equiv of ethyl oleate into a thermodynamic mixture ( $\sim 1:1$ ) of 9-octadecenes and diethyl 9-octadecenedioates in about 11,520 min (8 days). The initial turnover frequency (TOF) is ca. 0.38 TON/min (Fig. S1), which is much slower than that obtained for propene metathesis (ca. 28 TON/min, vide infra). Although inefficient compared with well-defined homogeneous [17–21] and silica-supported systems [22–26], it is noteworthy, because  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  is practically inactive (ca. 1 TON) without the use of a promoter such as alkyl tin reagents [5,27].

### 3.2. Active site, propagating species, and resting states in propene metathesis of $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$ ( $_{(500)}$ )

Although a recent study showed that  $[\text{Al}_5\text{CH}_2\text{ReO}_3]$  corresponds to an active species, pulses of Z 2-butene and  $^{13}\text{C}$  di-labeled ethene were used to evaluate whether the oxo ligands are also involved in the generation of the active sites, as well as to obtain complementary active site titration experiments [28,29]. When  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  is contacted with 2.6 equiv of Z 2-butene, 0.23 equiv of propene/Re and 0.082 equiv of 2-pentene/Re are formed, besides a fast Z/E isomerization of 2-butene through metathesis. The 2-pentenes (0.082 equiv) and a fraction of propene (ca. 0.082 equiv) are likely formed through the cross-metathesis of 2-butenes with 1-butene, present as traces in commercial Z 2-butenes (0.12%



Scheme 3. Possible way of decomposition of metallacyclobutanes.

of 1-butene, i.e., 0.003 equiv) and formed in situ by isomerization of 2-butenes on acid sites. The remaining part of propene (0.15 equiv) is formed by cross-metathesis of 2-butenes with  $[\text{Al}_5\text{CH}_2\text{ReO}_3]$ . Moreover, after evacuation of the gas phase, contacting this catalyst with 99%  $^{13}\text{C}$  di-labeled ethene gave 0.11 equiv of  $^{13}\text{C}$  mono-labeled propene along with 0.002 equiv of  $^{13}\text{C}$  mono-labeled 1-butene. Whereas  $^{13}\text{C}$  mono-labeled propene is expected from the cross-metathesis of an ethylidene propagating species and *Z* 2-butene, the presence of small amount of  $^{13}\text{C}$  mono-labeled 1-butene shows that propylidene propagating species are also present, as expected from the presence of 1-butene in *Z* 2-butene. Noteworthy, the number of active sites determined by this method is close to that obtained previously with  $^{13}\text{C}$ -di-labeled ethene (ca. 15% of total Re) [13], so that the oxo ligands are not involved in formation of the active species (in contrast to  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  [29]), so that the coordinated  $\text{CH}_3\text{ReO}_3$  on Lewis acid sites does not lead to active species.

For propene metathesis, two propagating carbenic species (methylidene and ethylidene) are expected. Whereas the former has been observed as the  $\mu$ -methylene species,  $[\text{Al}_5\text{CH}_2\text{ReO}_3]$ ,  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  was also contacted with 0.48 equiv of propene monolabeled on position 2 ( $2\text{-}^{13}\text{C}$  propene) to observe selectively the ethylidene species (or the corresponding resting state). After 15 min, the reaction mixture was composed of unlabeled ethene (0.1 equiv),  $^{13}\text{C}$  di-labeled *E* 2-butene (0.07 equiv), and  $^{13}\text{C}$  di-labeled *Z* 2-butene (0.02 equiv), the expected olefin metathesis products, along with  $^{13}\text{C}$  mono-labeled *E* 2-butene ( $4.2 \times 10^{-3}$  equiv) and  $^{13}\text{C}$  mono-labeled 1-butene ( $9.4 \times 10^{-4}$  equiv). These minor products are possibly formed through the decomposition of metallacyclobutane intermediates, as proposed previously (Scheme 3). The solid-state  $^{13}\text{C}$  CP MAS NMR spectrum of the catalyst displays a large, intense signal at 85 ppm along with a weaker broad signal at 30 ppm and a sharp signal at 146 ppm (Fig. 1a), no signal associated with carbene ligands being detected at lower fields. The two signals at 146 and 22 ppm also are observed when  $\gamma\text{-Al}_2\text{O}_3(500)$  is treated with mono-labeled  $2\text{-}^{13}\text{C}$  propene (Fig. 1b), and thus can be attributed to the  $\text{C}_{\text{sp}^2}\text{-H}$  and the  $\text{C}_{\text{sp}^3}\text{-H}$  carbons of adsorbed olefins [30]. Whereas the former is clearly observed in the  $^{13}\text{C}$  NMR spectrum of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$  contacted with monolabeled  $2\text{-}^{13}\text{C}$  propene, the latter is hidden under the broad peak at 30 ppm, which is associated with the major species of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$  (the coordination adduct of  $\text{CH}_3\text{ReO}_3$  onto the Lewis acid sites) [13]. The lower amount of adsorbed olefins on  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$  as evidenced by solid-state NMR is consistent with its lower acidity; in fact, this system has no Brønsted acidity and contains less Lewis acid sites than  $\text{Al}_2\text{O}_3$  (Fig. S2), which in turn is consistent with the fact that  $\text{CH}_3\text{ReO}_3$  has reacted with  $\text{Al}_5\text{-O}_5$  surface sites as-

