

Activation of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ metathesis catalyst by aryloxyaluminium complexes

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Abstract

Bis-aryloxyalkylaluminium complexes, previously involved in the synthesis of aryloxyaluminium perchlorate complexes that are active in olefin metathesis in homogeneous phase, are able to increase the activity of the supported $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ metathesis catalyst. They are also able to make active an otherwise inactive low temperature-treated $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. They can be used to regenerate, for the first time at room temperature, a previously deactivated catalyst. Until now, a high temperature calcination treatment was essential for the regeneration. These properties are attributed to the strong Lewis acidic character of these aluminium complexes due to the low coordination state of the aluminium, protected by the aryloxy ligands. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The metathesis reaction has drawn interest because of its technological and fundamental importance [1]. The first studies were carried out with molybdenum and tungsten-based catalysts, both homogeneous or heterogeneous. However, the comparison between homogeneous and heterogeneous catalysis is particularly interesting in the case of rhenium-based catalysts, because $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ is an excellent metathesis catalyst already at near-ambient temperatures, either in the gas phase or in the liquid phase [2]. There are only a few rhenium-based homogeneous metathesis catalysts, belonging to two main classes comprising the high valent rhenium trioxo complexes of Herrmann [3,4] and the carbene- or carbyne-containing rhenium complexes of

Schrock [5,6]. We have recently synthesised sterically hindered aryloxyaluminium perchlorate complexes that exhibit activity in olefin metathesis. They may be regarded as homogeneous models of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst [7,8].

There seems to be a general agreement that the active species comprises a rhenium carbene site in an environment possessing acidic properties, brought about either by an electron attracting ligand or a cocatalyst in homogeneous catalysis, or by an acidic carrier in a heterogeneous catalyst [2]. However, the nature of the effective acidity in the supported rhenium catalysts is debated. Xiaoding et al. have shown a relationship between activity and Br  nsted acidity [9]. Hsu claimed that both Lewis and Br  nsted acidity are responsible for the activity of the catalyst [10]. On the other hand, Buffon and Basset have found a clear relation between activity and Lewis acidity for the $\text{CH}_3\text{ReO}_3/\text{Nb}_2\text{O}_5$ catalyst [11]. We have, on our

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side, performed some studies on the influence of the acidity of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst on its catalytic performances which also seem to be in favour of the Lewis acidity [12,13].

Tetraalkyltin [14,15] or lead [16,17] complexes have been known to increase the activity of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst for the metathesis of alkenes, and their presence is essential for the metathesis of functional alkenes to occur. The attachment of alkyltin complexes onto the surface of the catalyst has been studied by Mol [2], Williams and Harrison [18] and Buffon et al. [19,20]. We now report in this paper that aryloxyalkylaluminium complexes are able to increase the activity of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst in the metathesis of propene [21]. For the first time, these complexes even make possible the activation and the regeneration of the catalyst at room temperature.

2. Experimental

Operations involving organometallic complexes and aryloxyaluminium-modified catalysts were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line and glove-box techniques. Toluene was distilled on sodium dispersion and stored over 3A molecular sieves. Pentane was distilled from LiAlH_4 and stored over 3A molecular sieves. Phenols, trialkylaluminium compounds and aqueous solution of perrhenic acid (H.C. Starck, Berlin, 54 wt.% aqueous solution) were commercially available and used as received. Aryloxyalkylaluminium complexes were prepared according to the methods described in the literature [8,22]. Alkoxyalkylaluminium complexes were prepared by careful alcoholysis of trialkylaluminium compounds with stoichiometric amounts of the corresponding alcohols.

NMR spectra were recorded on a Bruker CXP 200. Gas chromatography analyses were done on a HP 5890 series II with PONA or Al_2O_3 -plot columns.

2.1. Preparation of the catalysts

The catalysts were prepared using the incipient wetness impregnation of a gamma-alumina (surface area $180\text{ m}^2/\text{g}$, ball-shaped, diameter 1.8 mm) with an aqueous solution of perrhenic acid. Impregnation

is followed by drying overnight in an oven at 120°C . The standard activation (reference catalyst) is done by calcination at 550°C under a dry air flow ($<200\text{ ppm wt. H}_2\text{O}$) for 2 h, followed by cooling down under a dry nitrogen flow ($<10\text{ ppm wt. H}_2\text{O}$). The temperature of calcination has been varied during our study. The catalyst samples are kept and transferred under nitrogen before use in the metathesis reaction, or before modification by the aluminium complexes.

