# Reaction products and the mechanism in the dimerization of 2-methyl-1-alkenes over Lewis acid and Brønsted acid catalysts: anomalous reaction behaviors of 2-methyl-1-alkenes over $Re_2O_7$–$Al_2O_3$ metathesis catalyst

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## Abstract

2-Methyl-1-alkenes have exhibited anomalous reaction behavior over a $Re_2O_7$–$Al_2O_3$ metathesis catalyst. Self-metathesis of 2-methyl-1-alkenes did not occur at all and several kinds of dimers were formed as major products. The dimer structures using 2-methyl-1-pentene as a model compound were identified by using various methods, such as ozonolysis, hydrogenation, gas chromatography–mass spectrometry (GC–MS) and ^{1}H NMR and ^{13}C NMR. The dimerization mechanisms have been discussed. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The $Re_2O_7$–$Al_2O_3$ catalyst is well known for its high activity and selectivity in the metathesis of a variety of olefins. Indeed we have shown that *n*-alkenes [1,2], $\alpha,\omega$-dienes [3,4], 1,4-alkadienes[4–6], alkyl-substituted alkenes [7–10] excepting alkyl-substituted vinyl compounds, halogen-containing olefin [11] and vinylsilanes [12] were metathesized with high activity and

selectivity of > 94% over $Re_2O_7$–$Al_2O_3$ catalysts.

However, it has been found that the alkyl-substituted vinyl compounds have exhibited anomalous reaction behavior over $Re_2O_7$–$Al_2O_3$ catalysts [7–10]. In this case, self-metathesis did not occur at all and the main reaction products were cross-metathesis product between 2-methyl-1-alkene and 2-methyl-2-alkene formed by the double bond isomerization and dimers, e.g., in the reaction of 2-methyl-1-hexene (2-Me-1-$C_6'$), the cross-metathesis product was 88% selectivity and dimers 12% selectivity [10]. Further investigations revealed that the dimers were mainly obtained with > 70% selectivity

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over $Re_2O_7$–$Al_2O_3$ catalysts activated at temperatures lower than 140°C or reduced with hydrogen gas above 300°C [9,10]. The $WCl_6$–$Me_4Sn$ catalyst, which is also a well-known metathesis catalyst, showed similar anomalous reaction behaviors to the $Re_2O_7$–$Al_2O_3$ catalyst [10]. As it has been believed that $Re_2O_7$–$Al_2O_3$ and $WCl_6$–$Me_4Sn$ catalysts do not have activity for double bond shift isomerization and dimerization, these findings are of interest.

Studies on the metathesis of methyl-substituted vinyl compounds are limited as can be seen in the literatures [13–16]. 3-Me-2-$C_6'$ over $(n\text{-Bu})_4N[Mo(CO)_6Cl$–$MeAlCl_2$ [13] and 2-methyl-1-butene (2-Me-1-$C_4'$) over $WO(OPh)_4$–$AlCl_3$–$Et_3Al$ [14,15] were self-metathesized, but there was no mention of isomerization and dimerization in the papers. It has also been reported that 2-Me-1,5-hexadiene, analogous compound to 2-Me-1-alkene, produced 2,9-dimethyl-1,5,9-decatriene as a result of the exclusive metathesis in the presence of Schrock catalyst [16]. This shows that no isomerization of double bond takes place by the use of Schrock catalyst that is Lewis acid free metathesis catalyst [16]. The dimerization reaction of isobutene to diisobutene has been carried out on sulfuric acid, $SiO_2$–$Al_2O_3$ and zeolite, which are typical Brønsted acid catalysts [17,18]. Osokin et al. [19] has reported the dimerization reaction of 2-methyl-1-pentene (2-Me-1-$C_5'$) and 2-Me-2-$C_5'$ over $SiO_2$–$Al_2O_3$ catalyst. However, to our knowledge, there are no studies on the isomerization and dimerization of methyl-substituted vinyl compounds using Lewis acid catalysts such as $Re_2O_7$–$Al_2O_3$ and $WCl_6$–$Me_4Sn$ in the literature apart from the three papers originating from this laboratory [8–10].

