$Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4/1$-octene catalytic system
Part I: The influence of Cs^+ and PO_4^{3-} on the metathesis activity

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Abstract

The addition of small amounts ($\sim 2\%$) of Cs^+ and/or PO_4^{3-} ions to a 3% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4/1$-octene catalytic system led to a significant increase in the metathesis activity of the system. If Cs^+ and PO_4^{3-} ions are used, the activity of the system is determined by the sequence of impregnation on the $SiO_2 \cdot Al_2O_3$ support with the different compounds. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Re_2O_7 on Al_2O_3 is an excellent metathesis catalyst and the reaction may be performed at temperatures from room temperature up to 100°C with terminal or internal alkenes in the gas or liquid phase [1–4]. This system is also suitable for the metathesis of alkenes that contain functional groups [1,2,4,5] if $SnMe_4$ is used as cocatalyst [5,6].

The support material is an important factor to consider regarding the activity of the Re_2O_7 catalyst system [7]. There exists a clear relationship between the metathesis activity of the Re_2O_7 catalyst and the Brønsted acid character of the support material [7,8].

Re_2O_7 is fixed on to the support by using an aqueous solution of NH_4ReO_4 [9,10]. The ReO_4^- ion reacts with the Al_2O_3 surface through the replacement of a surface OH group and then bonds via an oxygen bridge to the Al_2O_3 surface [11–14].

Vuurman et al. [15] found two Re_2O_7 species after dehydration of the Al_2O_3 while the other was only present at the higher Re_2O_7 loading [14]. The ReO_4^- ions first react with Lewis acid centres on the Al_2O_3 but this species do not give metathesis active sites [7]. At the higher Re_2O_7 loading (76%), the interaction of ReO_4^- ions with Brønsted acid sites increase and therefore also the metathesis activity.

If Al_2O_3 is replaced by a silica–alumina ($SiO_2 \cdot Al_2O_3$) support, a highly active metathesis catalyst is obtained [16,17]. In the presence of suitable cocatalysts the $Re_2O_7/SiO_2 \cdot Al_2O_3$

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system is also active for the metathesis of functionalized alkenes [5,6]. Two types of OH groups on the silica–alumina support cause the Brønsted acid character [9,10,17]. One type of OH is bonded to the silicon while the other is a bridged OH between the silicon and aluminium [9,17]. During the activation of the system the ReO_4^- ions attach to the centres formerly occupied by the bridge OH groups [9,17].

If the impregnation of the Al_2O_3 support by a NH_4ReO_4 solution is preceded by the impregnation with a PO_4^{3-} containing solution, the system leads to a catalyst with a higher metathesis activity than the Re_2O_7/Al_2O_3 catalyst [10,18]. The higher activity may be ascribed to the change in strength of the Brønsted acidity on the support surface [10,18,19].

The metathesis activity of the silica–alumina-supported catalyst in general is much higher than the activity of the phosphated alumina. This is caused by the much stronger Brønsted acidity of these catalysts [20].

The addition of small amounts of alkali, alkali earth and thallium ions to heterogeneous catalyst systems, is especially effective in poisoning the acid points on the catalyst [1,21]. This will cause the decrease in double bond isomerisation and an increase in metathesis selectivity [22]. Sibeijn et al. [23] and Ellison et al. [24] reported that the addition of Cs^+ ions to the Re_2O_7/Al_2O_3 catalyst system is most effective for the inhibition of side reactions such as isomerisation, polymerisation and coke formation. With a 3% $Re_2O_7/SiO_2 \cdot Al_2O_3$ catalyst it was also found that with 1–2% Cs^+ the selectivity of the catalyst increased considerably [25].

The addition of a cocatalyst such as SnR_4 to the Re_2O_7/Al_2O_3 catalyst increases the catalytic metathesis activity [26,27] for alkenes and also causes the metathesis of functionalized alkenes [4,17].

The 3% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4$ system is an excellent catalyst system for the metathesis of 1-alkenes. It produces a high yield of homometathesis products with a relatively low yield of cross metathesis products. In this study we investigated the factors that influence the activity and selectivity of this system.

2. Experimental

2.1. Reagents

The reagents $SnMe_4$ (Merck) and 1-octene (Merck) were stored under N_2 after degassing. Other organic reagents were dried using standard methods and also stored under N_2.

NH_4ReO_4 (Strem Chemicals), $SiO_2 \cdot Al_2O_3$ (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 (Aldrich) were used as received.

2.2. Apparatus

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.

2.3. Catalyst preparation

The catalyst support was dried at 100°C for 1 h before use. The 3% Re_2O_7 containing catalyst was prepared by mixing 0.134 g of NH_4ReO_4 (5×10^{-4} mol) in 4 cm^3 water with 3 g of the support. This mixture was then dried at 100°C in air. In the cases where Cs^+ or PO_4^{3-} ions were added, $CsNO_3$ or $(NH_4)_4HPO_4$ in 4 cm^3 of water were used to impregnate the catalyst. After each impregnation step the catalyst was dried at 100°C. Analysis of the impregnated catalysts was done with ICP-AES methods.

