

Re₂O₇/SiO₂ · Al₂O₃/SnMe₄/1-octene catalytic system Part II. The influence of oxygen containing saturated hydrocarbons on the metathesis activity

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Abstract

Oxygen-containing Lewis bases and Brønsted acids deactivate the 3% Re₂O₇/SiO₂ · Al₂O₃/SnMe₄ catalyst system. The activity, selectivity, and stability of this system towards the presence of oxygen-containing compounds can be improved by the addition of PO₄³⁻ or Cs⁺ ions to the catalyst. The deactivation of the catalyst is influenced by the availability of an electron pair on the CO-containing Lewis base for bond formation with the active organometallic intermediate. The stronger the CO bond as measured by the IR stretching vibration, the less available the electron pair will be for bond formation. A relationship also exists between the strength of the OH bond, as indicated by the IR stretching vibration of the Brønsted acid and the deactivation of the catalyst. A higher value of the IR stretching vibration of the OH bond corresponds to a weaker deactivation of the catalyst system. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most metathesis catalyst systems are deactivated if polar groups in functionalized alkenes are present [1]. In the case of homogeneous catalysts, however, a number of additives are known that inhibits side reactions and so increase the selectivity of the metathesis reaction [2–4]. With the WCl₆/SnBu₄ catalyst system, the addition of small amounts of protic solvents such as ethanol, phenol, water or acetic acid increases the catalytic activity. Further addition

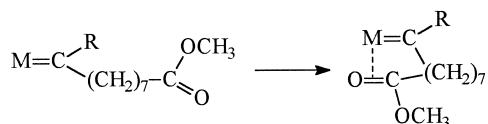
of these additives, however, deactivates the system and if the reaction temperature is increased (80–120°C), a larger amount of additive is needed to inhibit the reaction [4].

The Re₂O₇/SiO₂ · Al₂O₃ catalyst system shows a higher olefin isomerisation activity than the Re₂O₇/Al₂O₃ system because of the acid OH groups present on the support material. Sibeijn et al. [5] found that after the addition of methyl acetate during the metathesis of 1-octene the selectivity of the Re₂O₇/SiO₂ · Al₂O₃ catalyst system towards the major metathesis product, 7-tetradecene, increased from 85 to almost 100%. The activity of the system decreased during this process. The increase in selectivity

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was attributed to a decrease in the acid character of the system due to interaction of the ester with the acidic OH groups, while the decrease in activity was due to complexation of the ester groups with the Re atoms.

A special case of deactivation is the self-poisoning by reagents containing polar groups [6].



The presence of isobutene or 1,3-butadiene in propene deactivates the catalyst but the activity of the catalyst can be restored if pure propene is again used for the metathesis reaction [7].

The presence of polar compounds such as water, methanol, methyl *t*-butyl ether cause permanent deactivation of the catalyst probably by the protonation of the active rhenium atoms by these compounds [7].

Other polar compounds such as dimethylether deactivates the system also in a reversible manner. This ether is a nonprotic Lewis base that neutralises the Lewis acid character of the rhenium atoms by a reversible coordination equilibrium [8].

$\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4$ is one of the few metathesis catalyst systems that are active in the presence of a variety of alkenes including unsaturated esters and allyl compounds [1]. In this study, the metathesis activity of Re_2O_7 containing catalyst systems in the presence of functionalized saturated hydrocarbons were investigated.

2. Experimental

The same procedures were used as described before [9]. The influence of the oxygen-containing compounds was determined by adding the compound into the reactor with a syringe directly after the 1-octene was added to the reac-

tor. The amount of the oxygen-containing compound added is expressed as mol percentage with regard to the amount of 1-octene added. The values of the C=O and OH infrared stretching vibrations were obtained from literature [10].

3. Results and discussion

The 3% $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1$ -octene catalytic system has a high metathesis activity and selectivity. In the presence of the additives, butyl acetate (BuOAc), water, 2-pentanone (MeCOPr), acetic acid (HOAc) or butanol (BuOH) in 1-octene, the catalyst is deactivated partially (Fig. 1). Deactivation of the system by the additives increases in the following sequence: $\text{BuOAc} < \text{H}_2\text{O} < \text{MeCOPr} < \text{BuOH} < \text{HOAc}$.

BuOAc, however, gave an increase in the metathesis product yield if it was kept below 2%.