Our experiments have shown that 2-Me-1-alkenes undergo rapid double bond shift isomerization and dimerization over both Lewis acid catalysts and Brønsted acid catalysts [8–10]. Although $Re_2O_7$–$Al_2O_3$ catalysts possess both Brønsted and Lewis acid sites [20–24], the product distributions of dimers obtained from 2-Me-1-alkenes over the $Re_2O_7$–$Al_2O_3$ catalyst

were similar to those over $WCl_6$–$Me_4Sn$, suggesting that the major active sites of dimerization are Lewis acid in character. Further study revealed that the major active sites on the $Re_2O_7$–$Al_2O_3$ catalyst for the dimerization are Lewis acid sites [9,20]. The product distributions of dimers produced on Brønsted and Lewis acid sites differed from one another. The structures of dimer and mechanism have not been revealed [8–10].

This work is to clarify the structures of dimer and the mechanisms of the double bond shift isomerization and dimerization of 2-Me-1-alkenes over the $Re_2O_7$–$Al_2O_3$ catalyst, Lewis acid catalyst.

## 2. Experimental

### 2.1. Catalysts

A $Re_2O_7$–$Al_2O_3$ catalyst (40–60 mesh) was prepared by using impregnation technique described in previous papers [1,3]. The $Re_2O_7$ content was 17.4 wt.%, as determined by inductively coupled plasma on a Shimadzu ICPS-500 spectrometer. $WCl_6$ purified by sublimation of tungsten oxides at 110°C under vacuum was used. $Sn(CH_3)_4$ was used as purchased without further purification. The $SiO_2$–$Al_2O_3$ was obtained from Catalyst and Chemical Industries (IS-28, $Al_2O_3$ 29.07%, $Na_2O$ 0.01%, $SO_4$ 0.28%, 420 $m^2$ $g^{-1}$) was used as a Brønsted acid catalyst.

### 2.2. Reagents

2-Me-1-$C_4'$ obtained from Wako Pure Chemical Industries, 2-Me-1-$C_3'$, 2-Me-1-$C_5'$, and 2-Me-2-$C_5'$, 2,4,4-trimethyl-1-$C_5'$ obtained from Tokyo Kasei Kogyo, and 2-Me-1-$C_6'$ and 2,3,3-trimethyl-1-$C_4'$ obtained from Aldrich, were used as starting materials. These reagents were dried over 5-Å molecular sieves, and used without further purification. Monochlorobenzene used as solvent was dried over $P_2O_5$ and purified by rectification.

## 2.3. Procedure

The reactions were carried out in the liquid phase at atmospheric pressure using a continuous-flow system for the $Re_2O_7$–$Al_2O_3$ and $SiO_2$–$Al_2O_3$ catalyst. The reaction over $Re_2O_7$–$Al_2O_3$ catalyst activated at 140°C in dry nitrogen gas flow for 1.5 h was carried out at 40°C and W/F 7.4 g-cat h/mol. The reaction conditions over $SiO_2$–$Al_2O_3$ catalyst activated at 500°C in dry nitrogen gas flow for 1.5 h were temperature −38°C and W/F 0.92 g-cat h/mol. Other detailed experimental procedures are essentially identical as previously described [8–10]. For the homogeneous catalysts, the reactions were carried out at atmospheric pressure of nitrogen gas in a Schlenk-type glass reactor with stirring. In the reaction catalyzed by sulfuric acid, 50% sulfuric acid was used and the reaction time and temperature were 30 min and 20°C, respectively. The reaction conditions over the $WCl_6$–$Me_4Sn$ catalyst system were as follows: W/Sn/alkene = 1/2/125, temperature: 60°C, and time: 20min.

Hydrogenation of dimers was carried out over Pd/C catalyst at room temperature. Ozonolysis was carried out to determine the double bond position in the structure. Ozone was introduced to a hexanol solution of dimer at −30°C to make ozonide and its reductive decomposition was carried out at the same temperature under hydrogen gas over Pd/C catalyst.