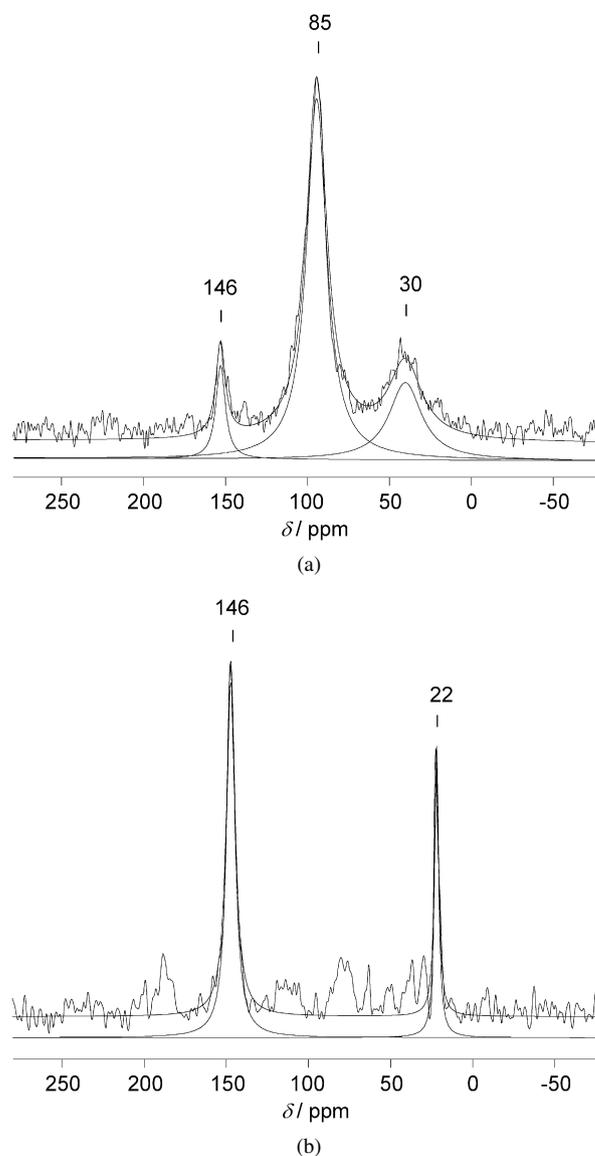


Fig. 1. (a)  $^{13}\text{C}$  CP-MAS solid state NMR spectrum of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$  after contact with mono-labeled  $2\text{-}^{13}\text{C}$  propene, under MAS of 10 kHz. The number of scan was 26,000 and the recycle delay was set to 2 s. A CP step of 2 ms was used. (b)  $^{13}\text{C}$  CP-MAS solid state NMR spectrum of  $\gamma\text{-Al}_2\text{O}_3(500)$  after contact with mono-labeled  $2\text{-}^{13}\text{C}$  propene under MAS of 10 kHz. The number of scan was 5021 and the recycle delay was set to 4 s. A CP step of 2 ms was used.

sociated with a strong Lewis acid aluminum center [13,14]. The signal at 85 ppm, down-field by 19 ppm with respect to  $[\text{Al}_5\text{CH}_2\text{ReO}_3]$ , is only present on  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3(500)$  contacted with mono-labeled  $2\text{-}^{13}\text{C}$  propene, and is assigned to  $[\text{Al}_5\text{CH}(\text{CH}_3)\text{ReO}_3]$ , resulting from the exchange of the  $\mu$ -methylene in  $[\text{Al}_5\text{CH}_2\text{ReO}_3]$  by an ethylidene fragment through cross-metathesis (Scheme 2,  $\text{Al}_5\text{CH}(\text{R})\text{-ReO}_3$ ,  $\text{R} = \text{CH}_3$  and  $\text{R}' = \text{H}$ ). Note also the absence of formation of oligomers upon treatment of  $\text{Al}_2\text{O}_3$  and  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  with propene, in contrast to what has been observed with ethene. Further contacting this solid with 1.08 equiv of  $^{13}\text{C}$  di-labeled ethene reveals both peaks at 66 and 85 ppm, which can be assigned to  $[\text{Al}_5\text{CH}_2\text{ReO}_3]$  and  $[\text{Al}_5\text{CH}(\text{CH}_3)\text{ReO}_3]$ , the two

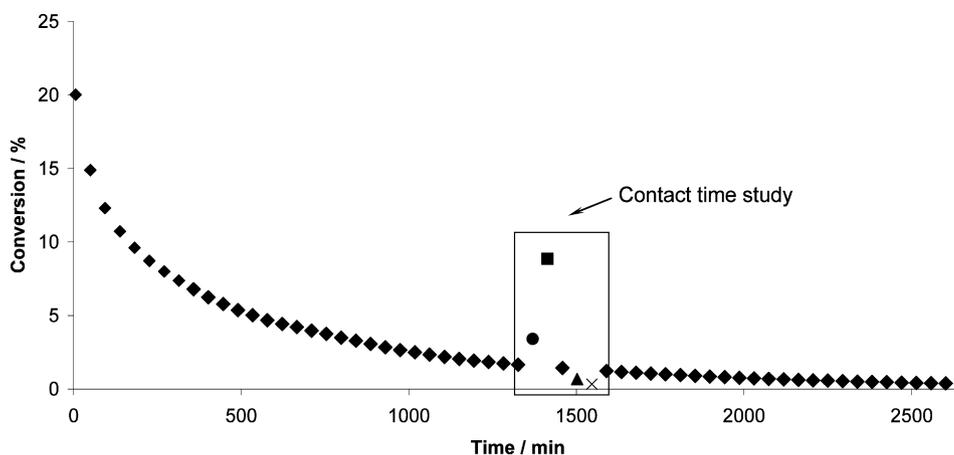


Fig. 2. Conversion as a function of time on stream at a flow rate of: (◆) 34.5, (●) 17, (■) 6.4, (▲) 77, and (×) 165 mL/min.

resting states of the expected propagating Re species associated with the metathesis of propene (Fig. S3, Scheme 2, R = H or CH<sub>3</sub>, respectively).

