

# Re<sub>2</sub>O<sub>7</sub>/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>/SnMe<sub>4</sub>/1-octene catalytic system. Part III: The influence of the carbon–carbon chain length of additives on the metathesis activity

J.A.K. du Plessis<sup>a,\*</sup>, A. Spamer<sup>b</sup>, H.C.M. Vosloo<sup>a</sup>

<sup>a</sup> SASOL Centre for Chemistry, Potchefstroomse Universiteit vir Christelike Hoër Onderwys, Potchefstroom 2520, South Africa

<sup>b</sup> Sastech R & D, PO Box 1, Sasolburg 9570, South Africa

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## Abstract

The metathesis reaction of 1-octene was studied by using a 3% Re<sub>2</sub>O<sub>7</sub>/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>/SnMe<sub>4</sub> catalyst system. The addition of oxygen containing Lewis bases and Brønsted acids, i.e., organic acids, alcohols, esters and 2-ketones, deactivate the catalytic system. A direct relationship exists between the chain length of the carbon chain associated with the Lewis base or the Brønsted acid, the activity of the catalyst and the IR stretching vibration of the C=O or OH group under investigation. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Re<sub>2</sub>O<sub>7</sub>/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>/SnMe<sub>4</sub>/1-octene; Carbon–carbon chain length; Metathesis

## 1. Introduction

The 3% Re<sub>2</sub>O<sub>7</sub>/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub>/SnMe<sub>4</sub>/1-octene catalytic system has a high metathesis activity and selectivity [1,2]. In the presence of the additives butyl acetate (BuOAc), water, 2-pentanone (MeCOPr), acetic acid (HOAc) or butanol (BuOH) the catalyst is deactivated.

In general, the order of deactivation of different Re<sub>2</sub>O<sub>7</sub>/SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> containing catalysts by the different additives was found to be H<sub>2</sub>O < BuOAc < MeCOPr < BuOH < HOAc [2].

The Lewis bases, HOAc, MeCOPr, heptanal and BuOAc, and the Brønsted acids water, BuOH and HOAc, showed a relationship between the value of the IR stretching vibration of the C=O of the Lewis bases and of the O–H of the Lewis acids and the degree of deactivation of the catalytic system used in the metathesis of 1-octene. A high IR stretching vibration corresponds with a weaker deactivation of the catalyst system [2].

In this investigation, we report on the relationship that we found to exist between the carbon–carbon chain length of the additive, the activity of the catalyst system and the IR

\* Corresponding author.

stretching vibration of the OH or CO present in the additive.

## 2. Experimental

The same procedures and techniques were used as described before [1,2]. This work was done on different 3%  $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$  catalytic systems at 25°C, reaction time 240 min and a Sn:Re molar ratio of 2:1. The additive content was 8% with regard to 1-octene (molar basis). The values of the C=O and OH infrared stretching vibrations of the different compounds were obtained from literature [3].

## 3. Results and discussion

The influence of the carbon chain length of additives containing C=O or OH on the activity of 3%  $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$  containing systems has been investigated.

### 3.1. Influence of alcohols ( $C_n\text{-OH}$ )

Fig. 1 shows the relationship between  $C_n$ , the OH stretching frequency of the alcohol and the

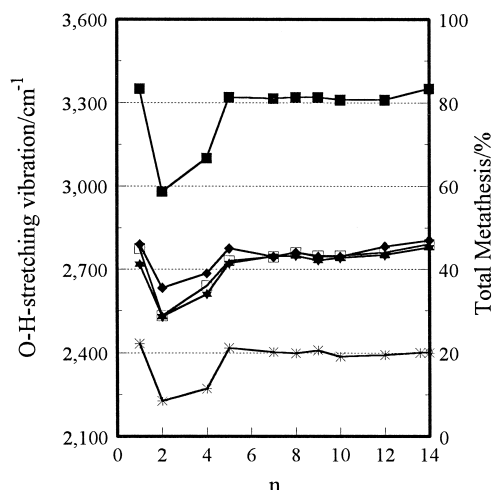


Fig. 1. The relationship between C–C chain length of the alcohols, the OH stretching vibration and the metathesis activity of different catalytic systems. ■:  $\text{IR}_{\text{OH}}$ ; \*: 3%  $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$  (= Cat), ★: 2%  $\text{Cs}^+/\text{Cat}$ , ◆: 2%  $\text{PO}_4^{3-}/\text{Cat}$ , □: 2%  $\text{Cs}^+ / 2\% \text{PO}_4^{3-} / \text{Cat}$ .