Results indicated that the deactivation of a 2% $\text{Cs}^+/3\%$ $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1$ -octene system with regard to the catalytic system without Cs^+ ions is less pronounced (Fig. 2). The order of deactivation by the different

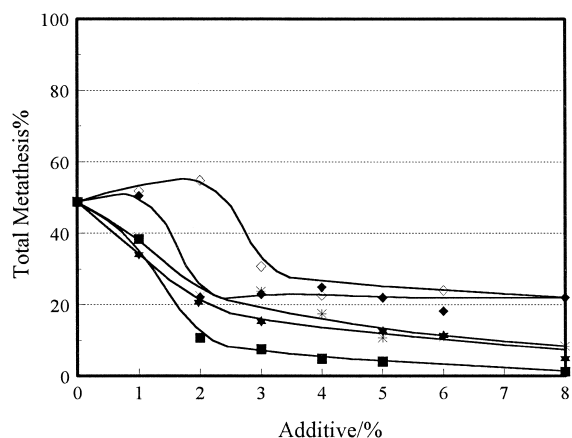


Fig. 1. The influence of additives on the metathesis activity of the 3% $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1$ -octene catalytic system at 25°C (Sn:Re molar ratio = 2:1; Reaction time = 240 min). ★: BuOH, ■: HOAc, ◆: H_2O , *: MeCOPr, ◇: BuOAc.

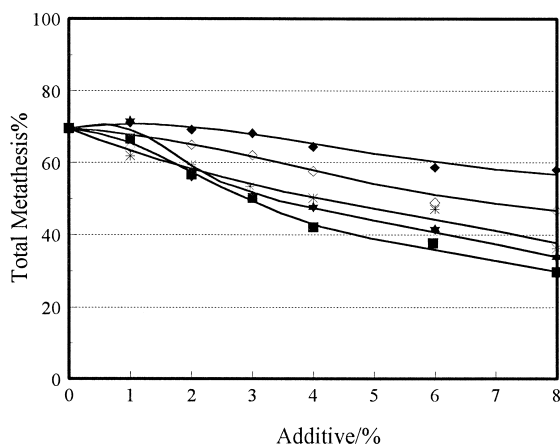


Fig. 2. The influence of additives on the metathesis activity of the 2% Cs^+ /3% $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1$ -octene catalytic system at 25°C (Sn:Re molar ratio = 2:1; Reaction time = 240 min). \star : BuOH, \blacksquare : HOAc, \blacklozenge : H_2O , \ast : MeCOPr, \diamond : BuOAc.

additives in this case was found to be $\text{H}_2\text{O} < \text{BuOAc} < \text{MeCOPr} < \text{BuOH} < \text{HOAc}$ (Fig. 2).

The influence of additives on the 2% $\text{PO}_4^{3-}/3\% \text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1$ -octene catalytic system also leads to the systematic deactivation of catalytic system (Fig. 3). The order of deactivation by the different additives was the same as in the Cs^+ -containing system.

Almost similar results were obtained with a 2% $\text{Cs}^+/2\% \text{PO}_4^{3-}/3\% \text{Re}_2\text{O}_7/\text{SiO}_2 \cdot$

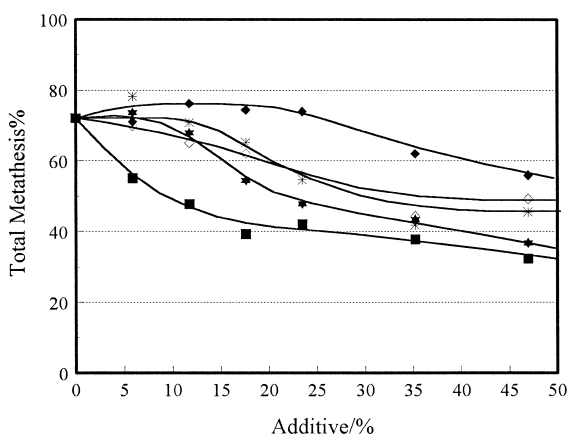


Fig. 3. The influence of additives on the metathesis activity of the 2% $\text{PO}_4^{3-}/3\% \text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1$ -octene catalytic system at 25°C (Sn:Re molar ratio = 2:1; Reaction time = 240 min). \star : BuOH, \blacksquare : HOAc, \blacklozenge : H_2O , \ast : MeCOPr, \diamond : BuOAc.

$\text{Al}_2\text{O}_3/\text{SnMe}_4/1$ -octene catalytic system when the influence of the additives was determined.

3.1. The influence of Lewis bases on the metathesis reaction of the $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1$ -octene catalytic system

BuOAc, MeCOPr and HOAc each contains a carbonyl group with an electron pair on the oxygen that can be donated. These three additives can act as Lewis bases and they can probably deactivate the metathesis reaction by donating an electron pair to the rhenium atom and so prevent the alkene to react.

To find an explanation for the sequence of deactivation of the catalyst by the additives, the Lewis base strength of the additives was investigated. This was done by comparing the IR stretching vibration of the C=O bond of the additives and the influence of the additive (8% content) on the total metathesis product yield with each other. The IR stretching vibrations used were obtained from literature [10]. We assumed that the stronger the C=O bonding, the weaker the electron donation ability of the carbonyl group and thus, the weaker the Lewis base properties of the additives will be, and the less the deactivation of the catalyst will be. The results of the catalyst system investigated are given in Fig. 4. The influence of heptanal and acetic anhydride, both as Lewis bases, is also indicated. Acetic anhydride is the only additive that does not fit into this scenario.

