

# Metathesis of halogen-containing olefin over $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst promoted with alkylmetal as a cocatalyst

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## Abstract

The 1-alkene containing bromide has been metathesized over  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst promoted with alkylmetal as a cocatalyst to elucidate the effects of addition of alkylmetal and reaction conditions. The reaction was carried out using a continuous flow apparatus under atmospheric pressure. Various kinds of alkylmetal were employed as cocatalyst. By the addition of small amounts of tetraalkyltin, the activity increased greatly in the sequence of  $\text{Bu} < \text{Me} < \text{Et}$ . The metal in alkylmetal also affected markedly the catalytic activity and the activity increased in the sequence of  $\text{Si}, \text{Al} \ll \text{Ge} < \text{Sn}$ . The most favorable catalyst system was found to be  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst promoted with  $\text{SnEt}_4$  at  $60^\circ\text{C}$ . The metathesis of olefin having halogen ( $\omega$ -bromo- $\alpha$ -olefin) easily occurred under very mild reaction conditions such as  $0^\circ\text{C}$  and  $W/F = 6.1 \text{ g}\cdot\text{cat}\cdot\text{h}/\text{mol}$ . The selectivity was always nearly 100% in spite of the differences in reaction conditions and kinds of cocatalyst. However, the catalytic activity decreased fairly faster compared to that of 1-hexene (1-C<sub>6</sub>'). The deactivation mechanism will also be discussed. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Metathesis; Rhenia–alumina catalyst ( $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst); Olefin containing halogen (halogenated olefin, functionalized olefin); Deactivation mechanism; Alkylmetal; Cocatalyst

## 1. Introduction

$\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst is one of the best metathesis catalysts due to its high activity and selectivity for various kinds of simple alkenes at low temperatures. Indeed, we have shown that *n*-alkenes [1,2], alkadienes [3–6], and alkyl-substituted alkenes [7,8], except alkyl-substituted vinylene compounds [9,10], were metathesized with high activity and selectivity of  $> 94\%$  over  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalysts.

Not only self-metathesis of functionalized olefin, but also cross-metathesis between a func-

tionalized olefin and a simple olefin are especially attractive, because they offer many important potential applications and new routes to a symmetrical di-functionalized olefin and mono-functionalized olefin which are hard to obtain by other methods. The reaction products are highly useful as raw material and intermediates. Numerous studies on metathesis of various kinds of functionalized alkenes have been reported [11]. However, metathesis of olefins containing halogen have been much less studied, and only limited data on allylbromide [12], allylchloride [13] and oleyl chloride [14] can be seen in the literature. Heterogeneous catalysts are more favorable than homogeneous ones with respect to

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easy separation of catalyst from reaction products, catalyst regeneration and suitability of continuous operation. It has been found that the addition of a small amount of tetramethyltin to  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst in the metathesis of methyl oleate leads to marked increase in reaction rate [15], and much efforts have been directed to find good cocatalysts (promoters). Various kinds of cocatalysts such as alkyltin [15–24], alkylaluminium [18,23], alkylsilane [18] and alkyllead [16,20–22] have been employed for the rhenium catalysts. However, systematic study on the effects of the addition of cocatalyst has not as yet been reported.

In the present paper, metathesis of olefin containing a halogen ( $\omega$ -bromo- $\alpha$ -olefin) have been investigated over  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalysts promoted with alkylmetal. The effects of alkyl group and metal in alkylmetal, and those of treatment conditions of the catalyst with alkylmetal on the catalytic activity have also been investigated in more detail. A deactivation mechanism has been proposed for the rapid deactivation in the metathesis.

## 2. Experimental

### 2.1. Catalyst

$\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst (80 ~ 100 mesh) was prepared by using impregnation technique described in previous papers [1,3]. The  $\text{Re}_2\text{O}_7$  content was 18.1 wt.%, as determined by inductively coupled plasma on a Shimadzu ICPS-500 spectrometer.

### 2.2. Reagents

4-Bromo-1-butene, 5-bromo-1-pentene, 3-bromo-1-pentene, 1-hexene (1- $\text{C}'_6$ ), 1,3-dibromo-propane and *n*-dodecane as an internal standard were dried over molecular sieves 5A. Monochlorobenzene (PhCl) used as solvent was dried over  $\text{P}_2\text{O}_5$  and distilled. Tetramethyltin

( $\text{SnMe}_4$ ), tetraethyltin ( $\text{SnEt}_4$ ), tetrabutyltin ( $\text{SnBu}_4$ ),  $\text{SnPh}_4$ ,  $\text{GeMe}_4$ ,  $\text{SiMe}_4$  and  $\text{AlMe}_2\text{Cl}$  were used as purchased without further purification as all have > 99% purity.