Finally, when CH<sub>3</sub>ReO<sub>3</sub>/Al<sub>2</sub>O<sub>3-(500)</sub> is treated first with <sup>13</sup>C mono-labeled propene for 15 min and then with unlabeled ethene (1.08 equiv), 0.05 equiv of mono-labeled propene/Re is detected. Considering the probable presence of a 1:1 mixture of methylene and ethylidene propagating species, and the titration of only the ethylidene species (formation of mono-labeled propene), the number of active sites has decreased from 15 to 10% of Re species, in agreement with partial catalyst deactivation. During this process, small amounts of unlabeled propene also are detected ( $6 \times 10^{-3}$  equiv), most likely formed by the decomposition of metallacyclobutanes as previously proposed (see Scheme 3, and vide infra for further comments on deactivation).

Overall, the active sites result from the methyl of CH<sub>3</sub>ReO<sub>3</sub> through the formation of a  $\mu$ -methylene complex, which can probably interconvert into an alkylidene species in the presence of olefins.

### 3.3. Activity, selectivity, and stability of CH<sub>3</sub>ReO<sub>3</sub>/Al<sub>2</sub>O<sub>3-(500)</sub> in the metathesis of propene as a function of time on stream

At 30 °C with a flow rate of 34.5 mL/min (227 mol propene/mol Re min), propene is transformed into a mixture of ethene and 2-butenes with an initial rate of 45 TON/min after 6 min (Fig. 2). Considering the amount of active sites at  $t = 0$  min (ca. 15%), the initial activity is at least 302 mol of propene transformed/min/active site, comparable to the best silica-supported well-defined systems [22–26] and much better than Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> (27 mol of propene transformed/min/active site considering 2% of active site) [28,29,31,32]. Over 530 min, conversion decreases from 20 to 5% due to a fast deactivation process. After 1330 min, a TON of 16,500 was achieved, corresponding to 110,000 TON/Re active site.

Noteworthy, a clear evolution of the selectivity in 2-butenes as a function of time (decreasing *E/Z* ratio) and conversion (increasing *E/Z* ratio) also is observed as the catalyst deactivates (Fig. 3). In addition, note that 1-butene is not detected

( $< 1 \times 10^{-4}\%$ ) and that isobutene is formed in only minute amounts (ca. 0.008%).

The change of selectivity at constant flow as a function of time on stream and deactivation can be explained according to the following hypotheses:

1. The catalyst has two types of two active sites, one more “*E* selective” and one more “*Z* selective,” with different lifetimes.
2. The nature of the Re-active site changes with time, leading to a more “*Z*-selective” catalysts (evolution of the structure).
3. The active site has an intrinsic selectivity that favors *Z* 2-butene, but a successive fast *Z*–*E* isomerization giving *E* 2-butene slows down with time, thus changing the selectivity as the catalyst ages. In the latter case, *Z/E* isomerization can occur through a degenerate metathesis reaction or can be acid-catalyzed. Therefore, it is important to distinguish the intrinsic selectivity of the catalyst (primary process) from the selectivity resulting from subsequent isomerization processes (secondary processes) or from a change of structure of the catalyst (Scheme 4).

Consequently, we have investigated the influence of the inverse space velocity on selectivity (contact time studies) to gain further insight into the catalytic system. Typically, the inverse space velocity is defined as a volume of catalyst crossed by a volume of reagent during a given unit of time:

$$vvh = \frac{V_{\text{cat}}}{F}, \quad (4)$$

where  $V_{\text{cat}}$  = volume of catalyst;  $F$  = flow rate expressed, e.g., in volume unit/h. It also can be expressed in mass or mol numbers:

$$mmh = \frac{M_{\text{cat}}}{D}, \quad (5)$$

where  $M_{\text{cat}}$  = mass of catalyst;  $D$  = flow rate expressed in mass unit/h, and they are all proportional. However, these definitions never take into account the number of active sites at a given time. Therefore, as the catalyst deactivates, the inverse