The same tendency was observed for all the other catalyst systems shown in Fig. 4. The value of the IR stretching vibration is related to the strength of the C=O bonding. The higher the IR stretching vibration, the stronger the C=O bond and therefore, the less available the electron pair on the oxygen atom will be for donation to the catalytic centre for bond formation; thus, deactivation of the catalyst system is observed. BuOAc is therefore a much weaker Lewis base than MeCOPr because of the higher IR stretching vibration and that explains the smaller deactivation influence of the additive.

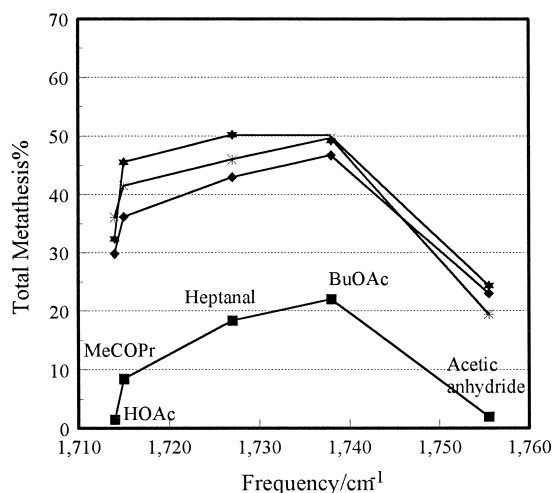


Fig. 4. The relationship between the total metathesis product yield and the C=O stretching vibration of different Lewis bases (8% with regard to 1-octene) on the catalyst system at 25°C. ★: 2% PO_4^{3-} /Cat, *: 2% Cs^+ /2% PO_4^{3-} /Cat, ◆: 2% Cs^+ /Cat, ■: Cat (3% $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$).

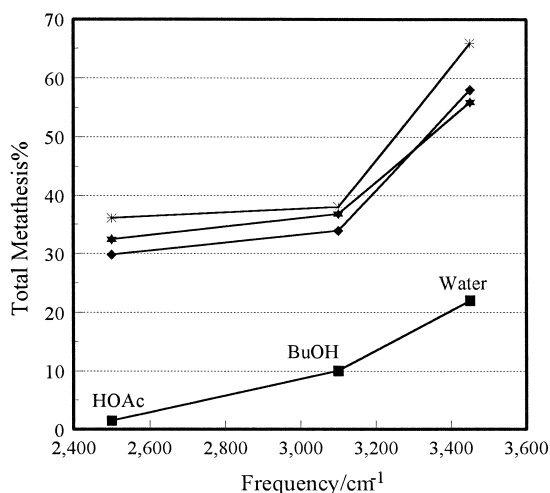


Fig. 5. The relationship between the total metathesis product yield and the O–H stretching vibration of different Brønsted acids (8% with regard to 1-octene) on the catalyst system at 25°C. ★: 2% PO_4^{3-} /Cat, *: 2% Cs^+ /2% PO_4^{3-} /Cat, ◆: 2% Cs^+ /Cat, ■: Cat (3% $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$).

For the systems containing the PO_4^{3-} , Cs^+ or a combination of the two ions, it is obvious that these systems are more resistant to deactivation by the additives than the $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4$ system.

3.2. The influence of Brønsted acids on the metathesis activity of the 3% $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4$ systems

HOAc, BuOH and H_2O have at their disposal a proton that can take part in reactions that can deactivate the active rhenium species. The O–H stretching vibration of the different Brønsted acids was used as an indication of the strength of the acids. The higher the frequency, the stronger the O–H bond and the weaker acid the compound will be.

In Fig. 5 the influence of HOAc, BuOH and H_2O is indicated.

The O–H bond of water has the highest stretching frequency with respect to that of BuOH and HOAc and it will be the weakest Brønsted acid. Therefore, deactivation by the stronger acids BuOH and HOAc will be more pronounced.

3.3. The influence of Lewis bases and Brønsted acids on the cross metathesis activity of $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4$ systems

In Fig. 6 the cross metathesis product yield in the presence of 8% of the different Lewis bases and Brønsted acids as indicated for the different Re_2O_7 -containing catalyst systems. The addition of Brønsted acids tends to give a higher

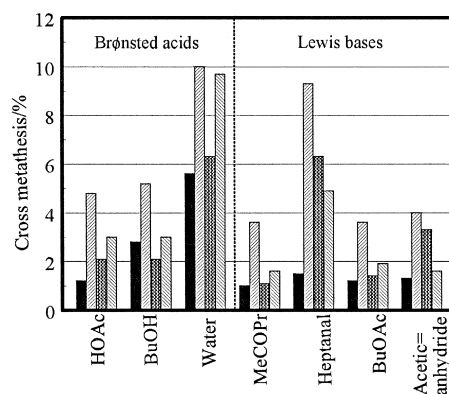


Fig. 6. The influence of different Brønsted acids and Lewis bases on the cross metathesis activity of Re_2O_7 containing catalyst systems. Additives: 8% with regard to 1-octene; Catalyst: ■ 3% $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$ (= Cat), ▨ 2% PO_4^{3-} /Cat, ▩ 2% Cs^+ /Cat, ▪ 2% Cs^+ /2% PO_4^{3-} /Cat.