Reaction products were analyzed by gas chromatography (GC) on a Shimadzu GC-12A equipped with an FID and a chemically bonded capillary column HP-5 (25 × 0.32 mm). Mass spectroscopy (MS) was performed on a Shimadzu GCMS-QP5000, gas chromatograph/mass spectrometer, equipped with Shimadzu GC-17A gas chromatograph with a chemically bonded capillary column DB-1(60 × 0.25 mm).

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL EX-270 (270 MHz). Chloroform-d was used as solvent and tetramethylsilane as the internal standard.

## 3. Results and discussion

### 3.1. Anomalous reaction behaviors of 2-methyl-1-alkene

2-Me-1-alkenes such as 2-Me-1-$C_4'$, 2-Me-1-$C_5'$ and 2-Me-1-$C_6'$ were easily isomerized to corresponding 2-Me-2-alkenes without exception over $Re_2O_7$–$Al_2O_3$ catalysts in a flow system. The self-metathesis did not occur at all and the main reactions were the cross-metathesis and dimerization [8–10]. Although $Re_2O_7$–$Al_2O_3$ catalysts possess both Lewis and Brønsted acidic sites [20–24], we have shown that the major active sites of dimerization reaction are Lewis acid sites [9,10]. The dimerization occurred not only over Lewis acid catalysts such as $Re_2O_7$–$Al_2O_3$ and $WCl_6$–$Me_4Sn$, but also Brønsted acid catalysts such as $H_2SO_4$ and $SiO_2$–$Al_2O_3$ [9,10]. The structures of dimers depended greatly on Lewis and Brønsted acid catalysts as shown in Fig. 1.
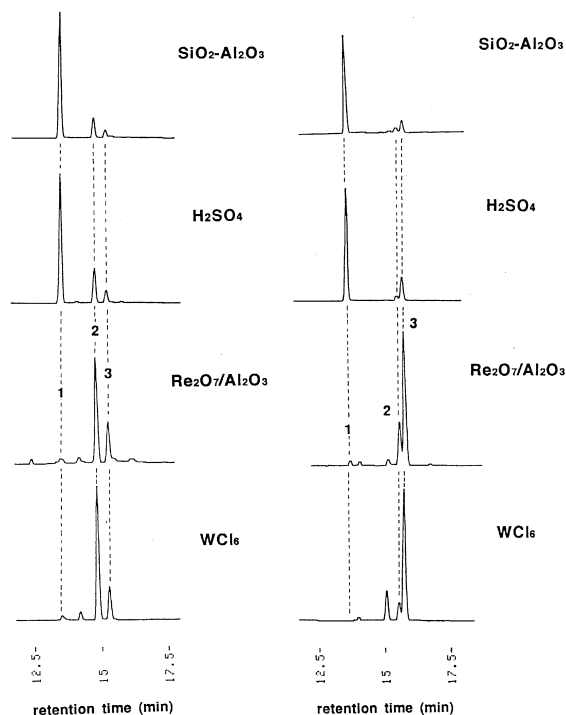


Fig. 1. Gas chromatogram of dimer region of 2-methyl-1-pentene (right) and 2-methyl-1-hexene (left).

However, irrespective of catalysts, mass spectra of the dimers with the same relative retention time showed the same pattern with each other.

### 3.2. Hydrogenation of dimers

2-Me-1-C$'_5$ was used as a model compound to clarify the structures of dimers produced over both Lewis and Brønsted acid catalysts. It has been found that the dimers are acyclic compound, and they have one double bond, confirmed by the bromination.

The hydrogenates of dimers (peak 2 and 3 in Fig. 1) formed over Lewis acid catalysts gave a newly formed single peak in GLC, suggesting that they are isomeric with each other and have double bond at different positions and the same carbon skeleton. By the hydrogenation of peak 1 formed as a main product over Brønsted acid catalysts, a newly single peak was obtained, indicating that peak 1 consists of one component or mixtures which have double bond at different positions and the same carbon skeleton. Also, the dimers of peaks 2 and 3 formed over Brønsted acid catalysts gave a single hydrogenate, which has the same retention time in GLC and shows the same GC–MS spectra as the hydrogenate of dimers 2 and 3 formed over Lewis acid catalysts.