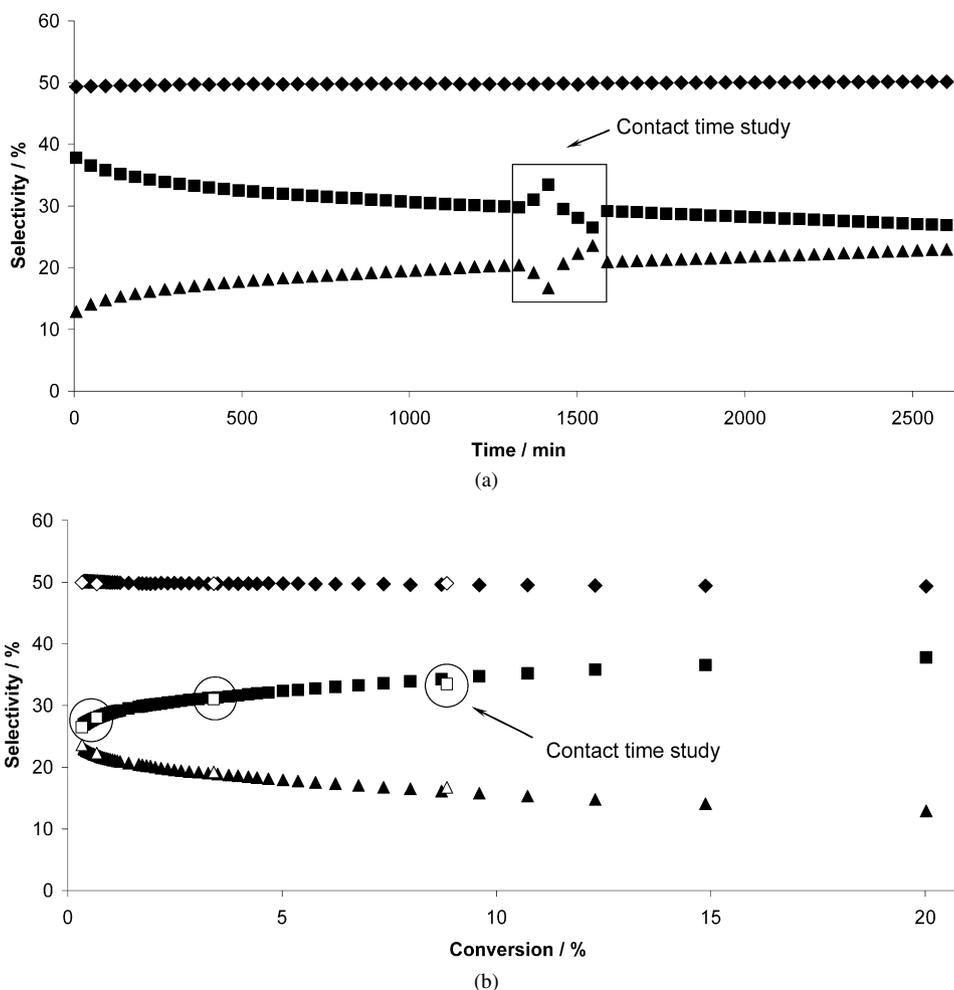


Fig. 3. Propene metathesis in a flow reactor: propene (34.5 mL/min; 227 mol P/(mol Re min)),  $P = 1$  atm, and  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3\text{-}(500)$  (31 mg). (a) Selectivity as a function of time: (◆) ethene, (■) *E* 2-butene, (▲) *Z* 2-butene. (b) Selectivity as a function of conversion: (◆) ethene, (■) *E* 2-butene, (▲) *Z* 2-butene.

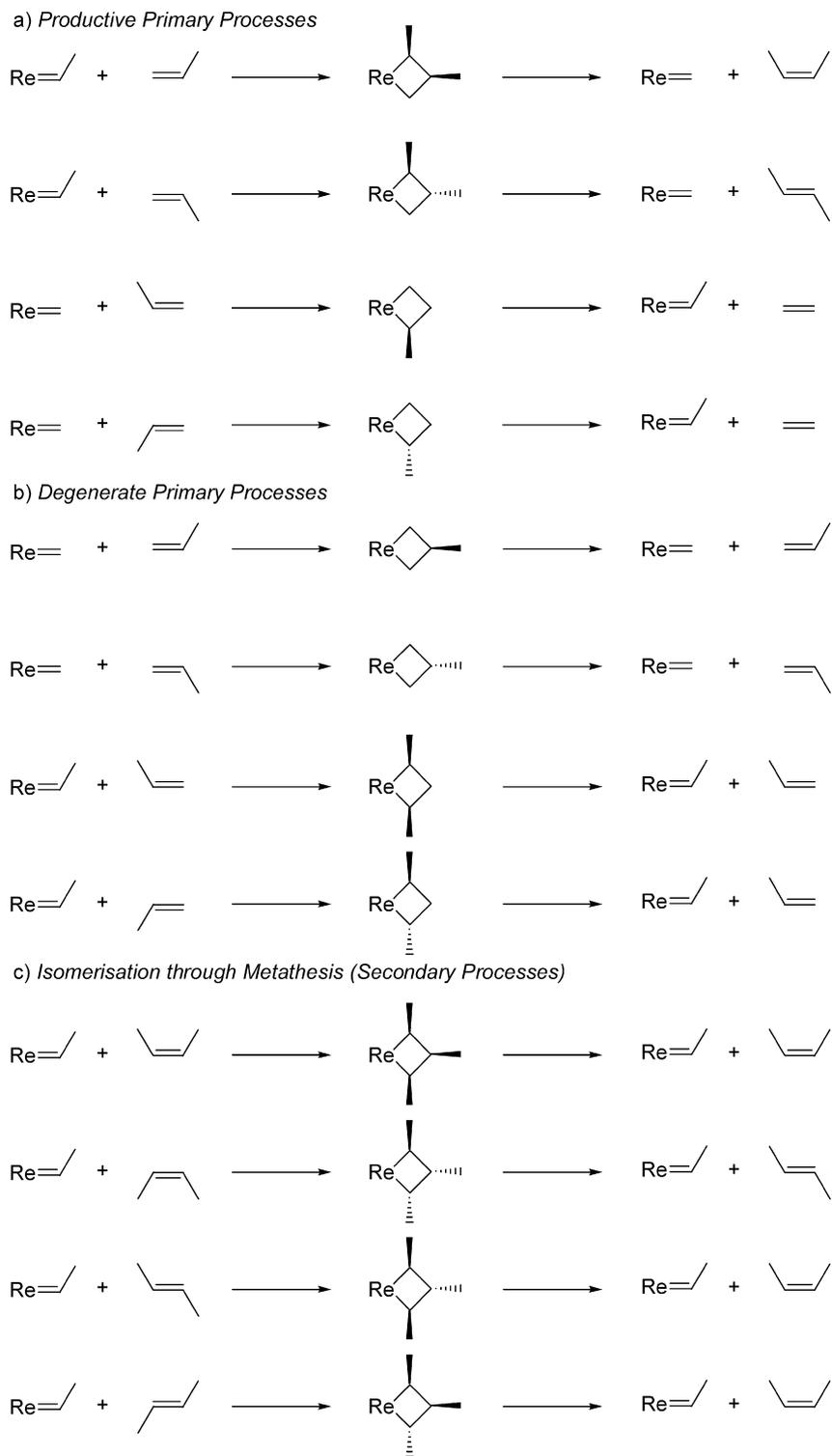
space velocity per active sites changes. To understand the system at a molecular level, it would be informative to express the inverse space velocity as a function of the number of active sites, hereinafter termed intrinsic contact time (ICT):