### 2.3. Procedure

The reactions were carried out in the liquid phase at atmospheric pressure in a single-path, continuous-flow system with a fixed catalyst bed in a tubular Pyrex glass reactor. The catalyst (0.27 g) was loaded in the lower part of the reactor, and the upper portion was filled with quartz chips to reduce dead volume. The catalyst was oxidized at 480°C for 1 h in dry oxygen gas flow and activated in situ at 500°C for 2 h in dry nitrogen gas flow, followed by cooling to reaction temperature. The treatment of the catalyst with alkylmetal was carried out by two ways; a continuous method and a pretreatment method. The continuous method is continuous addition of alkylmetal to the catalyst, that is, the solution composed of reactant, alkylmetal as cocatalyst, and PhCl as a solvent was fed to the catalyst. The pretreatment method is to use catalyst pretreated with alkylmetal before feeding the reactant. The reactant concentration was 0.383 or 0.0956 mol/l, the feed rate was 5 ml/h and  $W/F$  was 6.1 g-cat · h/mol. Metathesis products were analyzed by gas chromatography on a Shimadzu GC-9A equipped with an FID and a 50m OV-1 chemically bonded capillary column, and were identified by gas chromatograph-mass spectrometer on a Shimadzu GCMS-QP5000.

## 3. Results and discussion

### 3.1. Effects of the amount of alkyltin

The effects of the amount of  $\text{SnBu}_4$  were examined using 4-bromo-1-butene as a reactant over a  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst treated by the pretreatment method and the results are shown in Fig. 1 as a function of the amount of  $\text{SnBu}_4$ .

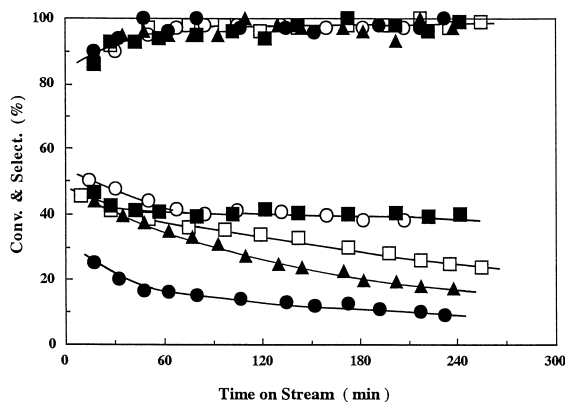


Fig. 1. Effects of the amount of  $\text{SnBu}_4$  by pretreatment method. Reactant: 4-bromo-1-butene, reaction temperature:  $25^\circ\text{C}$ , pretreatment temperature:  $25^\circ\text{C}$ , the total amount ( $\mu\text{mol}$ ) of  $\text{SnBu}_4$  fed to the catalyst (0.27 g): (●): 0 (▲): 3.0, (□): 9.1, (○): 18.2, (■): 36.2, reactant concentration: 0.0956 mol/l.

The activity decreased in the early stage of the reaction, while the selectivity increased to  $> 95\%$ , suggesting that the adsorption of the reactant and product occurred. The activity increased greatly by the addition of small amount of alkyltin and became constant for the catalyst treated with more than the amount of  $67 \mu\text{mol/g-cat}$ , which corresponds to Sn/Re molar ratio of 0.090. The activity increased about 4 times by the addition of  $\text{SnBu}_4$ . The decreases in activities were found with time on stream and were faster for the smaller addition of  $\text{SnBu}_4$ .

The activity of a deactivated catalyst could be restored several times by calcination in oxygen at  $480^\circ\text{C}$  for 1 h, followed by the activation and the new addition of cocatalyst on the same catalyst. The reaction product was 1,6-dibromo-3-hexene with only few by-products, and thus the selectivities were almost 100%. The ratio of *cis/trans* of 1,6-dibromo-3-hexene was about 0.23 independent on the reaction conditions and the kinds of cocatalysts.

### 3.2. Effects of treating method on catalytic activity

The activity changes over the catalyst treated by the pretreatment method are shown in Fig. 2

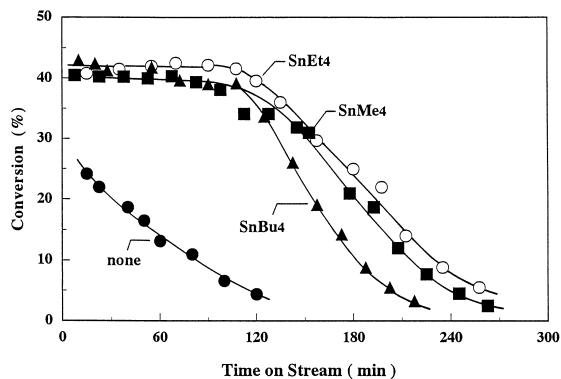


Fig. 2. Activity changes of catalyst pretreated with alkyltin. Reactant: 4-bromo-1-butene, reaction temperature:  $25^\circ\text{C}$ , pretreatment temperature:  $25^\circ\text{C}$ , the total amounts of  $\text{SnR}_4$  fed to the catalyst (0.27 g):  $36.2 \mu\text{mol}$ , Reactant concentration: 0.383 mol/l.

as a function of alkyltin. The selectivities were ca. 100% independent on the differences in alkyl group in alkyltin. The activities are almost constant until 2 h of process time, but decreased rapidly thereafter. The effects of alkyl group in alkyltin are not clear at the reaction conditions investigated here, but it seems that methyl and ethyl group works more effectively than butyl group.

