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Methyltrioxorhenium on silica–alumina as metathesis catalyst of 1-octene

T.M. Mathew [a], J.A.K. du Plessis [b,*], J.J. Prinsloo [a]

[a] *Department of Chemistry, University of the North, Private Bag X1106, Sovenga 0727, South Africa*
[b] *SASOL Centre for Chemistry, Potchefstroomse Universiteit vir CHO, Private Bag X6001, Potchefstroom 2520, South Africa*

Abstract

Methyltrioxorhenium (MTO) supported on silica–alumina acts as a heterogeneous catalyst for the metathesis of 1-octene. 7.5% (m/m) MTO on the support gave a maximum percentage of homo-metathesis products. The reaction reached equilibrium after 1.5 h at room temperature. Addition of cesium ions onto the silica–alumina support increased the selectivity towards homo-metathesis products but decreased the total metathesis activity. The optimum percentage of cesium ions on the support was found to be 3.3%. Addition of 1% oxygen-containing additives to the 1-octene like 2-hexanone, pentanal, butanol and pentanoic acid, increased the homo-metathesis products and decreased the cross-metathesis products of 1-octene catalysed by the $MTO/SiO_2 \cdot Al_2O_3$ catalytic system. Higher concentrations of additives decreased the activity of the catalytic system. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

By treating rhenium heptoxide in tetrahydrofuran with tetramethyltin, methyltrioxorhenium (MTO) can be isolated as fine crystals [1,2]. It is stable above its melting point (106°C), dissolves in organic solvents and in water and is stable in air.

MTO has exceptional catalytic qualities. In solution and in the presence of a suitable Lewis acid and an alkylating agent it acts as a metathesis catalyst of alkenes [3]. MTO also becomes a metathesis catalyst when supported on calcined silica–alumina, γ-alumina or niobium oxide [4,5].

When a silica–alumina surface is dehydrated by heating it to high temperatures, the surface can show Brønsted acidity, Lewis acidity or both depending on the pretreatment conditions [6]. According to Kawai et al. [7] the presence of some strong acid sites on the catalyst is responsible for the double bond isomerisation of alkenes. Migration of double bonds occurs on both Brønsted and Lewis acids. They also mentioned many publications which reported that the addition of small quantities of alkali or alkaline earth metal ions to heterogeneous catalysts can poison acid sites on the catalyst. This resulted in a decrease in the activity of isomeri-

* Corresponding author. Tel.: +27-182-992-358; Fax: +27-182-992-350; E-mail: chehcmv@puknet.puk.ac.za

sation and an increase in the selectivity of the homo-metathesis reaction.

Kawai et al. [8,9] and Mol and Andreini [10] reported that the selectivity of homo-metathesis reactions can be improved by the addition of cesium ions to the support. They further mentioned that the total conversion is lower, as a consequence of less side reactions.

Sibeijn et al. [11,12] reported that an interesting way to increase the catalytic activity of supported rhenium complexes is treating the support with phosphate ions prior to impregnation with rhenium complexes. During this process phosphate ions react with the acidic OH groups on the support and form acidic$\equiv$P–OH groups which will increase the activity.

The aim of this project was to investigate the activity of methyltrioxorhenium (MTO) supported on silica–alumina as heterogeneous catalyst in the metathesis of 1-octene. The influence of cesium ions and phosphate ions on the MTO/$SiO_2 \cdot Al_2O_3$ catalyst system was determined and also the influence of oxygen-containing organic additives to the 1-octene.

2. Experimental

The reagents, $SnMe_4$ (Merck) and 1-octene (Sigma) were stored under N_2 after degassing. Other organic reagents were dried with standard methods and also stored under N_2. $SiO_2 \cdot Al_2O_3$ (Akzo-Nobel, HA-1,5E, 22.4% Al_2O_3, 347 m^2 g^{-1}), $(NH_4)_2HPO_4$, $CsNO_3$, γ-Al_2O_3 (Merck, 196.4 m^2 g^{-1}), Re_2O_7 (Merck) were used as received. CH_3ReO_3 was synthesised according to the method reported in literature [1,2].