The structures of the isolated hydrogenates were identified by ^{1}H NMR, ^{13}C NMR and GC–MS. Spectra of COSY, DEPT and HETROCOSY were also examined to confirm their structures. It has been found that the hydrogenate of peak 1 is 3-ethyl-2,4,4-trimethyl-heptane and that of peaks 2 and 3 is 4,4,6-trimethyl-nonane.

### 3.3. Ozonolysis and structures of dimers

In order to determine the position of double bond, ozonolysis of the dimers obtained over Lewis and Brønsted acid catalysts was carried out. The reaction products were identified by authentic samples and estimated by GC–MS when the authentic samples are unavailable.

When the dimers formed over Lewis acid catalysts were used, propanal and formaldehyde were obtained together with only small amount of 2-pentanone. In the case of ozonolysis of the dimers from Brønsted acid catalysts, formaldehyde and acetone were formed together with only a small amount of propanal, which was derived from peak 2 and/or peak 3 existing in the dimer sample from Brønsted acid catalysts. Although ketones with parent peak of $m/z$ 142 and 170 were formed as the major products in the ozonolysis of the dimers obtained over both Lewis and Brønsted acid catalysts, it was difficult to identify whether the expected ketones derived from the position of double bond were formed or not. The compounds with $m/z$ 142 correspond to the ketones formed from L-1 and B-2 shown in Fig. 2, and similarly, $m/z$ 170 is formed from B-1 and L-2. The total ion chromatogram at $m/z$ 170 is larger than that of $m/z$ 142, suggesting that B-1 is formed much more than B-2 over Brønsted acid catalysts. From a similar consideration, it was estimated that L-1 is formed more than L-2 over Lewis acid catalysts.

The observations of the dimers and the hydrogenates by ^{1}H NMR, ^{13}C NMR, and the ozonolysis analysis revealed their structures as shown in Fig. 2. Considering not only the above mentioned analysis, but also the mechanistic considerations which will be discussed in Section 3.4, it is concluded that the peak 1 in Fig. 1 is assigned to B-1, and peaks of 2 and 3 to L-2 and L-1, respectively. B-2 and L-3 are formed only in small amounts.
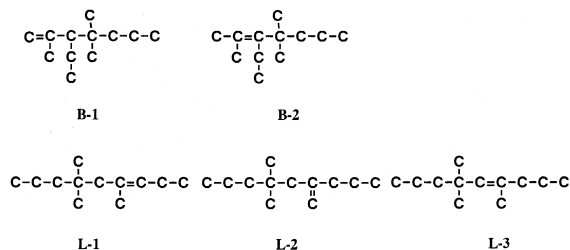


Fig. 2. Structures of dimers.

## 3.4. Mechanism of the dimer formation

### 3.4.1. Dimerization mechanism

The dimerization mechanism on Brønsted acid catalyst is well known and it occurs through the carbocation intermediate. According to this mechanism, five kinds of dimers are obtained as shown in Fig. 3, where the mechanism of double bond shift isomerization is also drawn.

When 2-Me-2-$C_5'$ was used as a starting material over Brønsted acid catalysts, the reactivity increased twice compared to 2-Me-1-$C_5'$ and the ratio of dimer products were consistent with those of 2-Me-1-$C_5'$. Thus, the main reaction path would be the reaction between 2-Me-2-$C_5'$ and the carbocation of monomer to produce B-1 and B-2. The dimers of L-1 and L-2 are formed through the other path shown in the mechanism. However, the formation of dimers, L-1 and L-2, should be in small amounts because 2-Me-1-$C_5'$ exists in small amounts under the reaction conditions [9,10]. According to the Saytzeff rule; the $H^+$ elimination occurs predominantly in the direction to yield the most substituted alkene, the structure B-2 is more favorable but the validity of structure of B-1 is judged by the analytical measurements as mentioned above. In the dimerization of 2-Me-$C_3'$ in the presence of Brønsted acid catalyst ($SiO_2$–$Al_2O_3$) at −35°C, 2,4,4-trimethyl-1-$C_5'$ was formed as the major product with 80% selectivity and 2,4,4-tri-methyl-2-$C_5'$ with 20% [10], in good agreement with the results reported previously [17,18]. These show that the direction of $H^+$ elimination in carbocation with the highly branched structure occurs in accordance with Hofmann rule, i.e., charged substrates yield the least substituted alkene, 2,4,4-trimethyl-1-$C_5'$. These data strongly support that the peak 1 in Fig. 1 would be B-1 together with a small amount of B-2. Although Osokin et al. [19] have reported that the dimers formed in the decreasing order: L-1 ≫ L-3, B-1 > L-2 in the dimerization of 2-Me-1-$C_5'$ over $SiO_2$–$Al_2O_3$ in the liquid phase, neither the identification of products, nor the product distribution are consistent with our data.