The activity changes over the catalyst treated by the continuous method are shown in Fig. 3 as a function of alkyltin. The activity itself and activity changes with time on stream are almost the same with those of the pretreated catalysts.

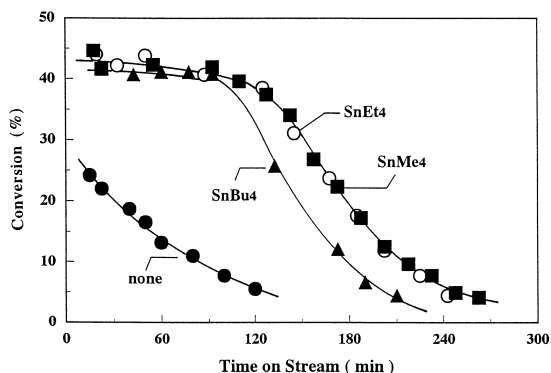


Fig. 3. Activity changes of catalyst by continuous feed of alkyltin. Reactant: 4-bromo-1-butene, reaction temperature:  $25^\circ\text{C}$ , the amount of  $\text{SnR}_4$  in feed solution:  $0.72 \mu\text{mol/h}$ , reactant concentration: 0.383 mol/l.

This indicates that the deactivated sites are not reactivated, and that new active sites cannot be formed during the reaction even by the continuous addition of alkyltin. This suggests also that the reaction between rhenium and alkyltin to create carbenes proceeds instantly at 25°C. This will be supported by the color change of catalyst from white to brown as soon as  $R_4Sn$  solution contacts with the catalyst. The rapid decrease in activities in Figs. 2 and 3 compared with Fig. 1 might come from the difference in reactant concentration as the reactant concentrations in Figs. 2 and 3 are 4 times higher than those in Fig. 1.

As can be easily seen from the comparison of Figs. 2 and 3, the apparent differences in the treatment methods on the catalytic activities cannot be found. The pretreatment method is much better than the continuous method as the alkyltin is not included in the reaction mixture.

### 3.3. Effects of reaction temperature on catalytic activity

The effects of reaction temperature on catalytic activity were examined and the results are shown in Figs. 4 and 5. The  $Re_2O_7/Al_2O_3$  catalyst promoted at  $-35^\circ C$  was used for experiments of the pretreatment method. The data

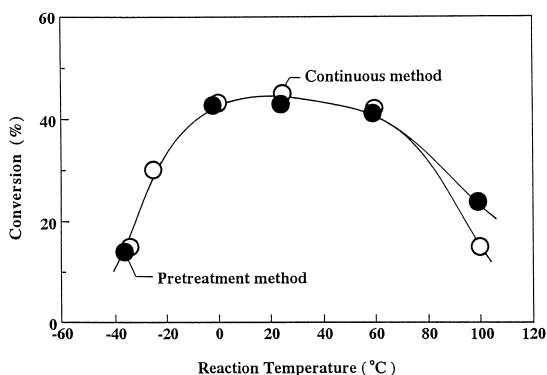


Fig. 4. Effects of reaction temperature on catalytic activity. Reactant: 4-bromo-1-butene, data: 0.5 h (process time), continuous method; the amount of  $SnBu_4$  in feed solution:  $0.72 \mu mol/h$ , pretreatment method; the total amount of  $SnBu_4$  fed for the pretreatment of catalyst (0.27 g) at  $-35^\circ C$ :  $36.2 \mu mol$ , reactant concentration:  $0.383 mol/l$ .