All glass apparatus were dried at 100°C and cooled under N_2 before use. Two-neck pear flasks were used as reactors. One of the necks was fitted with a septum so that liquid reagents could be introduced into the reactor by means of syringes.

The catalyst support was calcinated for 3 h under oxygen followed by 3 h under nitrogen at 550°C and then transferred to a 10 cm^3 pear flask containing a stirring bar under a nitrogen atmosphere. After cooling to room temperature under nitrogen atmosphere, 1 cm^3 solution of MTO in chlorobenzene was introduced via a syringe into the reactor and was stirred for 5 min. Then 0.3 cm^3 of 1-octene was injected into the reactor. The products were sampled and analysed after 24 h.

The Cs^+ and PO_4^{3-} containing supports were prepared by first impregnating the $SiO_2 \cdot Al_2O_3$ with a solution of cesium nitrate or diammonium hydrogen phosphate, then dried at 100°C before calcination.

All reactions were done under a dry nitrogen atmosphere and under the following conditions:

Reactor	10 cm^3 pear flask fitted with a septum
$SiO_2 \cdot Al_2O_3$	0.1100 g
MTO	0.0089 g in 1 cm^3 chlorobenzene (7.5% m/m MTO/$SiO_2 \cdot Al_2O_3$)
1-octene	0.3 cm^3
Reaction time	24 h
Temperature	25°C
Solvent (C_6H_5Cl)	Total volume was kept at 1 cm^3 and was also used as internal standard for GC analysis

GC analysis were performed with a Hewlett-Packard 5840 GC using the following conditions:

Column	2 m × 2 mm stainless steel containing 5% OV101 on chromsorb P AW-DM CS
Temperature	120–220°C (10°C min^{-1})
Carrier gas	N_2
Detector	FID

Products were identified by comparison with authentic samples and by GC–MS methods.

The terms used in presenting the results are defined as follows:

Total metathesis	The total yield of all the metathesis products in the product spectrum and is calculated as $2(\Sigma_{n=9}^{14} \% C_n)$ (C_n is the length of the carbon chain containing an alkene group)
Homo-metathesis	The sum of the primary metathesis products (C_2 and C_{14}) and is calculated as $2 \times \% C_{14}$.
Cross-metathesis	The sum of all the metathesis products with carbon chain lengths 3–7 and 9–13 and is calculated as $2(\Sigma_{n=9}^{14} \% C_n)$

3. Results and discussion

3.1. Influence of the MTO content

The increase in the MTO content of the $MTO/SiO_2 \cdot Al_2O_3$ catalytic system causes an increase in the metathesis product yield (Fig. 1). At a loading of 7.5% MTO, the product composition (mol%) is the following C_8: 11%, C_9: 16%, C_{10}: 4%, C_{11}: 4%, C_{12}: 7%, C_{13}: 9% and C_{14}: 10%. The homo-metathesis product yield is 20% and the cross-metathesis product yield is 80%. Further measurements were done at a MTO loading of 7.5%.

3.2. The influence of reaction time

The influence of the reaction time on the system is given in Fig. 2. The homo-metathesis product yield reached a maximum of 25% after 1.5 h and then decreased with longer reaction times. After 24 h the yield was 20%. After 6 h the cross-metathesis products reached a value of 75% and then flattened out as the time increased.

3.3. The influence of cesium ions

It is known that the addition of small quantities of cesium ions to the support of heterogeneous metathesis catalysts [8–10] improved the selectivity of the homo-metathesis reaction.

In Fig. 3 the influence of cesium ions added to the system is illustrated. The homo-metathesis product increased to a maximum of 46% at 3.3% cesium loading while the cross-metathesis
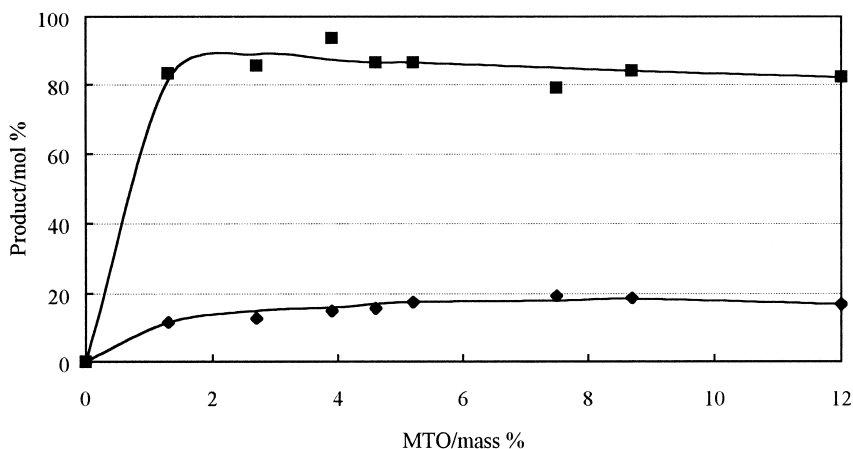