2.2. Modification of the catalysts by aryloxyaluminium complexes

The rhenium-impregnated and calcined catalysts were modified by aryloxyaluminium complexes using the incipient wetness impregnation method with pentane or heptane as the solvent. Typical procedure: 10 g of a catalyst prepared following the above method and containing 2.84 wt.% of rhenium (as metal) is transferred into a glass flask under nitrogen. A solution of 1 g of bis-(2,6-di-*t*-butyl-4-methylphenoxy)-isobutylaluminium (1.9 mmol Al) in 5 ml pentane is slowly added by means of a syringe into the manually agitated flask. The white catalyst balls rapidly become deep brown. The catalyst sample is then washed five times with 10 ml pentane. The washings are evaporated under vacuum, leaving 0.281 g of a white product which has been identified as the starting aluminium complex by $^1\text{H NMR}$.

2.3. Metathesis reactions

The laboratory scale experiments with a liquid propene feedstock were conducted in a semi-continuous mode as described in a previous paper [12]. The fixed bed reactor has a volume of 20 ml and is charged with 10 g of catalyst under a nitrogen flow. In experiments with modified catalysts, the modified catalyst samples are transferred directly after modification through a glass connexion device into the reactor under nitrogen. The liquid propene is introduced upflow into the reactor by means of a volumetric pump. Pressure is maintained constant by a back pressure valve, in which the reactor effluent is totally vaporised. Effluent is then analysed by means of an on-line gas chromatography.

2.4. Determination of the kinetic parameters

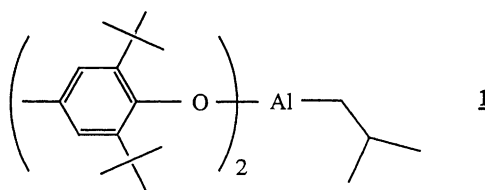
The experimental results are interpreted on the basis of a Langmuir–Hinshelwood model based on a second order equilibrated reaction, as previously described [12]. The rate constants calculated according to this model are plotted against time. The deactivation of the catalyst generally obeys a first order rate law. Some deviations to the first order deactivation may be observed in the case of the aryloxyaluminium-modified catalysts. Extrapolation at time zero gives the initial metathesis rate constant k_0 ($\text{mol}(\text{kg catalyst})^{-1} \text{s}^{-1}$). This initial metathesis rate constant k_0 and the deactivation rate constant k_d (s^{-1}) are the parameters used to quantify the performance of a catalyst sample.

3. Results and discussion.

3.1. Modification of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst with aluminium complexes

When a $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ metathesis catalyst (Re content: 3 wt.%), preactivated thermally at 550°C under an air flow, is impregnated with a solution of bis-(2,6-di-*t*-butyl-4-methylphenoxy) - isobutylalumi-

nium (**1**) in pentane under argon at room temperature, a colour change of the catalyst balls from white to deep brown is observed. A small quantity of gas is evolved during the process, the amount of which is irreproducible. Analyses show that it consists mainly of isobutane together with traces of isobutene.



This modified catalyst is seven times more active than the reference catalyst in the metathesis reaction of propene in the conditions reported in Table 1 (experiment 7 compared to 1). The deactivation of the modified catalyst is however more rapid. After deactivation, it is easily regenerated by calcination at 550°C , followed by reimpregnation with the aluminium complex (experiment 8). As a comparison, triisobutylaluminium has no effect (or slightly negative, experiment 2).

We have first studied the effect of the nature of the aryloxy ligand in the bis-aryloxy-isobutylaluminium complex. The results in Table 1 show that the improvement of the activity is dependent on the substituents

Table 1
Modification of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst with aluminium complexes^a

Run Nb	Aluminium complex (-Al)	Al/Re impregnation (mol) ^b	Al/Re fixed (mol) ^c	Activity $k_0 \times 10^3$ ($\text{mol kg}^{-1} \text{s}^{-1}$) ^d	Deactivation $k_d \times 10^6$ (s^{-1}) ^d
1 ^e	Without	0	0	2.3	3.0
2	Al <i>i</i> Bu ₃	2	nd ^f	1.7	13.9
3	[(EtO) ₂ Al <i>i</i> Bu] ₂	3.1	nd	2.6	11.1
4	[(PhO) ₂ Al <i>i</i> Bu] ₂	3	2.9	6.9	16.7
5	(2,6-Ph ₂ -PhO) ₂ Al <i>i</i> Bu	7.6	3.2	8.3	11.9
6	(2,6- <i>t</i> Bu ₂ -PhO) ₂ Al <i>i</i> Bu	2.5	0.8	15.5	19.7
7	(4-Me-2,6- <i>t</i> Bu ₂ -PhO) ₂ Al <i>i</i> Bu	3.2	nd	16.7	12.5
8	(4-Me-2,6- <i>t</i> Bu ₂ -PhO) ₂ Al <i>i</i> Bu ^g	3.2	nd	17.8	20.3
9	(4-Me-2,6- <i>t</i> Bu ₂ -PhO) Al <i>i</i> Bu ₂	2.3	1.5	12.5	11.1