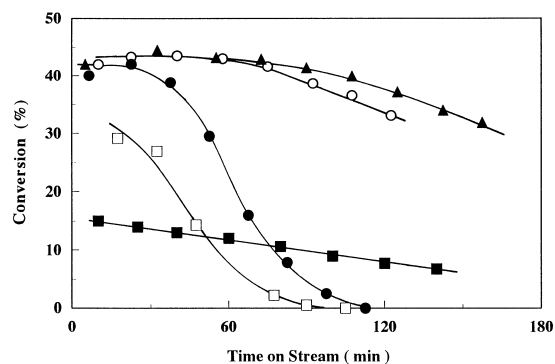


Fig. 5. Reaction temperature and catalytic activity. Reactant: 4-bromo-1-butene, pretreatment method; the total amount of  $SnBu_4$  fed for the pretreatment of catalyst (0.27 g) at  $-35^\circ C$ :  $36.2 \mu mol$ , reactant concentration:  $0.383 mol/l$ , reaction temperature ( $^\circ C$ ): (■):  $-35$ , (○): 0, (▲): 25, (●): 60, (□): 100.

show that there is no apparent differences between the two treatment methods of catalyst as shown in Fig. 4. It was found that the  $Re_2O_7/Al_2O_3$  catalyst treated with  $SnBu_4$  has fairly good activity even at such low temperature as  $-35^\circ C$ . The activity depended greatly on reaction temperature until  $0^\circ C$  and became constant during  $0$ – $60^\circ C$  and then decreased at  $100^\circ C$ . The catalytic activity decreased much faster at 60 and  $100^\circ C$  in comparison with lower reaction temperatures than  $25^\circ C$  as shown in Fig. 5. The selectivities were almost 100% below  $60^\circ C$ , but decreased to ca. 75% at  $100^\circ C$ . By-products estimated as cross-metathesis between 4-bromo-1-butene and 1-bromo-2-butene, and self-metathesis of 1-bromo-2-butene were formed together with small amount of other unidentified by-products at  $100^\circ C$ . The activity changes in the metathesis by the continuous method were almost the same with those shown in Fig. 5. This shows that there is no effect on the improvement in catalytic activity and prolongation of catalytic life even by the continuous addition of alkyltin, in agreement with the discussion in Section 3.2. We will discuss the reason why the activity decreases rapidly at higher reaction temperatures in Section 3.7.

The increase in activity with increasing reaction temperatures must be attributed to the increase in reaction rate as the number of active

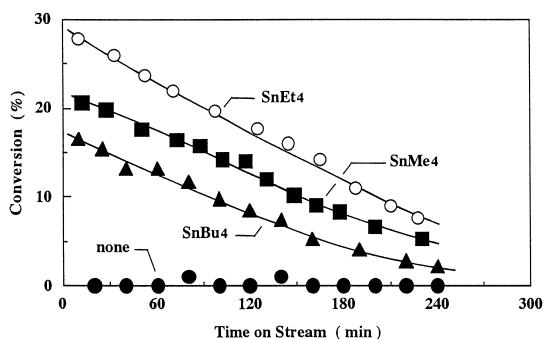


Fig. 6. Effects of alkyl group in tetraalkyltin on catalytic activity. Reactant: 4-bromo-1-butene, reaction temperature:  $-35^{\circ}\text{C}$ , the total amount of alkyltin fed for the pretreatment of catalyst (0.27 g) at  $-35^{\circ}\text{C}$ :  $36.2\ \mu\text{mol}$ , Reactant concentration:  $0.383\ \text{mol/l}$ .

sites formed at  $-35^{\circ}\text{C}$  is the same at least for the pretreatment method. As another factor, it is considered that the additional active sites are generated by the reaction between adsorbed  $\text{SnBu}_4$  and rhenia with increasing reaction temperatures.

### 3.4. Effects of alkyl group in alkyltin

The effects of alkyl group in alkylmetal were investigated at  $-35^{\circ}\text{C}$  reaction temperature over the catalyst pretreated at  $-35^{\circ}\text{C}$  by the pretreatment method, and the results are shown in Fig. 6. The alkyl group in alkyltin affected the catalytic activity and the effectiveness increased in the following order:  $\text{Bu} < \text{Me} < \text{Et}$ .  $\text{SnPh}_4$  did not promote metathesis at all as expected, as it does not contribute to make carbene species. The order could be attributed to the reactivity to generate carbene. The order agrees with the data obtained for the metathesis of methyl oleate over  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst [23]. However, the order differs from the sequence  $\text{SnMe}_4 < \text{PbEt}_4 < \text{SnBu}_4 < \text{SnEt}_4$  in the metathesis of methyl oleate over 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  catalyst under reaction conditions at  $20^{\circ}\text{C}$  [16], and the sequence  $\text{SnMe}_4 < \text{SnEt}_4 < \text{SnOct}_4$  (Oct = octyl)  $< \text{SnBu}_4$  in the metathesis of propene over 12 wt.%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst at  $60^{\circ}\text{C}$  [20]. Since the average bond energy between tin or lead, and alkyl group are; Sn–Me 218, Sn–Et 193, Sn–Bu 195 and Pb–Me 153 kJ/mol, it

was found that the bond energy is not a critical parameter. Reasonable explanations for the differences in the order cannot be found to date.

Apparent differences in activity changes with time on stream could not be found, suggesting that the carbenes created by alkyltin having different alkyl group are the same in the chemical nature and are deactivated in the same manner.