Fig. 1. The influence of MTO concentration on the support on the metathesis activity of 1-octene after 24 h. [(■)—cross-metathesis; (♦)—homo-metathesis].
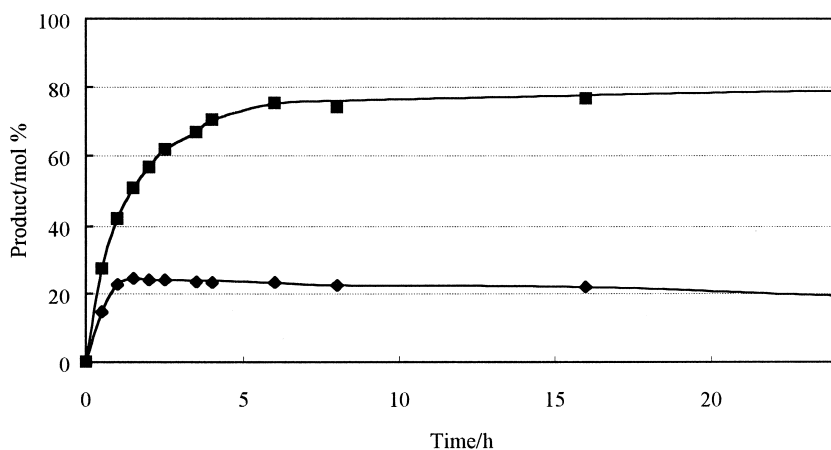
Fig. 2. The influence of reaction time on the metathesis activity of 1-octene with the 7.5% $MTO/SiO_2 \cdot Al_2O_3$ catalytic system. [(■)—cross-metathesis; (♦)—homo-metathesis].

products decreased until it reaches 1% at a 10% cesium loading.

3.4. The influence of phosphate ions

The addition of phosphate on the silica–alumina before calcination does not show any marked influence. The homo-metathesis products are almost constant at 19% with a slight increase from 80% to 85% of cross-metathesis products is noticed when the phosphate content was increased from 0 to 9%.

In Fig. 4 the influence is shown of the phosphate content on the metathesis of 1-octene with a 7.5% $MTO/3.3\%$ $Cs^+/SiO_2 \cdot Al_2O_3$ catalytic system. The homo-metathesis products is kept almost constant at 45%. At 3% PO_4^{3-} content the cross-metathesis products reached a maximum of 22%.

3.5. The influence of additives added to 1-octene on the metathesis activity of the catalytic system

Most metathesis catalytic systems are deactivated in the presence of polar groups present in the functionalized alkenes [13]. We investigated the metathesis activity of the 7.5% MTO/SiO_2
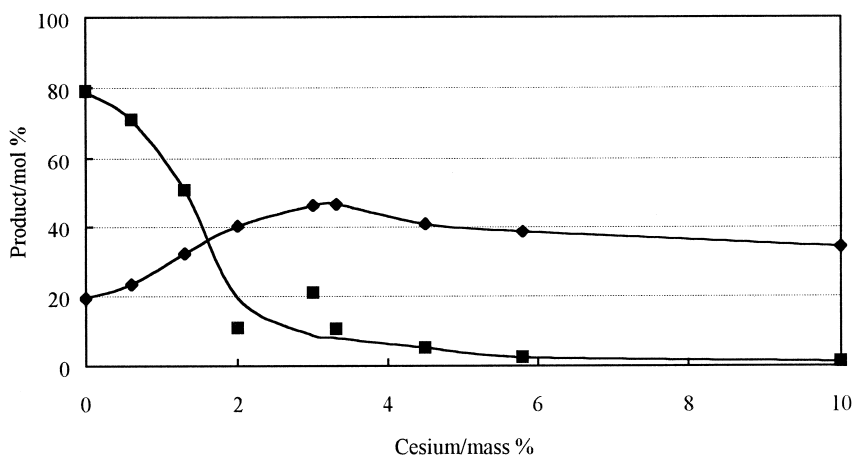