The dimerization mechanism on Lewis acid, in the case of $Re_2O_7$–$Al_2O_3$ and $WCl_6$–$Me_4Sn$ catalyst, is not well established. One of the most famous mechanisms on transition metals must include a π-ally complex intermediate. Although the possibility has been checked, the expected structures indicated in Fig. 2 could not be formed according to the mechanism.

Through the oxidative coupling and reductive elimination mechanism [25], the metal induces a coupling reaction between two alkene ligands to give a metallacyclopentane and β-hydrogen elimination to give dimers. According to the mechanism, 10 kinds of intermediates will be considered as shown in Fig. 4.

Among the intermediates, 3, 4 and 10 are inadequate conformations due to large steric hindrance among four substituents on positions 3 and 4 of the metallacyclopentane ring. As the intermediates 1, 7 and 8 have four substituents on positions 2 and 5 of the metallacyclopentane ring, their formation through the interaction with the coordination sites in case of homogeneous
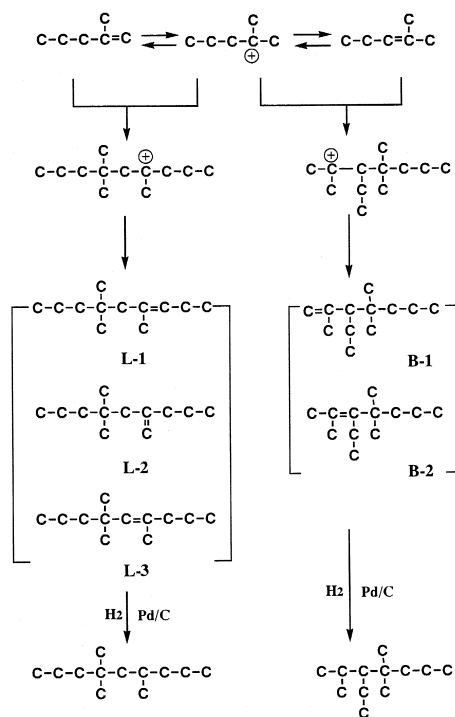


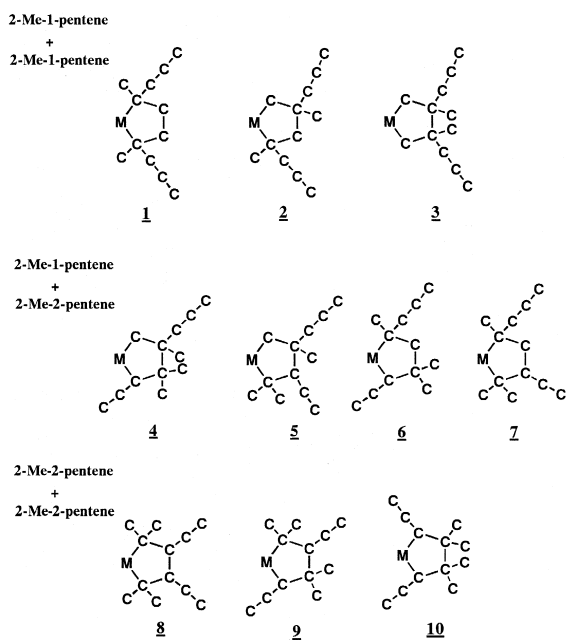Fig. 3. Dimerization mechanism over Brønsted acid catalyst.