2.4. Activation of the catalyst

The catalysts (0.11 g) were activated by heating in a glass tube in a stream of dry O_2 for 3 h followed by a stream of dry N_2 at 500°C for 2

h. The catalyst was then transferred under N_2 to the reactor.

2.5. Catalytic reactions

In a typical reaction 1 cm^3 of PhCl containing 6.26×10^{-6} mol SnMe$_4$ was added to the catalyst in the reactor. After stirring the mixture for 5 min 0.3 cm^3 of 1-octene (2×10^{-3} mol) was added. The reaction was terminated after a specific period by the removal of the catalyst. The remaining liquid was analysed by GC and GC-MS methods.

GC analyses were performed with a Fisons 8000 series GC equipped with a SE 30 (15 m $\times$ 0.53 mm $\times$ 1.2 μm) capillary column and FID using the following conditions: inlet temperature 250°C, oven programmed from 40–250°C at 6°C min^{-1}; N_2 carrier gas and FID temperature 300°C.

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 $2(\sum_{n=9}^{14} \%C_n)$

Homometathesis: 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 $2(\sum_{n=9}^{13} \%C_n)$.

3. Results and discussion

Different factors that can influence the catalytic activity and selectivity of the Re$_2$O$_7$/SiO$_2 \cdot$ Al$_2$O$_3$/SnMe$_4$/1-octene catalytic system, were studied.

3.1. Reaction time

The influence of reaction time on a 3% Re$_2$O$_7$/SiO$_2 \cdot$ Al$_2$O$_3$/SnMe$_4$ catalyst system with a Sn:Re molar ratio = 2 (Fig. 1) indicates that the metathesis reaction equilibrium is

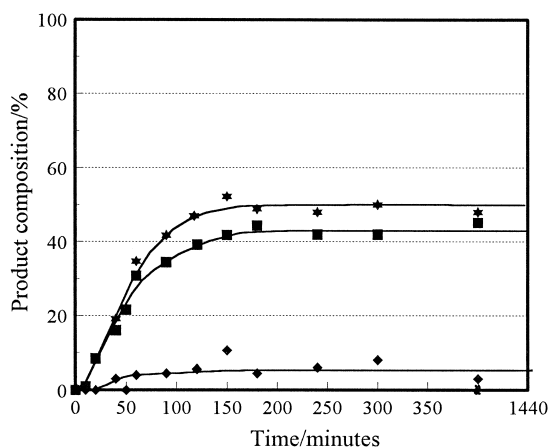Fig. 1. The product yield as a function of reaction time for a 3%Re$_2$O$_7$/SiO$_2 \cdot$ Al$_2$O$_3$/SnMe$_4$/1-octene catalytic system. ★: Total metathesis, ■: homometathesis products, ◆: cross metathesis products.

reached after 240 min. This reaction time was used in all the further investigations.

3.2. Re$_2$O$_7$ content

By increasing the Re$_2$O$_7$ content of the Re$_2$O$_7$/SiO$_2 \cdot$ Al$_2$O$_3$/SnMe$_4$ system and keeping the Sn:Re molar ratio = 2 an increase in the homometathesis product yield is obtained up to a 3% Re$_2$O$_7$ content. Above 4% a decrease in
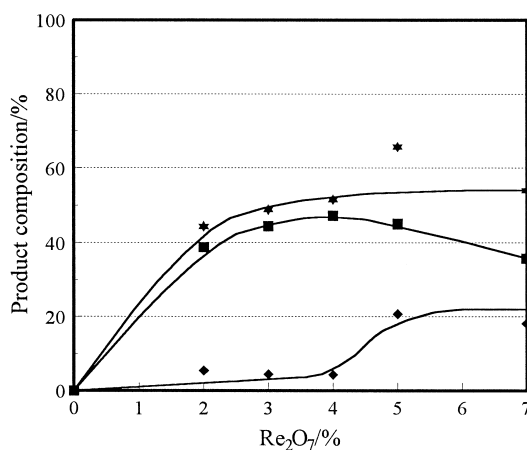

Fig. 2. The influence of the Re$_2$O$_7$ content on the metathesis activity of the Re$_2$O$_7$/SiO$_2 \cdot$ Al$_2$O$_3$/SnMe$_4$/1-octene catalytic system. ★: Total metathesis, ■: homometathesis, ◆: cross metathesis.

the homometathesis product yield takes place while a rapid increase of the cross metathesis product yield is observed (Fig. 2). For further investigations a 3% Re_2O_7 content was used.

3.3. The Sn:Re molar ratio

From Fig. 3 it can be concluded that the maximum homometathesis product yield is reached at a Sn:Re molar ratio between 1:1 and 2:1 and the ratio 2:1 was used in the other experiments.

3.4. Addition of Cs^+

The addition of 1% Cs^+ to the 3% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4/1$-octene catalytic system increased the total metathesis product yield from 46 to 70% and the homometathesis product yield from 44 to 53% (Fig. 4). It also resulted in the increase of the cross metathesis product yield from 4–16%.