Effect of the nature of the complex.

^a Catalyst preactivation temperature 550°C , Re = 3 wt.% (unless otherwise stated).

^b Molar ratio of aluminium complex to Re, at impregnation.

^c Molar ratio of aluminium complex to Re, fixed after washings.

^d Metathesis of propene, $T = 35^\circ\text{C}$, $P = 3.5 \text{ MPa}$; LHSV = $1.1 \times 10^{-3} \text{ s}^{-1}$.

^e Re = 2.84 wt.%.

^f nd: not determined.

^g Catalyst from run 7 after calcination and reimpregnation with the same Al complex.

of the aryloxy ligand. Unsubstituted diphenoxy-isobutyl-aluminium, known to be a dimer, is the less effective (experiment 4). When *ortho*-substituted aryloxy ligands are used, like bis-(2,6-diphenyl-phenoxy)-isobutylaluminium (experiment 5) or bis-(2,6-di-*t*-butyl-phenoxy)-isobutyl-aluminium (experiment 6), more active catalysts are obtained. Additional substitution in the *para* position of the aryloxy ligand has only a small positive effect (compare experiments 6 and 7). A mono-aryloxy-diisobutyl-aluminium (experiment 9) is less efficient than a bis-aryloxy-isobutylaluminium. The addition of 2,6-di-*t*-butyl-4-methylphenol, a hydrolysis product of (**1**), to the reference catalyst (4-Me-2,6-*t*Bu₂-PhOH /Re = 5.6/1 molar ratio) completely suppressed its activity in the metathesis of propene.

Alkoxy ligands, instead of aryloxy ligands, in the aluminium complex do not improve the activity of the catalyst. The modification of the catalyst with diethoxy-isobutylaluminium dimer affords only a very small enhancement of the activity (experiment 3). Surprisingly, diisopropoxy-isobutylaluminium dimer leads to a completely inactive catalyst.

The best results are thus observed with aryloxy ligands, and especially with the sterically crowded complex (**1**), which has already been found to be the most efficient in the homogeneous models of the catalyst. The following experiments have thus been conducted with this complex.

3.2. The mode of impregnation and the continuous injection of the aluminium complex (**1**)

The mode of impregnation of the aluminium complex (**1**) was studied more thoroughly. The results are reported in Table 2. Washings with pentane after impregnation give a slightly less active catalyst than the non-washed one (experiments 10 and 11). Yet the amount of aluminium complex which is fixed onto the catalyst at the end of the metathesis run is not very much different. There is no noticeable elution of aluminium or rhenium in the effluent of the reactor during the propene metathesis experiments, provided that the catalyst has been washed after the impregnation (experiment 11). Otherwise, some aluminium, but no rhenium, is eluted during the metathesis run, roughly in the same amount as during washings.

Note that the catalyst in experiment 11 is less active than that in experiment 7 (Table 1) because of a different amount of the aluminium complex introduced, an effect that will be discussed in the following.

Drying of the catalyst under vacuum at 20 °C at the end of the impregnation gives a more active catalyst, but the deactivation is faster (experiment 12). On the contrary, drying of the modified catalyst at 90 °C almost completely suppress the benefit of the modification by the aluminium complex (experiment 13). It is then not surprising that calcination at 550 °C of the

Table 2
Modification of the Re₂O₇/Al₂O₃ catalyst with aluminium complex (**1**)^a