### 3.5. Effects of metal in alkylmetal and the pretreatment temperature of catalyst

The effects of metal in alkylmetal and the pretreatment temperature on the catalytic activities were examined for  $\text{SnBu}_4$ ,  $\text{GeMe}_4$ ,  $\text{SiMe}_4$  and  $\text{AlMe}_2\text{Cl}$ , and some of the results are shown in Figs. 7 and 8. With increasing the pretreatment temperatures in case of  $\text{SnBu}_4$ , the catalytic activity increased up to  $60^{\circ}\text{C}$  and then decreased greatly at  $100^{\circ}\text{C}$ . The lower activity at  $100^{\circ}\text{C}$  corresponded to the data at Fig. 4, but the deactivation of the catalyst was much smaller and the selectivity was ca. 100% as the reaction temperature was  $-35^{\circ}\text{C}$ .  $\text{GeMe}_4$  showed similar behavior, but its activity was lower than  $\text{SnBu}_4$ , and it was about one-third. The selectivities are always ca. 100% independent of the kind of metals. Both  $\text{SiMe}_4$  and  $\text{AlMe}_2\text{Cl}$  showed no enhancement in activities under the

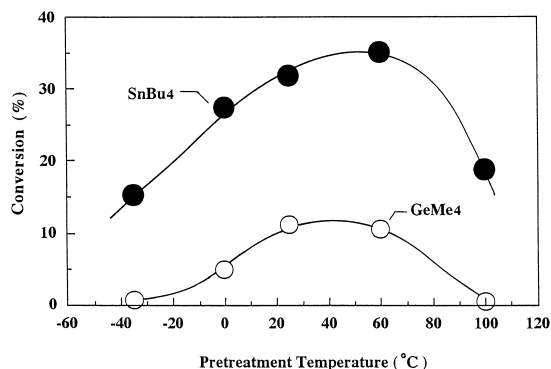


Fig. 7. Effects of pretreatment temperature of catalyst on catalytic activity. Reactant: 4-bromo-1-butene, data: 0.5 h (process time), reaction temperature:  $-35^{\circ}\text{C}$ , the total amount of alkylmetal fed for the pretreatment of catalyst (0.27 g) :  $36.2\ \mu\text{mol}$ , reactant concentration:  $0.383\ \text{mol/l}$ .

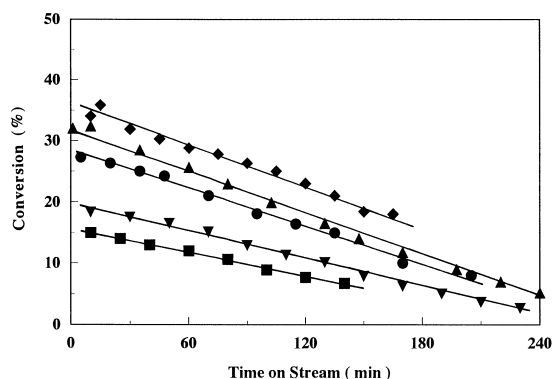


Fig. 8. Changes in catalytic activity as a function of pretreatment temperature of catalyst. Reactant: 4-bromo-1-butene, reaction temperature:  $-35^{\circ}\text{C}$ , the total amount of  $\text{SnBu}_4$  fed for the pretreatment of catalyst (0.27 g):  $36.2 \mu\text{mol}$ , reactant concentration:  $0.383 \text{ mol/l}$ , pretreatment temperature ( $^{\circ}\text{C}$ ): (■):  $-35$ , (●):  $0$ , (▲):  $25$ , (◆):  $60$ , (▼):  $100$ .

reaction conditions examined here. It has been reported that the effectiveness of alkylmetal increased in the sequence  $\text{AlMe}_3 < \text{SiMe}_4 < \text{SiHEt}_3 < \text{SnMe}_4$ , in the metathesis of propene over 6 wt.%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst pretreated at  $25^{\circ}\text{C}$  under reaction conditions  $25^{\circ}\text{C}$  and 1 atm [18], and  $\text{LiBu}_4 < \text{Al}_2\text{Me}_3\text{Cl}_3 < \text{SnBu}_4 < \text{SnMe}_4 < \text{SnEt}_4$ , in the metathesis of methyl oleate over  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst [23]. The order of effectiveness of cocatalyst could not be explained by the average bond energy between metal and alkyl groups.