The sequence of the addition of Cs^+ and ReO_4^- ions onto the $SiO_2 \cdot Al_2O_3$ has no influence on the metathesis product yield distribution.
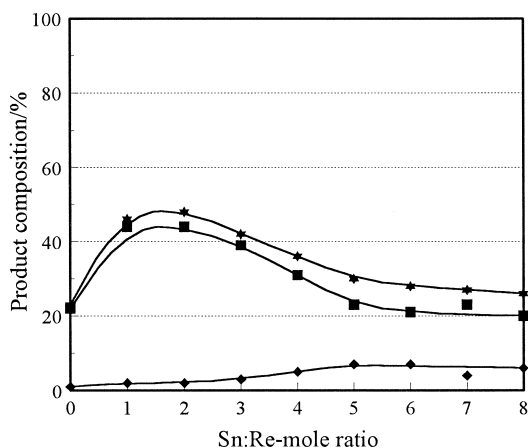

Fig. 4. The influence of the Cs^+ content on the metathesis activity of a 3% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4/1$-octene catalytic system. ★: Total metathesis, ■: homometathesis, ◆: cross metathesis.

3.5. Addition of PO_4^{3-} ions

The addition of PO_4^{3-} ions did not only increase the metathesis product yield but also the products resulting from isomerisation and cross metathesis of the 1-octene (Fig. 5).

Maximum homometathesis yield of 52% is obtained with a 2% PO_4^{3-} content while a maxi-
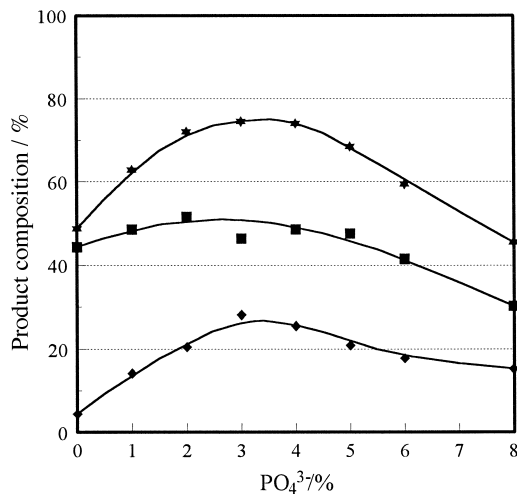

Fig. 3. The influence of the Sn:Re molar ratio on the metathesis activity of a 3% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4/1$-octene catalytic system. ★: Total metathesis, ■: homometathesis, ◆: cross metathesis.

Fig. 5. The influence of the PO_4^{3-} content on the metathesis activity of a 3% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4/1$-octene catalytic system. ★: Total metathesis, ■: homometathesis, ◆: cross metathesis.

Table 1
Comparison of the metathesis activity of different $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4/1$-octene catalytic systems

Catalyst system	Total metathesis (%)	Homo metathesis (%)	Cross metathesis (%)
3% $Re_2O_7/$[a]	48	44	4
2% $Cs^+/$3% $Re_2O_7/$[a]	69	53	16
2% [b]$PO_4^{3-}/$3% [c]$Re_2O_7/$[a]	72	52	20
2% [c]$PO_4^{3-}/$3% [b]$Re_2O_7/$[a]	89	30	58
2% [c]$Cs^+/$2% [d]$PO_4^{3-}/$3% [b]$Re_2O_7/$[a]	72	53	19
2% [d]$Cs^+/$2% [c]$PO_4^{3-}/$3% [b]$Re_2O_7/$[a]	69	54	15

[a]$SiO_2 \cdot Al_2O_3/SnMe_4/1$-octene.
[b]Added second.
[c]Added first.
[d]Added third.

mum cross metathesis yield of 25% is reached with a 3% PO_4^{3-} content.

The sequence of impregnation with $(NH_4)_2HPO_4$ and NH_4ReO_4 has a pronounced effect on the product yield. If the $SiO_2 \cdot Al_2O_3$ was first impregnated with NH_4ReO_4 the product yield was as follows: Total metathesis 89%, homometathesis 30% and cross metathesis 58%. If the $SiO_2 \cdot Al_2O_3$ was first impregnated with $(NH_4)_2HPO_4$ the product yield was: total metathesis 74%, homometathesis 52% and cross metathesis 21% (Table 1). In our work we used the last mentioned system.

3.6. Addition of PO_4^{3-} and Cs^+ ions

In Table 1 the combined effect on the product distribution is also given if both Cs^+ and PO_4^{3-} ions are present in the rhenium catalyst. Similar results of about 53% homometathesis products and about 17% cross metathesis products are obtained irrespective the order of addition.

4. Conclusions

The addition of Cs^+ and PO_4^{3-} ions to the 3% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4$ catalyst system with a Sn:Re molar ratio of 2:1 causes an increase in the metathesis product yield with 1-octene but it also causes the increase in the

isomerisation and cross metathesis activity of the different catalysts.

A 2% Cs^+, 2% PO_4^{3-} and also a combination of these two ions on a 3% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4$ catalytic system gives the best result because it causes a high yield of homometathesis products and a relatively low yield of cross metathesis products. The activity of the system if a combination of the ions on the 3% Re_2O_7 system is used, is determined by the sequence of impregnation with the different ions (Table 1).

Acknowledgements

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