Run Nb	Mode of impregnation of the aluminium complex	Al/Re impregnation (mol) ^b	Al/Re fixed (mol) ^c	Al/Re fixed (mol) ^d	Activity $k_0 \times 10^3$ (mol kg ⁻¹ s ⁻¹) ^d	Deactivation $k_d \times 10^6$ (s ⁻¹) ^d
10	In pentane, $T = 20^\circ\text{C}$, no washings	1.3	–	1.05	11.9	11.4
11	In pentane, $T = 20^\circ\text{C}$, five washings with pentane	1.3	0.93	0.93	8.9	11.9
12	In pentane, $T = 20^\circ\text{C}$, drying vacuum at 20°C	1.3	–	1.16	20.5	18.0
13	In heptane, $T = 90^\circ\text{C}$, drying vacuum at 90°C	1.3	–	1.3	4.4	31.4
14	In pentane, $T = 20^\circ\text{C}$, five washings with pentane, then calcined at 550°C	1.3	nd ^e	nd	0.8	nd

Effect of the mode of impregnation of the complex.

^a Catalyst preactivation temperature 550 °C, Re = 2.84 wt.%.

^b Molar ratio of aluminium complex to Re, at impregnation.

^c Molar ratio of aluminium complex to Re, fixed after washings (where any).

^d Molar ratio of aluminium complex to Re, after 48 h metathesis run.

^e nd: not determined.

modified catalyst leads to a catalyst which is even less active than the reference (experiment 14).

The first washing with pentane is yellow coloured, while the fifth one is completely colourless. The coloured washings contain aluminium, but only traces of rhenium. NMR analyses show that aluminium is present as the starting complex (**1**). Washing of the catalyst after impregnation of the aluminium complex thus eliminates the part of the complex which has not reacted with the surface of the catalyst.

On the other hand, we have conducted a few propene metathesis runs in the gas phase. The deactivation of the catalyst is the same as in the liquid phase. No elution of the aluminium complex is expected in the gas phase. Therefore, elution of the complex is not the reason for the more rapid deactivation of the modified catalyst.

Two propene metathesis runs were performed during which variable amounts of the aluminium complex (**1**) were dissolved in the propene feedstock (0.23 and 0.46 wt.% Al complex) in addition to the initial impregnation of the catalyst as above. This continuous injection of the complex (**1**) results in a three times slower deactivation rate of the catalyst with time ($k_d = 4.4 \times 10^{-6} \text{ s}^{-1}$ with 0.23 wt.% Al, $k_d = 4.7 \times 10^{-6} \text{ s}^{-1}$ with 0.46 wt.% Al, to be compared with k_d values in Table 2, experiments 10–12). Surprisingly, the deactivation rate is not dependent on the concentration of (**1**) in the propene feedstock. At the present time, we have not been able to completely suppress the deactivation of the catalyst by that means.

In these last experiments, some aluminium, but no rhenium, is eluted into the liquid effluent of the reactor during the metathesis runs. The aluminium material balance between the feedstock and the effluent of the reactor indicates that, although the deactivation rate of the catalyst is regular with time, the aluminium present on the catalyst (apart from the aluminium of alumina) rapidly reaches a steady state which is maintained during the first 50 h, and then declines down to the end of the run (72 h).

3.3. Effect of some parameters of the activation by the aluminium complex (**1**)

We have compared the efficiency of the modification by the complex (**1**) with different rhenium-loaded catalysts. The results reported in Table 3 show that the relative increase of activity due to the aluminium complex is roughly independent of the rhenium content of the starting catalyst up to 3 wt.% Re. For an 8 wt.% Re catalyst, the gain in activity is lower and, due to its faster deactivation rate, the modified catalyst becomes less active than the reference catalyst during a metathesis run.

The gain in activity is dependent on the amount of the complex (**1**) which is contacted with the reference catalyst *in one time*. Indeed, when this amount is varied, the more aluminium is contacted (Al/Re impr.), the more is fixed, and the higher the activity of the modified catalyst is, as seen in Table 4. It is noteworthy that when the same amount of aluminium complex is contacted with the reference catalyst *in three times*

Table 3
Modification of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst with aluminium complex (**1**)^a

Run Nb	Re content (wt.%)	Aluminium complex (-Al)	Al/Re impregnation (mol) ^b	Al/Re fixed (mol) ^c	Activity $k_0 \times 10^3$ ($\text{mol kg}^{-1} \text{ s}^{-1}$) ^d	Deactivation $k_d \times 10^6$ (s^{-1}) ^d
1	2.84	Without	0	0	2.3	3.0
11	2.84	With	1.3	0.93	8.9	11.9
15	8	Without	0	0	13.3	2.2
16	8	With	2.3	0.88	26.4	10.3
17	0.92	Without	0	0	0.5	11.7
18	0.92	With	3.8	nd ^e	1.7	14.7

Effect of the Re content.