It was found that the activity depends greatly on the pretreatment temperatures as shown in Fig. 7. The reaction between rhenium and alkylmetal to form carbene proceeds easily even at  $-35^{\circ}\text{C}$ , in agreement with the results obtained for the continuous method as described in Section 3.2. Since the reaction temperature is constant at  $-35^{\circ}\text{C}$ , the increase in activity attributes to the increase in the active sites, carbene complexes. Almost the same decreases in activity were observed for the reactions over the catalysts treated at  $-35^{\circ}\text{C}$  and reaction temperature  $100^{\circ}\text{C}$  (Fig. 4), and over the catalyst treated at  $100^{\circ}\text{C}$  and reaction temperature  $-35^{\circ}\text{C}$  (Fig. 7). This must be caused by the decrease in active sites, which become unstable and decompose at higher temperatures such as  $100^{\circ}\text{C}$ . The

activity changes with time on stream are almost the same regardless of the pretreatment temperatures as shown in Fig. 8.

### 3.6. Metathesis of olefin containing halogen

The metathesis of 4-bromo-1-butene has been extensively investigated here, but 3-bromo-1-propene and 5-bromo-1-pentene were also examined as another olefin containing halogen. Their reactivities and the degrees of catalyst deactivation with process time were similar to those in the metathesis of 4-bromo-1-butene as shown in Fig. 9 and the selectivities were nearly 100%, respectively. The ratio of *cis* to *trans* of 1,4-dibromo-2-butene and 1,8-dibromo-4-octene was ca. 0.27, which is close to 0.23 of 1,6-dibromo-3-hexene.

When 1-hexene, as a sample of alkene, has been metathesized over the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalysts unpromoted or promoted with  $\text{SnBu}_4$  at  $25^{\circ}\text{C}$ , the activity decrease was only a little within the 6 h of process time examined and the selectivity to 5-decene was ca. 100%.

### 3.7. Deactivation

Several mechanisms have been proposed for the deactivation of heterogeneous catalysts in

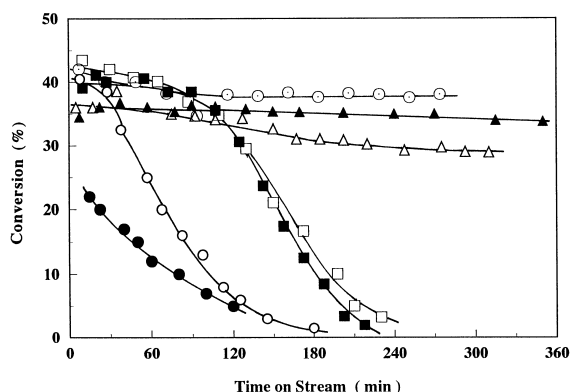
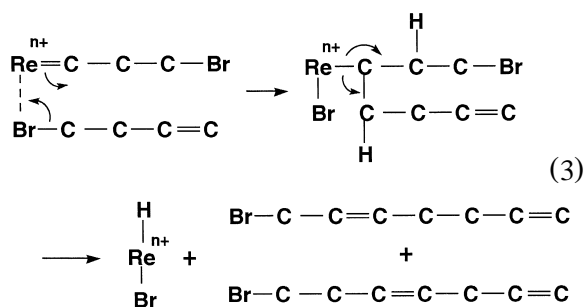
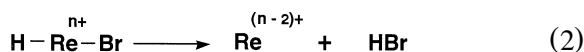
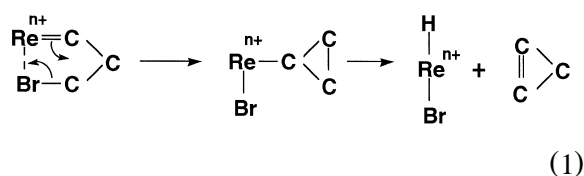


Fig. 9. Changes in catalytic activity of various kinds of olefin. Reaction temperature:  $25^{\circ}\text{C}$ , the total amount of  $\text{SnBu}_4$  fed for the pretreatment of catalyst (0.27 g) at  $25^{\circ}\text{C}$ :  $36.2 \mu\text{mol}$ , reactant concentration:  $0.383 \text{ mol/l}$ , reactant: (○): 3-Br-1-C'<sub>3</sub>, (●): 4-Br-1-C'<sub>4</sub> (unpromoted), (■): 4-Br-1-C'<sub>4</sub>, (□): 5-Br-1-C'<sub>5</sub>, (Δ): 1-C'<sub>6</sub> (unpromoted), (▲): 1-C'<sub>6</sub>, (⊙): 1-C'<sub>6</sub> + 1,3-diBr-C'<sub>3</sub>.

the metathesis [16,17,20,24]. However, there is no general understanding of the reason why rapid decrease in activity occurs in the metathesis of functionalized olefin such as halogen-substituted olefin as shown in this study and methyl oleate [17] compared with nonfunctionalized olefin. It is important to make clear the mechanism of the rapid deactivation of catalyst in the metathesis of functionalized olefin to use the metathesis as a potential tool to synthesize valuable chemicals.