$$\text{ICT} = \frac{\text{AS}(t)}{F_m}, \quad (6)$$

where  $\text{AS}(t)$  = number of active sites over time;  $F_m$  = molar flow rate expressed in mol unit/h, but this value is difficult to obtain for heterogeneous catalysts, because doing so requires knowledge of the number of active sites at a given time. Note that if only one type of active site is present and if the reaction is not performed under mass transport limiting conditions, then conversion will be directly proportional to the number of active sites and thus can be used to monitor the ICT (vide infra).

Inverse space velocity studies show that the conversion varies linearly with respect to contact time: mass transport is therefore not rate limiting so that chemical information can be inferred (Figs. S4–S5). Conversely, inverse space velocity is also proportional to the mass of the catalyst and the flow rates on independent experiment, which further confirms that mass transport (intragranular diffusion) is not rate-limiting (Fig. S6).

Moreover, the same behavior has been observed when contact time studies are performed at two different time-on-stream periods (Figs. S7–S8). The *E/Z* ratio decreases at shorter contact times (moving away from the thermodynamic ratio of 3) but obtaining the intrinsic selectivity still requires the use of much shorter contact times. In addition, when the selectivities of 2-butenes are plotted as a function of conversion, all the data points for each butene isomer (including those obtained at various contact times) are aligned on the same curve (circled data, Figs. 3b and S8). Therefore, the *E/Z* ratio depends only on conversion, which is consistent with the presence of only one type of active site, not evolving (structurally) with time. Thus, the conversion is proportional to the number of active sites and thereby to the intrinsic contact time, so that reaching very low conversion should allow the intrinsic selectivity to be obtained (kinetic–product ratio). In fact, when the metathesis of propene is run at a higher flow rate of 77 mL/min (261 mol/(mol Re min)), the conversion decreases from 12 to 3% within 710 min (~12 h), and reaches 0.03% after about 12,000 min (200 h) (Fig. S9). At this conversion (0.03%), the *E/Z* ratio of 2-butenes decreases to about 0.42, a value probably very close to the kinetic ratio of 2-butenes (Fig. 4).



Scheme 4. (a) Productive, (b) degenerated, and (c) isomerization metathesis processes.

The need to use such low contact time to obtain the intrinsic selectivity is due to the strong adsorption of olefins on the alumina support ( $\Delta H \sim 80$  kJ/mol) [33]. In fact, it was previously shown that desorption can be rate-determining even under chemical regime for  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  [34,35], so that isomerization becomes faster than desorption; thus, the difficulty in obtaining the intrinsic selectivity at low contact time. Noteworthy,

the isomerization rate of *Z*-2-butene/g of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  is at least 15 faster than on  $\gamma\text{-Al}_2\text{O}_3\text{-(500)}$  alone, so that isomerization occurs mainly through olefin metathesis (Scheme 4). The kinetic ratio of 2-butenes (*E/Z* ratio  $\sim 0.42$ ) must be related to the structure of the active sites of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$ . Typically, terminal olefins give the *E* products as favored isomers (Scheme 5) [36], but it has been shown that in certain cases (and