^a Catalyst preactivation temperature 550 °C.

^b Molar ratio of aluminium complex to Re, at impregnation.

^c Molar ratio of aluminium complex to Re, fixed after washings.

^d Metathesis of propene, $T = 35 \text{ °C}$, $P = 3.5 \text{ MPa}$; LHSV = $1.1 \times 10^{-3} \text{ s}^{-1}$.

^e nd: not determined.

Table 4
Modification of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst with aluminium complex (**1**)^a

Run Nb	Impregnation of the aluminium complex	Al/Re impregnation (mol) ^b	Al/Re fixed (mol) ^c	Activity $k_0 \times 10^3$ (mol kg ⁻¹ s ⁻¹) ^d	Deactivation $k_d \times 10^6$ (s ⁻¹) ^d
11	In one time	1.3	0.93	8.9	11.9
19	In one time	3.2	1.56	20.5	16.1
20	In three times	3.8	0.80	8.3	nd ^e
21	In one time	0.64	0.47	3.6	11.9

Effect of the amount and the way of introduction of the aluminium complex.

^a Catalyst preactivation temperature 550 °C, Re = 2.84 wt.% (3 wt.% for 19).

^b Molar ratio of aluminium complex to Re, at impregnation.

^c Molar ratio of aluminium complex to Re, fixed after washings.

^d Metathesis of propene, $T = 35$ °C, $P = 3.5$ MPa; LHSV = 1.1×10^{-3} s⁻¹.

^e nd: not determined.

(experiment 20) instead of in one time (experiment 19), the amount which is fixed, and the resulting activity, correspond to that observed with one-third of the amount of aluminium complex (experiment 11). As the volume of the solution used for the impregnation of (**1**) and the amount of the catalyst are the same in all these experiments, increasing the ratio Al/Re at the impregnation (Al/Re impr.) is done by increasing the aluminium concentration in the solution. Thus, there is a relation between the concentration of the aluminium complex in the impregnation solution and the amount of the complex which is anchored onto the surface.

Most important is the effect of the temperature of preactivation of the catalyst before impregnation with the aluminium complex (**1**). The results in Table 5 show that the best activity is obtained for a preactivation temperature of 550 °C. Preactivation at 760 °C

leads to a much smaller amount of fixed aluminium complex, and therefore, to a small gain in activity. For the lower activation temperatures, we were surprised that preactivation at only 200 °C followed by impregnation of the aluminium complex (**1**) gives a fairly active catalyst. Even preactivation at 100 °C leads to some activity (experiments 23 and 24). We have verified that the reference catalyst activated at 200 °C without modification with the aluminium complex is completely inactive in the same metathesis conditions.

We have then investigated the possibility of the regeneration of a non-modified, deactivated, catalyst by means of an aryloxyaluminium complex. A reference catalyst sample, activated at 550 °C, and not modified with complex (**1**), was first deactivated during a propene metathesis run. The initial activity was $k_0 = 3 \times 10^{-3}$ and the activity at the end of this 50 h run was

Table 5
Modification of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst with aluminium complex (**1**)^a

Run Nb	T , activ (°C) ^a	Al/Re impregnation (mol) ^b	Al/Re fixed (mol) ^c	Activity $k_0 \times 10^3$ (mol kg ⁻¹ s ⁻¹) ^d	Deactivation $k_d \times 10^6$ (s ⁻¹) ^d
11	550	1.3	0.93	8.9	11.9
22	760	1.3	0.18	3.6	17.5
23	200	1.3	nd ^e	8.3	nd
24	100	1.3	nd	0.5	nd
25	– ^f	1.3	nd	2.8	18.6

Effect of the temperature of preactivation of the catalyst.

^a Catalyst Re = 2.84 wt.%, aluminium complex: (4-Me-2,6-*t*Bu₂-PhO)₂Al*i*Bu; T (active), temperature of preactivation of the catalyst before impregnation of the Al complex.

^b Molar ratio of aluminium complex to Re, at impregnation.

^c Molar ratio of aluminium complex to Re, fixed after washings.

^d Metathesis of propene, $T = 35$ °C, $P = 3.5$ MPa; LHSV = 1.1×10^{-3} s⁻¹.

^e nd: not determined.

^f Regeneration of a deactivated catalyst by addition of the Al complex at room temperature without any thermal treatment (see text).