Fig. 3. The influence of cesium content on the metathesis activity of 1-octene with the 7.5% $MTO/SiO_2 \cdot Al_2O_3$ catalytic system after 24 h. [(■)—cross-metathesis; (♦)—homo-metathesis].
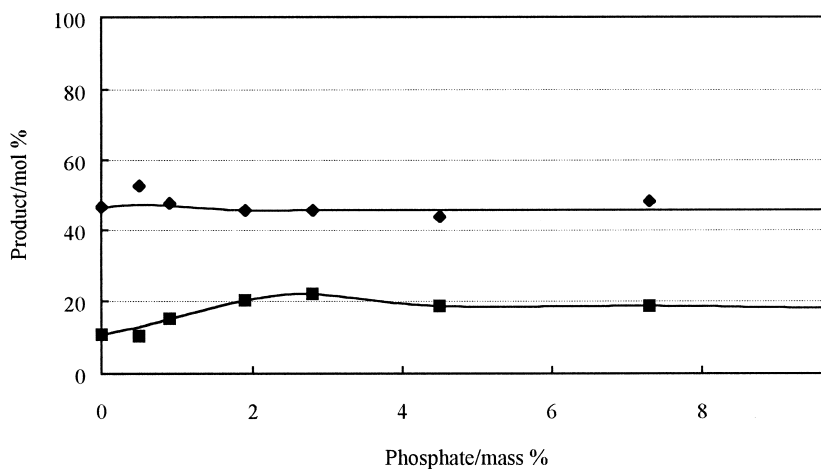
Fig. 4. The influence of the phosphate content on the metathesis activity of 1-octene with the 7.5% MTO/3.3% Cs/$SiO_2 \cdot Al_2O_3$ catalytic system after 24 h. [(■)—cross-metathesis; (◆)—homo-metathesis].

$\cdot Al_2O_3$ and the 7.5% MTO/3.3% Cs^+/$SiO_2 \cdot$ Al_2O_3 catalytic systems in the presence of functionalized saturated hydrocarbons.

3.6. The influence of pentanoic acid

Fig. 5 shows the influence of pentanoic acid on the metathesis activity of the 7.5% MTO/$SiO_2 \cdot Al_2O_3$ catalytic system with 1-octene. Addition of pentanoic acid to 1-octene increases the homo-metathesis products and it reaches a maximum of 30% at 1.3% pentanoic acid after which it declines. The cross-metathesis products decrease from 80% at 0% to 10% at 9.5% pentanoic acid added.

Fig. 6 shows the influence of the pentanoic acid on the metathesis activity of the 7.5% MTO/3.3% Cs^+/$SiO_2 \cdot Al_2O_3$ catalytic system. Addition of pentanoic acid decrease the homo-metathesis products from 46.6% at 0% to 5.8% at 9.5% pentanoic acid added. The cross-metathesis products decrease from 10.6% at 0% to 0% at 6.1% pentanoic acid added and stays like that for further addition of pentanoic acid.
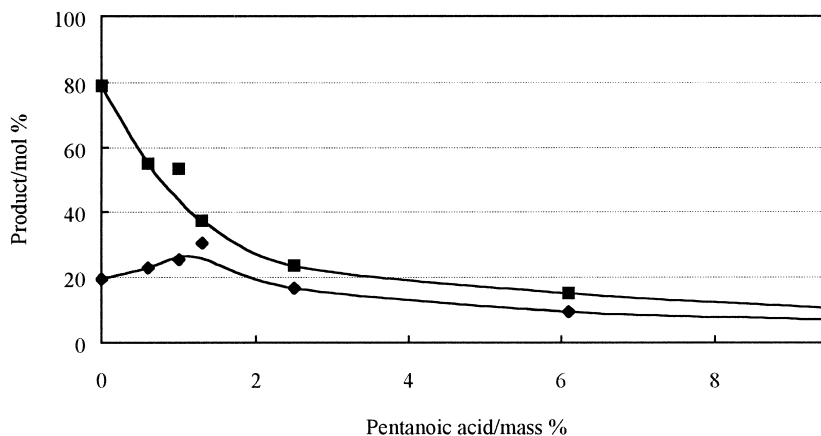