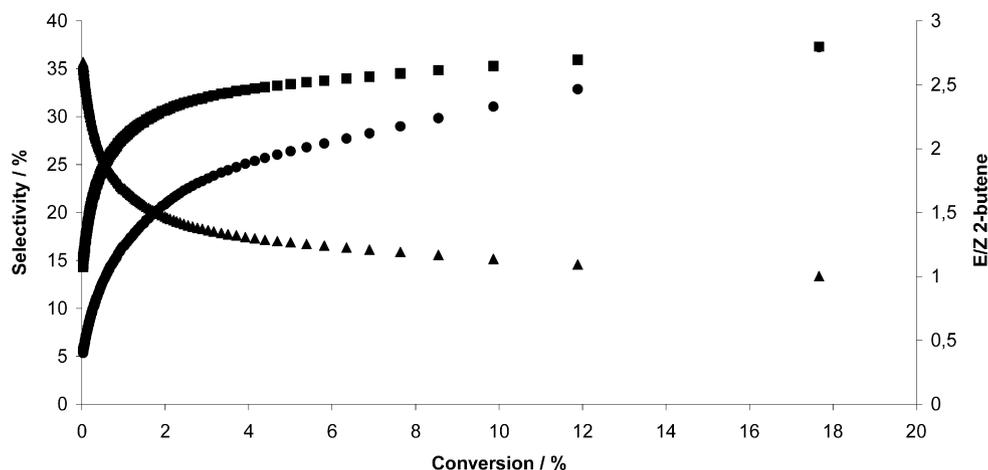
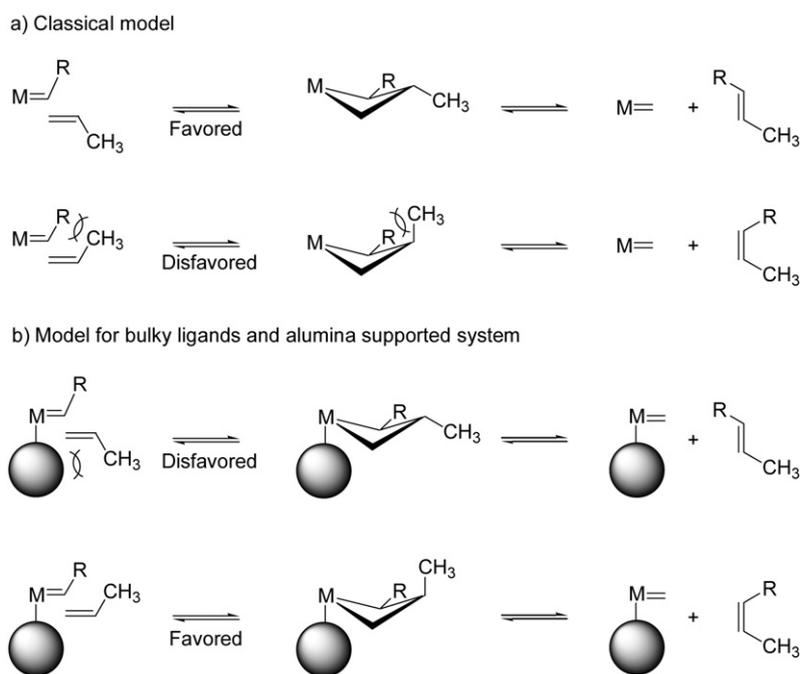


Fig. 4. Propene metathesis in a flow reactor: propene (77 mL/min; 261 mol P/(mol Re min)),  $P = 1$  atm, and  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_{3-(500)}$  (60 mg) (see Fig. S3 for conversion and selectivity as a function of time on stream). Selectivity as a function of conversion: (●) E/Z 2-butene ratio, (■) E 2-butene, (▲) Z 2-butene.



Scheme 5. Ways of approach of the olefin towards the metallic center.

typically for alumina-supported catalysts) [37], the Z isomer is preferred, and this can be associated with a favored pathway involving the approach of propene toward the ethylidene ligands, whose respective methyl substituents point away from the surface.

#### 3.4. Deactivation of $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_{3-(500)}$ in the propene metathesis

The deactivation of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  is relatively fast, and modeling this phenomenon shows that this process is much faster than a simple first order decay of the active site ( $e^{-ax}$ , Eq. (7), Fig. S10) and is faster at higher than at lower conversions. The major deactivation process cannot therefore be due to either a poison in the feed or to an intrinsic deactivation phe-

nomenon because both would only depend on the concentration of active sites for a constant flow of propene (of a given purity). A satisfactory model shows that deactivation is first order in the concentration in products or in one of the products formed, i.e. ethene and/or butenes (Eq. (8), Fig. 5a, see Section 2 for more details on the simulation). Ethene has been used for simulation, but using 2-butenes leads to the same expression for the deactivation rate law (see Fig. S11). This model can be improved if one includes a second deactivation pathway, such as a first order decay of the number of active sites (Eq. (9), Fig. 5b). Overall, the first order deactivation in the concentration in ethene and/or butenes requires that they are involved in this process (Eqs. (8) and (9)).