Fig. 4. Metallacyclopentane intermediates.

catalyst and with the active sites on the surface of the $Re_2O_7$–$Al_2O_3$ catalyst becomes difficult, resulting in inadequate conformations. The contribution of intermediate *9* should be small due to the six alkyl substituents. The most favorable intermediate is *2* due to the least steric effect. Taking into account the fact that B-1 was formed over Lewis acid catalysts, the formation of intermediates *5* and *6* with five substituents should be considered, although they have relatively highly steric hindrances. The main reaction products, L-1–L-3, can be formed mostly through the β-hydrogen elimination from the intermediate *2* and with a small contribution of intermediate *6*. The intermediate *5* gives the dimers B-1 together with a small amount of B-2. The overall reaction mechanism on Lewis acid catalysts is shown in Fig. 5.

When 2-Me-2-$C_5'$ was used as a starting material over Lewis acid catalysts, the reactivity decreased greatly to 22% compared with 51% of 2-Me-1-$C_5'$ and the B-1 selectivity in dimers increased to 70%. 2-Me-1-$C_5'$ exists in only a few, indicating that the isomerization of 2-Me-2-$C_5$' to 2-Me-1-$C_5'$ is very slow. This indicates

that the contribution of the main route of L-1 and L-2 formation through the intermediate *2* should be only a few, because the intermediate can be formed with the interaction between 2 mol of 2-Me-1-$C_5'$ and Lewis acid catalysts. The main route of the formation of L-1 and L-2 should involve the intermediate *6*, which can be formed by coupling 2-Me-1-$C_5'$ and 2-Me-2-$C_5'$. In the same way, B-1 is formed through the intermediate *5*, which can be formed by coupling 2-Me-1-$C_5'$ and 2-Me-2-$C_5'$.

In the dimerization of 2-Me-1-$C_3'$ in the presence of Lewis acid catalyst ($Re_2O_7$–$Al_2O_3$), 2,4,4-trimethyl-1-$C_5'$ is formed as the major product with 94% selectivity and 2,4,4-trimethyl-2-$C_5'$ with 6% selectivity. As the isomerization does not occur in the case of 2-Me-1-$C_3'$, the analogous intermediates *1*, *2* and *3* to those of intermediates *1–3* shown in Fig. 4 will be formed from 2 mol 2-Me-1-$C_3'$. The intermediate *2* is the most favorable one due to the
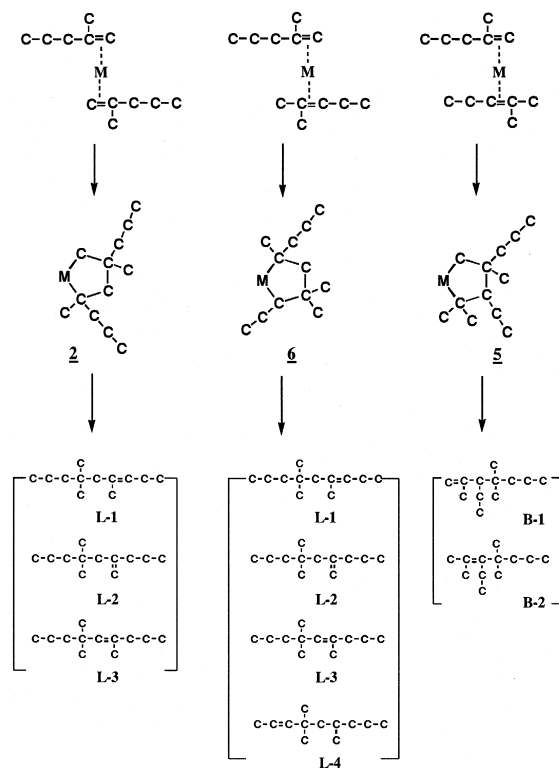


Fig. 5. Dimerization mechanism over Lewis acid catalyst.

least steric hindrance and it produces 2,4,4-tri-methyl-1-C$'_5$ and 2,4,4-trimethyl-2-C$'_5$. The participation of the intermediates *1* and *3* must be small due to steric hindrance as mentioned above. If they are formed, neither the intermediate *1* nor *3* give the expected dimers. The product distribution suggests that the β-hydrogen elimination from the alkyl groups should occur much faster than that from the metallacyclopentane ring. The data support strongly that the dimerization mechanism over Lewis acid catalyst undergoes through the metallacyclopentane intermediates, and that L-1 and L-2 are obtained in larger amounts than L-3.