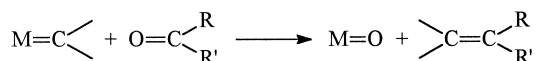
yield of cross metathesis products than the Lewis bases. Water gives the highest cross metathesis activity. Heptanal, a Lewis base, unexpectedly showed a high yield of cross metathesis products especially in the presence of the catalyst containing PO_4^{3-} ions.

Deactivation of the catalyst system can be caused by a reaction with the additive, which destroys the active intermediate necessary for the metathesis reaction or by a reaction between the additive and the co-catalyst, or by a reaction between the additive and the OH groups present on the surface. We came to the conclusion that the deactivation is caused by an attack on the metal intermediate. The reason is that all the catalyst systems tested reacted in the same manner after addition of the additives. This was not only found for the Re_2O_7 -containing catalysts but also for the $\text{CH}_3\text{ReO}_3/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ system (J.A.K. du Plessis, unpublished results) that contained no co-catalyst and for homogeneous catalyst systems such as $\text{WCl}_6/\text{SnMe}_4$ and $\text{W}(\text{O}-2,6-\text{C}_6\text{H}_3\text{Cl}_2)_2\text{Cl}_4/\text{SnBu}_4$ [11,12]. Nishiguchi et al. [4] also found similar results in their study of the $\text{WCl}_6/\text{SnBu}_4$ system.

The additives may be classified according to the functional groups they contain as Lewis bases or Brønsted acids, and two different types of reactions can take place with a metal carbene centre.

4. Lewis base

The Lewis bases containing a C=O bond and available electron pairs on the oxygen can react with the metal carbene according to a Wittig type reaction [13]:



Agnero et al. [13] found, in their study of the reaction of ketones and esters with metal carbenes of the type $(t\text{-BuCH}_2\text{O})_2\text{Br}_2\text{W}=\text{CHR}$,

that the above-mentioned reaction is easier with the ketone than with the ester. This explains the higher degree of deactivation of the metathesis reaction by ketones than by esters (Fig. 4).

With heptanal, a high degree of isomerisation of the alkene and thus, also a higher degree of cross-metathesis products can be observed (Fig. 6). This leads to the conclusion that heptanal may also act as a Brønsted acid in donating a proton to the rhenium system.

Acetic anhydride is not expected to deactivate the catalyst system to such an extent as shown in Fig. 6 because of its high C=O stretching frequency. This phenomenon may be the result of the decomposition of the anhydride to acetic acid through a reaction with the OH groups on the catalyst surface [14]. Acetyl groups formed on the surface may then also react with acid –OH groups to form acetaldehyde [15].

5. Brønsted acids

H_2O , BuOH and HOAc act as Brønsted acids. In HOAc , the OH stretching frequency is the lowest and its proton will more easily react with the rhenium intermediate than BuOH or H_2O to prevent the metathesis reaction to take place.

The Brønsted acids also cause a higher degree of isomerisation of 1-octene and the formation of cross metathesis products especially in the cases where PO_4^{3-} ions were present. Although H_2O has the highest OH stretching frequency, it gives the highest yield of cross-metathesis products and shows the least deactivation of the catalyst system. This may indicate an interaction with the $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ support to form Brønsted acid sites with fewer interactions with the rhenium species.

The deactivation of the catalytic system in the presence of the Brønsted acids or Lewis bases additives is permanent. By rinsing the system with pure 1-octene, the activity could not be restored.

6. Conclusions

The metathesis activity, selectivity, and stability of the $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1$ -octene catalytic system towards the presence of oxygen-containing compounds can be improved by the addition of PO_4^{3-} or Cs^+ ions to the catalyst.

The deactivation of the catalyst is influenced by: (a) The availability of an electron pair of the oxygen on the $\text{C}=\text{O}$ containing Lewis base for donation. The stronger the $\text{C}=\text{O}$ bond as measured by the IR stretching vibration, the less available the electron pair will be for bond formation; (b) The strength of the $\text{O}-\text{H}$ bond (as indicated by the IR stretching vibration) of the Brønsted acid. The deactivation declines with a stronger $\text{O}-\text{H}$ bond.

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