As shown in Fig. 9, the deactivation rates of olefins containing bromide are much faster than that of 1-hexene over  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst, where the same amounts of carbene are preformed at the initial stage of the reaction. The results strongly suggest that another plausible deactivation mechanism, other than mechanisms proposed for nonfunctionalized olefin, should be considered. The difference in the interaction between carbene and reactant and in the stability of carbenes might reflect the deactivation rate. The rapid deactivation will occur as a result of the interaction between Re and functional group, bromide in this case. The following two mechanisms are considered as candidate.



By intramolecular interaction between Re and Br in carbene, the coordination site needed for metathesis is blocked and the intermediate forms and followed by  $\beta$ -elimination of a hydrogen atom as shown in Eq. (1). A reductive elimination of HBr from  $\text{H}-\text{Re}^{n+}-\text{Br}$  occurs according to Eq. (2), resulting to the overreduction of  $\text{Re}^{n+}$  to  $\text{Re}^{(n-2)+}$ . In the same way, Eq. (3) will occur by intermolecular interaction between Re and Br in reactant and/or reaction products to form the intermediate and the following  $\beta$ -elimination of a hydrogen atom (there are two possibilities). There is no possibility of these mechanisms in the metathesis of alkene which does not contain functional group. When an equimolar mixture of 1- $\text{C}_6'$  and 1,3-dibromopropane was metathesized, the activity itself and the activity changes with time processes were almost the same with those of 1- $\text{C}_6'$  alone as shown in Fig. 9. This result rules out the participation of Eq. (3) in the deactivation mechanism.

The deactivation rates were almost constant at same reaction temperatures (Figs. 2, 3, 6 and 8) and increased greatly when reaction temperatures were increased, especially in temperatures higher than  $60^\circ\text{C}$  (Fig. 5). As the alkenyl carbenes are stable at  $60^\circ\text{C}$  (Fig. 8), the rapid decrease of carbenes at temperatures higher than  $60^\circ\text{C}$  must be caused by the mechanism shown in Eqs. (1) and (2).

The deactivation rate is strongly temperature-dependent as shown in Fig. 5, suggesting that the rate of  $\beta$ -elimination of a hydrogen atom from intermediates must be largely dependent on the reaction temperature.

The deactivation rate differed according to the concentration of reactant, but the total turnover was almost the same, in agreement with the proposed mechanism. Although it has been reported that the addition of  $\text{R}_4\text{Sn}$  during the reaction is effective for improving the catalytic life [20], such an effect could not be found in this study as can be seen from the comparison of Figs. 2 and 3. The influence of a different alkyl group in alkyltin on the stability of the catalyst was only small (Fig. 6).

The deactivation rate of promoted catalyst is much faster than that of the unpromoted one, suggesting that there are two types of active sites, carbenes (Figs. 1–3 and 9). It has been reported that new sites generated upon addition of  $\text{Me}_4\text{Sn}$  differ from those present in the untreated  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst [19]. Although there are many studies on the characterization, structure and the nature of these carbenes, it is still under debate [11,24–29]. The carbene created by the promoter appeared to be less stable than one generated by reactant itself, in agreement with the result obtained for the metathesis of propene [20]. Delicate differences between two carbenes in valence and conformation of active sites might be caused by changes in the environment of the rhenium atom. More favorable electronic valence and steric interaction between Re and Br in carbene will occur on the carbenes created by promoter, resulting in the rapid deactivation.

#### 4. Conclusions

The effects of addition of alkylmetal as a cocatalyst to  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst and the reaction conditions were investigated in the metathesis of  $\omega$ -bromo- $\alpha$ -olefin in liquid phase at atmospheric pressure using a continuous flow apparatus. The effects of the amount of alkylmetal, the kind of metal, the kind of alkyl group, treatment temperature and treatment method were examined in detail. The main results can be summarized as follows.

(1) The catalytic activity increased greatly by addition of a small amount of alkyltin and the activity became constant when the amount is more than  $67 \mu\text{mol/g-cat}$ .

(2) The alkyl group in alkyltin affected the catalytic activity and the effectiveness increased in the following order:  $\text{Bu-} < \text{Me-} < \text{Et-}$ .

(3) The metal in alkylmetal affected the catalytic activity and the activity increased in the sequence of  $\text{Al, Si} \ll \text{Ge} \ll \text{Sn}$ .

(4) The treatment temperature of catalyst affected the activity and the optimal temperature appeared to be  $60^\circ\text{C}$ .

(5) There are no differences in both treatment methods, i.e., pretreatment and continuous method, on the effects on the activity, selectivity and catalytic life. The pretreatment method is the recommended one.

(6) The metathesis of  $\omega$ -bromo- $\alpha$ -olefin occurred under very mild reaction conditions with  $> 95\%$  selectivity. The use of catalyst pretreated with tetraalkyltin at treatment temperature  $60^\circ\text{C}$  was the most favorable.