$$-\frac{d\text{cat}}{dt} = k[\text{cat}], \quad (7)$$

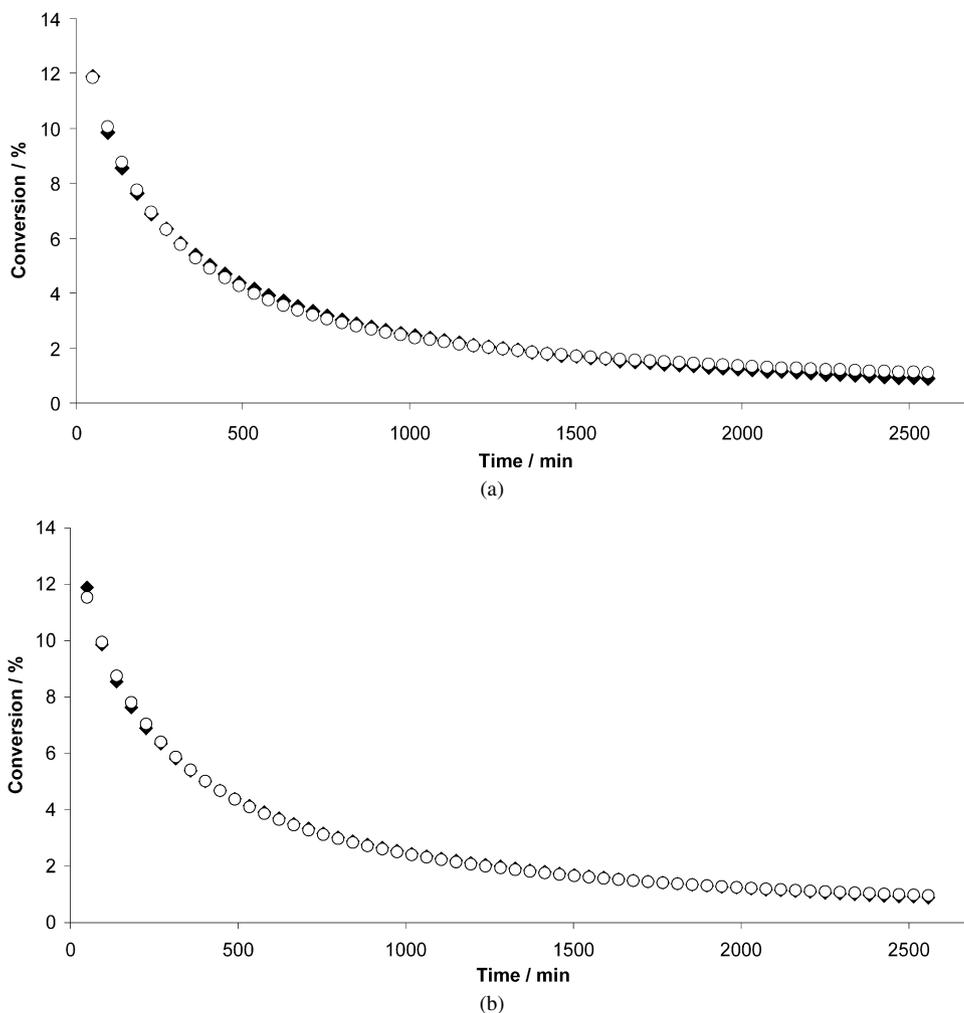


Fig. 5. Modeling deactivation of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  ( $\blacklozenge$ ) conversion at a flow rate of 77 mL/min, ( $\bullet$ ) deactivation model with (a) deactivation model of Eq. (5) ( $A_0 = 14.3$ ;  $k = 5.92 \times 10^4 \text{ mol}^{-1} \text{ min}^{-1}$ ) and (b) deactivation model of Eq. (6) ( $A_0 = 13.8$ ;  $k = 5.26 \times 10^4 \text{ mol}^{-1} \text{ min}^{-1}$ ;  $k' = 0.006 \text{ min}^{-1}$ ).

$$-\frac{d\text{cat}}{dt} = k[\text{cat}][=], \quad (8)$$

$$-\frac{d\text{cat}}{dt} = k[\text{cat}][=] + k'[\text{cat}], \quad (9)$$

where  $k$  is the rate constant of deactivation,  $[\text{cat}]$  is the concentration of active sites, and  $[=]$  is the concentration of ethene in the feed.

To test this hypothesis, we contacted the catalyst in a flow reactor with either ethene or *Z* 2-butene, the metathesis of propene was monitored (77 mL/min), and these experiments were compared with those from a catalytic test with only propene (Fig. 6). The flow rates of ethene or *Z* 2-butene were set to 5 mL/min (21,000 equiv/Re over 1188 min), which corresponds to the amount of ethene or *Z* 2-butene formed during the same amount of time for the metathesis of propene carried out at 77 mL/min (Fig. S9a). A strong deactivation of the catalyst is observed with pure ethene (decrease of ca. 80% of the conversion in propene metathesis and thereby amount of active sites). Although ethene has been used previously to titrate the active sites of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  with no major sign of deactivation, the amount and the pressure of ethene used in titration studies was always very small ( $\ll 1$  equiv/Re and ca. 0.04 bar).

In the case of *Z* 2-butene, the deactivation was less severe (decrease of ca. 50% of conversion, i.e. active sites), and in fact, the presence of 1-butene in the feed (1.8% and overall ca. 375 equiv/Re over 1188 min), could in fact be solely responsible for deactivation because it can form ethene via metathesis.

Overall, all the data show that deactivation of  $\text{CH}_3\text{ReO}_3/\text{Al}_2\text{O}_3$  in the metathesis propene is probably mainly due to its metathesis products, and most likely ethene, but it is not possible to completely exclude the participation of 2-butenes or even propene in the deactivation process. Based on these data, several deactivation pathways can be proposed. First, the formation of stable metallacyclopentane intermediates, as already proposed for well-defined homogeneous  $d^0$  catalysts [38], is not likely because no signal associated with this species have been observed by solid state NMR. Second, the formation of oligomers, as evidenced by NMR, can possibly interfere with the active sites and be responsible for deactivation; this phenomenon is observed mainly for ethene. Finally, the active site can convert into an inactive species by reaction with an olefin, for instance through the insertion of ethene into the Al–C bond of  $[\text{Al}_5\text{CH}_2\text{ReO}_3]$  in place of reacting with the methylidene ligand for metathesis (Scheme 6). Again, this process should be