### 3.4.2. Reactions to support the mechanisms

It has been found that the reaction behavior of 2-Me-1-C$'_3$ and 2-Me-2-C$'_5$ over both Lewis and Brønsted acid catalyst can be rationally explained according to the mechanisms discussed above. Further studies to support the mechanisms were also carried out.

When 2,3,3-trimethyl-1-C$'_4$ was reacted, only one dimer was formed over the SiO2–Al$_2$O$_3$ catalyst with 29% conversion and 100% selectivity. As there is no possibility of isomerization to the corresponding 2,3,3-trimethyl-2-C$'_4$, dimers corresponding to B-1 and B-2 in Fig. 3 are not formed. The dimer corresponding to L-1 cannot be formed due to quaternary carbon adjacent to the carbocation. The product would be 2-*t*-butyl-4,4,5,5-tetramethyl-1-C$'_6$ as L-2 formation is greater than L-3 as discussed above. Over the Re$_2$O$_7$–Al$_2$O$_3$ catalyst, the same dimer was formed with only a small amount, suggesting that the formation of metallacyclopentane intermediates, which are similar to those *1–3* in Fig. 4 is difficult due to steric hindrance. Among the intermediates *1–3*, only *2* has possibility due to the least steric hindrance. In this case, the product is a dimer corresponding to L-2, 2-*t*-butyl-4,4,5,5-tetramethyl-1-C$'_6$, in complete agreement with the result over Brønsted acid catalyst.

In the reaction of 2,4,4-trimethyl-1-C$'_5$, three kinds of dimer with similar product distribution

(about 4:2:1) were formed over both SiO$_2$–Al$_2$O$_3$ and Re$_2$O$_7$–Al$_2$O$_3$ catalyst. Over the Brønsted acid catalyst, the corresponding products to B-1 and B-2 cannot be formed due to the steric hindrance, and those to L-1, L-2 and L-3 are formed with 20% conversion and 100% selectivity. Over the Re$_2$O$_7$–Al$_2$O$_3$ catalyst, the intermediate corresponding to the intermediate *2* would be formed as a sole intermediate as discussed above, and it produces the corresponding products to L-1, L-2 and L-3. Their structures formed over both Lewis and Brønsted acid catalysts are estimated from the mechanism shown in Figs. 3 and 5 to be 4,4,6,6-tetramethyl-2-neopentyl-1-heptene, 2,2,4,6,6,8,8-heptamethyl-3-nonene and 2,2,4,6,6,8,8-heptamethyl-4-nonene, respectively.

The behaviors of these two reactions over both Lewis and Brønsted acid catalysts strongly support the validity of the reaction mechanisms proposed.

## 4. Conclusion

In the reaction of 2-Me-1-alkenes over Re$_2$O$_7$–Al$_2$O$_3$ catalyst, the major products were dimers together with cross-metathesis products as minor products. The structures of dimers obtained from 2-Me-1-C$'_5$ were identified by using ^{1}H NMR and ^{13}C NMR, ozonolysis, hydrogenation, and GC–MS. It was clarified that the mechanism of the dimerization reaction over the Brønsted acid catalysts such as H$_2$SO$_4$ and SiO$_2$–Al$_2$O$_3$ proceeds via the carbocation mechanism. The H$^+$ elimination from the highly branched structure of carbocation occurs in accordance with Hofmann's rule, giving preferential product 3-ethyl-2,4,4-trimethyl-1-heptene (B-1). Over the Lewis acid catalysts such as WCl$_6$–Me$_4$Sn and Re$_2$O$_7$–Al$_2$O$_3$, the dimerization reaction proceeds via the metallacyclopentane intermediates and 4,4-dimethyl-2-propyl-1-heptene (L-2) was formed as the major product together with a small amount of 4,6,6-trimethyl-3-nonene (L-1). The β-hydrogen elimi-

nation from the alkyl substituents occurs much faster than that from the metallacyclopentane ring.

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