Fig. 5. The influence of pentanoic acid on the metathesis activity of 1-octene with the 7.5% MTO/$SiO_2 \cdot Al_2O_3$ catalytic system after 24 h. [(■)—cross-metathesis; (◆)—homo-metathesis].
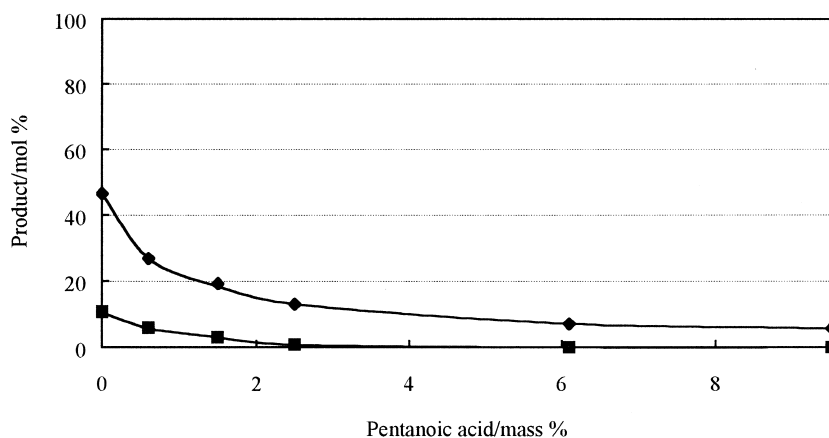
Fig. 6. The influence of pentanoic acid on the metathesis activity of 1-octene with the 7.5% MTO/3.3% Cs/SiO$_2$ · Al$_2$O$_3$ catalytic system after 24 h. [(■)—cross-metathesis; (♦)—homo-metathesis].

3.7. The influence of other additives

The influence of butanol, 2-hexanone, pentanal, water and butylamine was also investigated. In Table 1 the influence of a 1% and 2% addition to the 1-octene is illustrated (the influence of pentanoic acid is also presented in Table 1).

3.8. Yield of homo-metathesis products

Only MTO supported on the silica–alumina is activated towards homo-metathesis products by 1% additive added except in the case of water and butyl amine. 2-Hexanone gives the highest metathesis products at 1% of 2-hexanone added. Addition of 2% of the additives drastically decrease the homo-metathesis products in the case of butanol and pentanal. Water, butyl amine, pentanoic acid and 2-hexanone slightly decrease the homo-metathesis products.

Addition of 1% of the organic additives deactivates the MTO catalyst supported on the silica–alumina loaded with cesium. Butanol gives the highest deactivation and butyl amine gives the lowest deactivation. Increased concentrations of additives also deactivates the MTO/ Cs$^+$/SiO$_2$ · Al$_2$O$_3$ catalytic system.

3.9. Yield of cross-metathesis products

The cross-metathesis products of 1-octene catalysed by MTO supported on silica–alumina decreased with the addition of 1% of additives.

Table 1

The influence of 1% and 2% addition of butanol, 2-hexanone, pentanal, pentanoic acid, water and butylamine added to 1-octene on the metathesis activity of the MTO containing catalytic system

Additive	Butanol		2-Hexanone		Pentanal		Pentanoic acid		Water		Butylamine		No addition
% addition	1	2	1	2	1	2	1	2	1	2	1	2	0
System	7.5% MTO/SiO$_2$ · Al$_2$O$_3$/1-octene												
% homo-metathesis	25	9	36	28	30	10	25	17	13	10	18	20	19
% cross-metathesis	32	11	22	16	42	12	53	23	21	16	56	41	79
System	7.5% MTO/3.3% Cs$^+$/SiO$_2$ · Al$_2$O$_3$/1-octene												
% homo-metathesis	9	6	23	11	11	6	23	16	16	13	34	28	47
% cross-metathesis	0	0	2	0	4	0	4	2	2	2	5	5	11

Water gives the highest and butyl amine the lowest deactivation. Addition of 2% of butanol gives the highest deactivation of $MTO/SiO_2 \cdot Al_2O_3$ catalytic system.