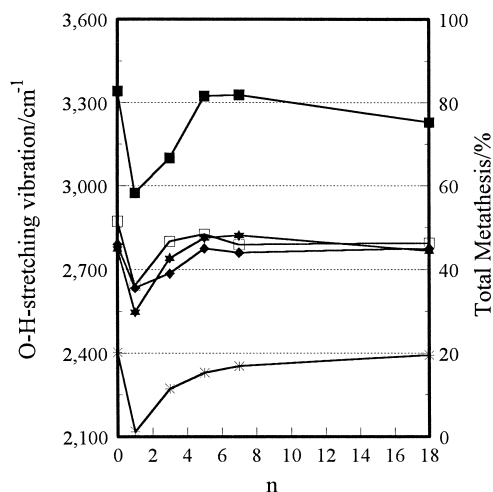


Fig. 2. The relationship between the C–C chain length of the acids, the OH stretching vibration, and the metathesis activity of different catalytic systems. ■:  $\text{IR}_{\text{OH}}$ ; \*: 3%  $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$  (= Cat), ★: 2%  $\text{Cs}^+/\text{Cat}$ , □: 2%  $\text{PO}_4^{3-}/\text{Cat}$ .

total metathesis product yield. The OH stretching frequency for  $n = 1$ ,  $3380 \text{ cm}^{-1}$ , decreases to  $3000 \text{ cm}^{-1}$  for  $n = 2$  and increases again until  $n = 5$  is reached. For  $n \geq 5$ , the frequency stays more or less constant at  $3350 \text{ cm}^{-1}$ . The same tendency can also be observed between the chain length,  $n$ , and the total metathesis product yield for the different catalyst systems tested. The same profile is shown for the relationship between  $n$  and the OH stretching vibration and  $n$ , and the activity of the catalytic system in terms of the total metathesis product yield.

### 3.2. Influence of acids ( $C_n\text{-COOH}$ ) as Brønsted acids

In Fig. 2, the relationship between the chain length ( $C_n$ ) of the acids, the OH stretching frequency and total metathesis product yield is indicated. A relationship almost similar to that for the alcohols (Fig. 1) has been found. From  $n = 0$  to  $n = 1$ , a sharp drop in the OH frequency is observed, and thereafter an increase is found till  $n = 4$ . This is followed by a small decline in frequency as  $n$  increases. A similar

relationship is shown between  $n$  and the total metathesis product yield. It is also obvious that the catalyst containing  $\text{PO}_4^{3-}$  and/or  $\text{Cs}^+$  ions is more resistant towards deactivation by the acids.

### 3.3. Influence of acids ( $\text{C}_n\text{-COOH}$ ) as Lewis bases

The relationship between the CO stretching frequency of the different acids and their chain length (Fig. 3) differs from the relationship that exists between the OH frequency of the different acids and their chain length,  $\text{C}_n$  (Fig. 2). The CO stretching frequency at  $n = 0$  decreases from  $1722\text{ cm}^{-1}$  until it reaches  $1710\text{ cm}^{-1}$  at  $n \geq 3$ . This profile differs from that obtained for the relationship between  $n$  and the total metathesis product yield.

### 3.4. Influence of esters ( $\text{C}_n\text{-OAc}$ )

In Fig. 4, the relationship between the carbon chain length  $\text{C}_n$ , of the esters  $\text{C}_n\text{-OAc}$ , the CO stretching frequency and the total metathesis product yield, is illustrated. The CO stretching

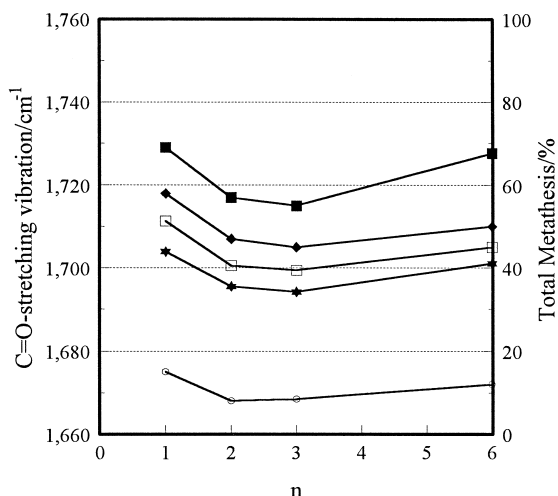


Fig. 3. The relationship between the C–C chain length of the acids, the C=O stretching vibration and the metathesis activity of different catalytic systems. ■:  $\text{IR}_{\text{OH}}$ ; ○: 3%  $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$  (= Cat), \*: 2%  $\text{Cs}^+/\text{Cat}$ , ◆: 2%  $\text{PO}_4^{3-}/\text{Cat}$ , □: 2%  $\text{Cs}^+/2\% \text{PO}_4^{3-}/\text{Cat}$ .