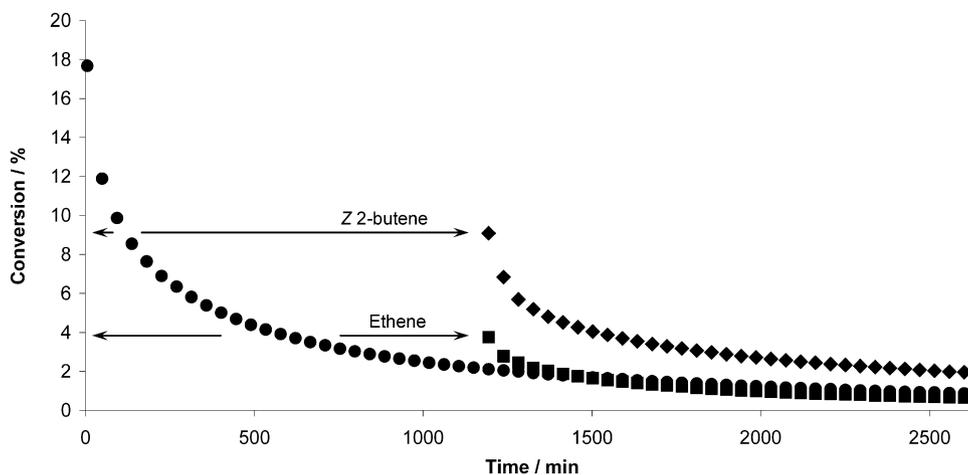
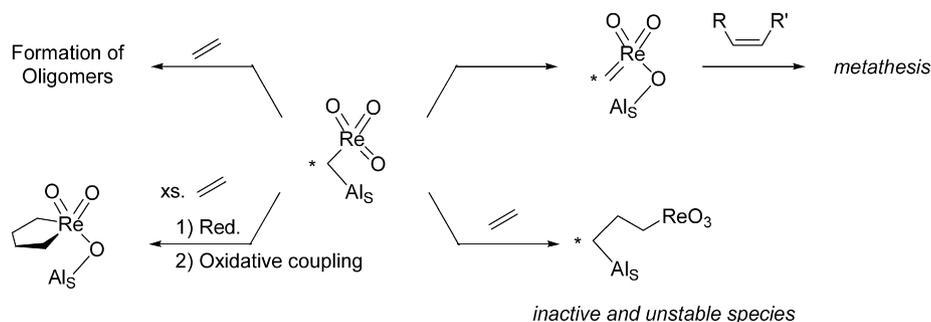


Fig. 6. Conversion as a function of time: (a) conversion of propene at a flow rate of 77 mL/min (●), (b) conversion of propene at a flow rate of 77 mL/min, after contacting the catalyst for 1188 min with ethene at a flow rate of 5 mL/min (◆) and (c) conversion of propene at a flow rate of 77 mL/min after contacting the catalyst for 1188 min with Z 2-butene at a flow rate of 5 mL/min (■).



Scheme 6. Possible deactivation pathways.

more favored for ethene and would lead to a new Re species that cannot form the propagating carbene species (no tautomerization is possible) and which could probably decompose because longer alkyl trioxorhenium ( $C_nH_{2n+1}-ReO_3$ ) complexes are usually much less stable than the parent methyl complex ( $CH_3 \gg C_2H_5 > Me_2CH \gg tBu$ ) [39].

#### 4. Conclusion

The specificity of  $CH_3ReO_3$  supported on alumina compared with  $Re_2O_7/Al_2O_3$  is that it already contains the carbenic propagating center as a protected  $\mu$ -methylene between Re and  $Al_5$  in  $[Al_5CH_2ReO_3]$ . This corresponds to the resting state of the catalyst, and the propagating carbenic species is probably formed in situ in the presence of olefins. The active sites,  $[Al_5CH_2ReO_3]$ , arise solely from the reaction of the C–H bond of  $CH_3ReO_3$  with reactive  $Al_5-O_5$  sites, whereas the inactive major species corresponds to  $MeReO_3$  chemisorbed on Lewis acid sites of alumina through its oxo ligand(s). Noteworthy  $[Al_5CH_2ReO_3]$  resembles the Tebbe reagent, one of the first well-defined homogeneous catalysts, which contains a carbene protected by an Al Lewis center [40,41]. Although this study is limited to alumina, our findings suggest that other heterogeneous systems based on  $MeReO_3$  and supported on silica-alumina, zeolite, or  $Nb_2O_5$  generate similar active species

that are likely present only in small amounts; thus the difficulty of obtaining spectroscopic evidence of such species or even to titrate them, which has led to long-standing debates in this area [42]. The presence of the carbenic species in  $CH_3ReO_3/Al_2O_3$ , even if not observed directly but formed in situ from a protected form, is consistent with the activity of this system in the metathesis of functionalized olefins without the need for a co-catalyst, in contrast to  $Re_2O_7/Al_2O_3$ . In fact, the latter requires to generating the carbenic species in situ from the olefin, and it is likely that ethyl oleate, a Lewis base, hinders such a step [38]. Moreover, kinetic studies show that this system is highly active (i.e., having activities similar to those of some of the best catalysts) but undergoes fast deactivation in the metathesis of propene, due to the propene metathesis products, and most likely ethene. Overall, this catalyst behaves more like a molecular system (i.e., well-defined active site, deactivation by ethene), and we are currently investigating ways to improve the catalytic performances of this system.

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## Supporting information

Supporting information for this article may be found on ScienceDirect, in the online version.

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