Addition of 1% butanol drastically decreases the cross-metathesis products of 1-octene catalysed by the $MTO/Cs^+/SiO_2 \cdot Al_2O_3$ catalytic system. Addition of 1% butyl amine gives the least deactivation. Higher concentrations of additives also deactivates the $MTO/Cs^+/SiO_2 \cdot Al_2O_3$ catalytic system.

4. Conclusions

In the presence of the MTO containing metathesis catalyst, 1-octene is converted into a series of alkene products stretching from C_2 to C_{14}. To form these products 1-octene must undergo an alkene isomerisation reaction.

Metathesis activity and rhenium oxide loading can be related to the number and Brønsted acidity of OH-groups on the support. At low MTO loading, there will be more Brønsted acid sites on the support which favour isomerisation and result in low selectivity towards the homo-metathesis reaction.

The addition of alkali metal ions to heterogeneous catalysts improve the selectivity of homo-metathesis reaction. Fig. 3 illustrates that the addition of cesium clearly improves the selectivity of MTO supported on the silica–alumina towards homo-metathesis reaction. The addition of cesium before calcination interfere with the active sites on silica–alumina involved in isomerisation. The cesium ions displace the hydrogen ions on the silica–alumina surface, inhibit the isomerisation reaction and no cross-metathesis products can be generated. Higher concentrations of cesium on the support also reduced the percentage yield on homo-metathesis products.

It is important to note that the added phosphate ions do not influence the yield of homo-metathesis products of 1-octene and only a slight increase in cross-metathesis products as can be seen in Table 2.

It can be concluded from the data given in Table 1 that a low percentage of organic additives to 1-octene increase the metathesis activity. However, an excess of the additive lowers the metathesis yield. The type and also the amount of additive added to the 1-octene has an influence on the activity on the MTO-containing catalyst.

The metathesis activity of MTO supported on the silica–alumina loaded with cesium decreased with the addition of the organic additives, but the selectivity towards homo-metathesis reaction increased, as a consequence of less side reactions. These results correlate with the result of Nishiguchi et al. [14]. They reported that Brønsted acid sites of the silica–alumina interact preferentially with the polar additives as a result the activity decreased. If the organic additive is in excess, it competes with the alkene double bond for the active site.

The additive used can be classified as Lewis bases which are 2-hexanone, butyl amine and pentanal, each containing a lone pair of electrons on the oxygen or nitrogen atom, and Brønsted acids which are water, pentanoic acid and butanol.

Table 2
The influence of 3.3% Cs^+ and of 2% PO_4^{3-} on the metathesis product yield of 1-octene catalysed by a 7.5% $MTO/SiO_2 \cdot Al_2O_3$ catalyst. Reaction time 24 h at room temperature

Catalytic systems	Homo-metathesis products	Cross-metathesis products
7.5% $MTO/SiO_2 \cdot Al_2O_3$	20	80
2% $PO_4^{3-}/7.5\%$ $MTO/SiO_2 \cdot Al_2O_3$	20	85
3.3% $Cs^+/7.5\%$ $MTO/SiO_2 \cdot Al_2O_3$	47	11
2% $PO_4^{3-}/3.3\%$ $Cs^+/7.5\%$ $MTO/SiO_2 \cdot Al_2O_3$	46	20

The presence of acidic hydrogen in the functional group of additive, increases isomerisation. That could be the reason why the cross-metathesis products in Table 1 for pentanal is higher than that of the 2-hexanone.

The Lewis bases containing a C=O group and an electron pair on the oxygen may react with the metal carbene according to a Wittig type of reaction [15] to form a Re=O containing species and so deactivates the system.

The Brønsted acids may protonate the rhenium and lowers the possibility of the rhenium nucleus to reacts with an alkene and to form a metal carbene [16].

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