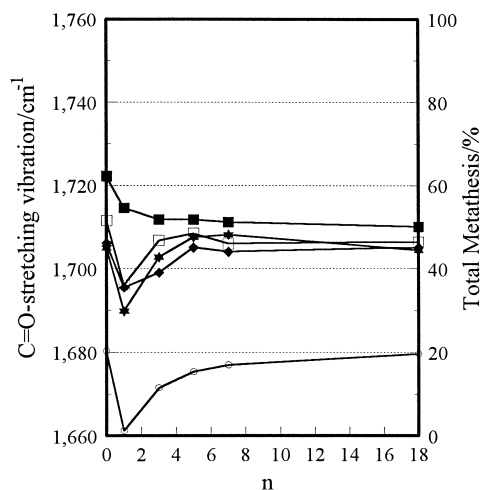


Fig. 4. The relationship between the C–C chain length of the alkyl acetates, the C=O stretching vibration and the metathesis activity of different catalytic systems. ■:  $\text{IR}_{\text{OH}}$ ; ○: 3%  $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$  (= Cat), \*: 2%  $\text{Cs}^+/\text{Cat}$ , ◆: 2%  $\text{PO}_4^{3-}/\text{Cat}$ , □: 2%  $\text{Cs}^+/2\% \text{PO}_4^{3-}/\text{Cat}$ .

frequency increases from  $1716\text{ cm}^{-1}$  for  $n = 1$  to  $1755\text{ cm}^{-1}$  for  $n = 2$  and then decreases again till it remains constant at  $1744\text{ cm}^{-1}$  for  $n \geq 5$ . The influence of the carbon chain length on the total metathesis product yield shows the same profile as that for the CO stretching frequency.

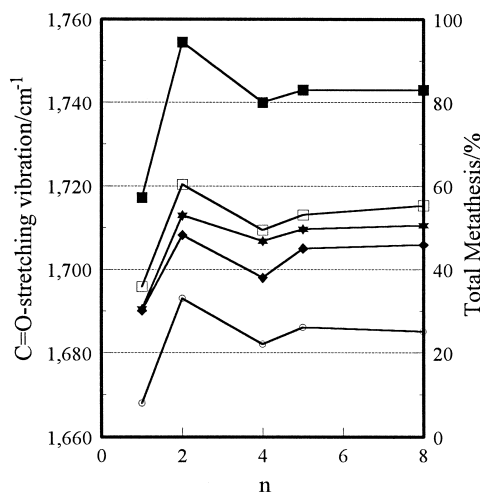


Fig. 5. The relationship between the C–C chain length of the 2-ketones, the C=O stretching vibration and the metathesis activity of different catalytic systems. ■:  $\text{IR}_{\text{OH}}$ ; ○: 3%  $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3/\text{SnMe}_4/1\text{-octene}$  (= Cat), \*: 2%  $\text{Cs}^+/\text{Cat}$ , ◆: 2%  $\text{PO}_4^{3-}/\text{Cat}$ , □: 2%  $\text{Cs}^+/2\% \text{PO}_4^{3-}/\text{Cat}$ .

### 3.5. Influence of 2-ketones ( $C_n$ -Ac)

A clear relationship exists also between the CO stretching frequency of the 2-ketones, the chain length  $C_n$  and the total metathesis product yield (Fig. 5). The frequency and total metathesis product yield decrease for  $n = 1$  to 3 and the increases again.

## 4. Conclusions

From these results, it is obvious that the higher the IR stretching vibration of the functional group the smaller the interaction between the additive and the catalytic system will be, and that causes a lesser degree of deactivation of the catalyst. This relationship is well illustrated by the additives with chain lengths smaller than 4.

It is also obvious that the  $PO_4^{3-}$  and  $Cs^+$  containing catalyst systems have a greater resistance towards the deactivation by the additives than the 3%  $Re_2O_7/SiO_2 \cdot Al_2O_3/SnMe_4/1$ -octene catalytic system.

For a certain type of additive with a carbon-carbon chain length greater than 4 the same degree of deactivation is found while the IR stretching vibration of the CO or OH also stays at their same relative values.

Deactivation of the catalytic systems by the additives can be caused by electronic or by steric factors. Nishiguchi et al. [4] found in their study of ketones and esters of different C-C chain lengths that the shorter chain length ketones and esters deactivate the metathesis reaction much easier than the longer chain compounds. They explained this phenomenon by stating that the shorter chain additive is less steric-hindered and will react easier with the

metal carbene, and so deactivate the catalytic metathesis reaction.

If steric effects were the more important factor during the deactivation of the catalytic system, the metathesis activity should have increased with the increase in chain length because the longer chain additive would be less inclined to interact with the active intermediate. The direct relationship between the C=O and O-H stretching vibrations and the metathesis activity indicates, however, that the electronic effects rather than the steric effects are the most important factor to consider in explaining the decrease in activity of the catalyst in the presence of additives.

In the case of the acids (Figs. 2 and 3), the metathesis activity in the presence of the different acids shows a relationship with the change in O-H stretching vibration and not with that of the C=O stretching vibration. These acid compounds deactivate the system by interacting as a Brønsted acid and not as a Lewis base.

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