Table 6
Compared effects of aryloxyaluminium and alkyltin complexes^a

Run Nb	Al/Re impregnation (mol) ^b	Sn/Re impregnation (mol) ^b	Activity $k_0 \times 10^3$ (mol kg ⁻¹ s ⁻¹) ^c	Deactivation $k_d \times 10^6$ (s ⁻¹) ^c
26	1.3	0	8.3	13.6
27	0	0.1	8.3	14.2
28 ^d	1.3	0.1	10.3	13.0
29 ^e	1.3	0.1	8.3	11.4

^a Catalyst Re = 2.71 wt.%, aluminium complex: (-Al), (**1**), tin complex: (-Sn), SnBu₄.

^b Molar ratio of aluminium or tin complex to Re, at impregnation.

^c Metathesis of propene, $T = 35^\circ\text{C}$, $P = 3.5\text{ MPa}$; LHSV = $1.1 \times 10^{-3}\text{ s}^{-1}$.

^d (-Al) impregnated first, then (-Sn).

^e (-Sn) impregnated first, then (-Al).

$k_{50} = 0.8 \times 10^{-3}$). Then it was impregnated with the aluminium complex (**1**) at room temperature without any thermal treatment (Table 5, experiment 25), and engaged in a second propene metathesis run. The activity which was reached ($k_0 = 2.8 \times 10^{-3}$) indicated that the catalyst has been fully regenerated. The level of activity is that of the non-modified catalyst, and not that of a catalyst which would have been thermally activated, then modified with (**1**). As far as we know, it is the first time that the regeneration of a rhenium-based metathesis catalyst by a chemical treatment at room temperature is observed. However, for a reason which is not fully understood at the present time, this room temperature regeneration can be accomplished only one time. Work is continuing to overcome this drawback.

3.4. Compared effects of aryloxyaluminium and alkyltin complexes

We have been interested in comparing the activation by the aryloxyaluminium complex (**1**) with the long-known activation by tetraalkyltin complexes. In our hands, these two methods of activation give the same gain in activity in the metathesis of propene, as shown in Table 6 (experiments 26 and 27). Even when the catalyst is activated by both aluminium and tin complexes, the activity remains at the same level as that reached with each of the activator, whatever the order of introduction of the two complexes is (experiments 28 and 29).

On the other hand, we have impregnated with SnEt₄ a 3 wt.% Re catalyst thermally preactivated at only 200 °C (Sn/Re = 0.1/1 M). The initial activity in the

metathesis of propene is extremely low in these conditions ($k_0 < 5 \times 10^{-4}$), compared to the activation with an aryloxyaluminium complex (Table 5, experiment 23). We already know [17] that a tetraalkyltin complex is not able to regenerate a deactivated catalyst at room temperature without any thermal treatment. The ways tin and aluminium complexes activate the rhenium catalyst thus appear quite different. Activation and regeneration of a rhenium-based metathesis catalyst at room temperature is specific of the sterically crowded aryloxyaluminium complexes.

4. Conclusion

Bis-aryloxyalkylaluminium complexes, especially the complex (**1**), previously involved in the synthesis of aryloxyaluminium perrhenate complexes that are active in olefin metathesis in homogeneous phase, have been shown to increase the activity of the supported Re₂O₇/Al₂O₃ metathesis catalyst. They are also able to make active an otherwise inactive low temperature-treated Re₂O₇/Al₂O₃ catalyst. They can be used to regenerate, for the first time at room temperature, a previously deactivated catalyst. Until now, a high temperature calcination treatment of the catalyst was essential for the regeneration.

The bis-(2,6-di-*t*-butyl-4-methylphenoxy)-methylaluminium complex is known to exist as a monomer with a tricoordinated aluminium atom stabilised by the steric crowding brought by the *ortho-ortho t*-butyl substituents [23]. It is likely that the isobutyl analog (**1**) is also a monomer. Such a tricoordinated aluminium centre is expected to exhibit a strong

Lewis acidity. We propose that this acidity, usually resulting from the high temperature calcination, is responsible for the improvement of the activity of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ metathesis catalyst.

List of symbols

k_0	initial (at time zero) metathesis rate constant ($\text{mol kg}(\text{catalyst})^{-1} \text{s}^{-1}$)
k_d	deactivation rate constant (s^{-1})
(-Al)	aluminium complex
(-Sn)	tin complex
LHSV	liquid hourly space velocity ($\text{kg}(\text{propene}) \text{kg}(\text{catalyst})^{-1} \text{s}^{-1}$)

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