(7) The continuous addition of alkylmetal did not affect the catalytic life.

(8) The selectivities were not affected by the amount of addition, the kind of metal and alkyl group in alkylmetal, treatment temperature lower than  $60^\circ\text{C}$ , treatment methods and reaction temperatures lower than  $60^\circ\text{C}$ , and were nearly 100%.

(9) There are two types of carbenes. The carbene created by promoter was much less stable than one created by reactant itself.

(10) As the plausible mechanism for the rapid deactivation in the metathesis of  $\omega$ -bromo- $\alpha$ -olefin, the intramolecular interaction between  $\text{Re}^{n+}$  and Br in the carbene and the following reactions to yield cycloalkene and overreduced  $\text{Re}^{(n-2)+}$  formation (Eqs. (1) and (2)) are considered.

(11) The reaction between rhenium and alkylmetal to form carbene proceeds easily at such conditions as  $-35^\circ\text{C}$  and very short contact time. The carbenes are stable until  $60^\circ\text{C}$  and the amounts of carbenes increased with increasing amount of  $\text{R}_4\text{Sn}$  and the treatment temperature till  $60^\circ\text{C}$ .

#### References

- [1] T. Kawai, Y. Yamazaki, A. Tokumura, Sekiyu Gakkai Shi 26 (1983) 332.
- [2] T. Kawai, H. Goto, Y. Yamazaki, T. Ishikawa, J. Mol. Catal. 46 (1988) 157.
- [3] T. Kawai, Y. Yamazaki, T. Taoka, K. Kobayashi, J. Catal. 89 (1984) 452.



- [4] T. Kawai, Y. Yamazaki, M. Nishikawa, Sekiyu Gakkai Shi 27 (1984) 378.
- [5] T. Kawai, H. Goto, T. Ishikawa, Y. Yamazaki, J. Mol. Catal. 39 (1987) 369.
- [6] T. Kawai, H. Goto, Y. Yamazaki, Sekiyu Gakkai Shi 29 (1986) 212.
- [7] T. Kawai, N. Maruoka, M. Goke, T. Ishikawa, J. Mol. Catal. 49 (1989) 261.
- [8] T. Kawai, N. Maruoka, T. Ishikawa, J. Mol. Catal. 60 (1990) 209.
- [9] T. Kawai, T. Okada, T. Ishikawa, J. Mol. Catal. 76 (1992) 249.
- [10] T. Kawai, M. Furuki, T. Ishikawa, J. Mol. Catal. 90 (1994) 1.
- [11] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, New York, 1997.
- [12] J.C. Mol, E.F.G. Woerlee, J. Chem. Soc., Chem. Commun. (1979) 330.
- [13] E.I. Bogolepova, I.V. Vygodskaya, G.A. Kliger, S.M. Loktev, Petrol. Chem. 32 (1992) 461.
- [14] R. Nakamura, E. Echigoya, Chem. Lett. (1977) 1227.
- [15] E. Verkuiljen, F. Kapteijin, J.C. Mol, C. Boelhouwer, J. Chem. Soc., Chem. Commun. (1977) 198.
- [16] J.C. Mol, J. Mol. Catal. 65 (1991) 145.
- [17] J.C. Mol, J. Mol. Catal. 90 (1994) 185.
- [18] R. Nakamura, S. Nakano, M. Nakamura, H. Niiyama, Proceedings of Symposium, The Japan Petroleum Institute, 1996, p. 265.
- [19] K.G. Moloy, J. Mol. Catal. 91 (1994) 291.
- [20] R. Spronk, A. Andreini, J.C. Mol, J. Mol. Catal. 65 (1991) 219.
- [21] X. Xiaoding, P. Imhoff, G.C.N. Aardweg, J.C. Mol, J. Chem. Soc., Chem. Commun. (1985) 273.
- [22] X. Xiaoding, J.C. Mol, J. Chem. Soc., Chem. Commun. (1985) 631.
- [23] R.H.A. Bosma, G.C.N. van den Aardweg, J.C. Mol, J. Organomet. Chem. 255 (1983) 159.
- [24] J.A. Moulijn, J.C. Mol, J. Mol. Catal. 46 (1988) 1.
- [25] R. Buffon, U. Schuchardt, A. Abras, J. Chem. Soc., Faraday Trans. (1995) 3511.
- [26] X. Xiaoding, A. Andreini, J.C. Mol, J. Mol. Catal. 28 (1985) 133.
- [27] R. Buffon, M.J.D.M. Jannini, A. Abras, J. Mol. Catal. 115 (1997) 173.
- [28] K.P.J. Williams, K. Harrison, J. Chem. Soc., Faraday Trans. (1990) 1603.
- [29] W.A. Herrmann, F.E. Kuhn, Acc. Chem. Res. (1997) 169.