

A Novel Metathesis Catalyst Consisting of Non-transition Elements.  
The Metathesis of Alkenes over Tetramethyltin/Dehydroxylated Alumina

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$\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$  prepared by the deposition of  $\text{Sn}(\text{CH}_3)_4$  to alumina which was previously dehydroxylated by heating at 773-1223 K was found to be an active catalyst for the metathesis of alkenes. The catalytic activity greatly depended on the pretreatment temperature of the alumina and the amount of  $\text{Sn}(\text{CH}_3)_4$  deposited.

A variety of catalysts which are active for the metathesis of olefins have been reported up to date. It is worth noting that any of the known metathesis catalysts comprises a certain transition metal(W, Mo or Re in usual cases; Ti, Nb, Ta, etc. in some particular cases);<sup>1)</sup> therefore, it has been believed that such transition metals are essential catalytic components for the metathesis of olefins. In this paper we report the fact that the metathesis of alkenes proceeds even over a "non-transition metal" catalyst system, i.e.  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$ , describing some catalytic features of the new system in the metathesis of propene or some other alkenes.

The metathesis of propene was examined by a pulse method by using a gas-flow-typed reaction apparatus having a quartz tubular reactor and gas chromatographs. The catalysts were prepared in the reactor just before the reaction was started. These experiments were performed under flowing helium according to a series of the procedures as follows.

Divided alumina(80-100 mesh, usually 0.5 g) was placed in the reactor and it was dehydroxylated by heating in a He flow( $50 \text{ cm}^3 \text{ min}^{-1}$ ) for 1 h at a temperature in the range of 723-1223 K, where the degree of dehydroxylation of the alumina being controlled by altering the pretreatment temperature(see Table 1). Tetramethyltin was then deposited onto the dehydroxylated alumina, under flowing He at 298 K, by introducing a pentane solution of  $\text{Sn}(\text{CH}_3)_4[2.0 \times 10^{-2} \text{ mol dm}^{-3}]$  into the reactor, followed by evaporating the

solvent. During this stage the evolution of  $\text{CH}_4$  was observed. In some cases the amount of  $\text{CH}_4$  evolved was measured by gas chromatography. A variety of  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$  catalysts were thus prepared. Since the evolution of  $\text{CH}_4$  was completed in 25 min, the metathesis of propene was started 30 min after the introduction of the  $\text{Sn}(\text{CH}_3)_4$  solution. The reaction was conducted at 298 K by introducing a series of the pulses of propene (each pulse size:  $2.5 \text{ cm}^3 = \text{ca. } 1.0 \times 10^{-4} \text{ mol}$ ) into the carrier gas (He;  $30 \text{ cm}^3 \text{ min}^{-1}$ ) through a six-way valve. The reaction products were analyzed by gas chromatography.

Besides, the metathesis of 1-hexene or 2-pentene in benzene was briefly studied. These liquid phase reactions were conducted at 298 K under a helium atmosphere by using a conventional batch method.

The alumina mainly employed in this work was JRC-ALO-4 [a reference catalyst provided by the Catalysis Society of Japan; extra pure  $\gamma$ -alumina containing traces of Na, Si and Fe (each <70 ppm)]. In some cases, it was purified by washing with  $\text{HNO}_3$  ( $0.1 \text{ mol dm}^{-3}$ ) and with pure water, and then calcined in air at 773 K for 1 h before the use. This purification allowed to reduce each content of Na and Fe in the alumina to below 5 ppm. Besides, other pure alumina (see Fig. 2) and silica gel (Davidson 62) were used instead of JRC-ALO-4 for comparison. Tetramethyltin (Kanto Chemicals) was purified with Molecular Sieve 5A. Helium used as the carrier gas, etc. was purified by passing through a column of Molecular Sieve 13X dipped in a liquid nitrogen bath. Propene (propane <0.5%, ethene and butenes <0.01%) was purified by passing through a  $\text{Mn}^{2+}/\text{SiO}_2$  column ( $\text{O}_2$  and moisture trap).

Figure 1 shows that the metathesis of propene occurs over a

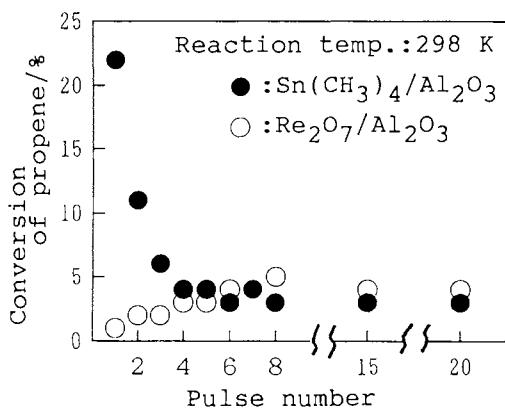


Fig. 1. Metathesis of propene over  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$  ( $7.3 \mu\text{mol}/0.5 \text{ g}$  pre-heated at 1223 K) or 4wt%  $\text{Re}/\text{Al}_2\text{O}_3$  ( $0.5 \text{ g}$ , activated at 773 K for 1 h in a He flow).

Table 1. Properties of the alumina preheated at different temperatures and amounts of  $\text{CH}_4$  evolved during the deposition of  $\text{Sn}(\text{CH}_3)_4$  to the alumina<sup>a)</sup>

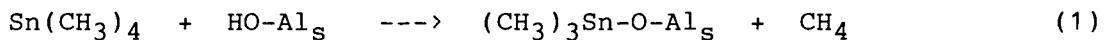
$T_p$ K	SA $\text{m}^2 \text{g}^{-1}$	$N_{\text{OH}}$ $\mu\text{mol g}^{-1}$	$N_{\text{Al}}$ $\mu\text{mol g}^{-1}$	$N_M$	$R_M$
723	175	1300	1125	14.6	1.00
773	173	750	1400	14.3	0.98
823	165	400	1575	13.9	0.95
1073	155	130	1685	8.2	0.56
1223	130	7	2046	7.4	0.51

a) Starting alumina : JRC-ALO-4,  $T_p$ : pretreatment temp, SA : BET surface area,  $N_{\text{OH}}$ :  $(\text{OH})_s$  content by a TGA,  $N_{\text{Al}}$ :  $(\text{Al}^{3+})_s$  or  $(\text{Al}^{3+}-\text{O}^{2-})_s$  content calculated from  $N_{\text{OH}}$ ,  $N_M$ :  $\text{CH}_4$  evolved,  $R_M$ : molar ratio of  $\text{CH}_4$  evolved/ $\text{Sn}(\text{CH}_3)_4$  deposited ( $N_M/14.6$ ).

$\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$  catalyst, where the alumina was preheated at 1223 K in this case. The reaction products were only ethene and 2-butene. The molar ratio of ethene to 2-butene produced was approximately unity for every pulse. Although the catalytic activity sharply decreased in the few initial pulses, it became almost constant after several pulses, indicating that the reaction is certainly catalytic. Figure 1 also shows that the activity of this catalyst is comparable to that of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  (a conventional metathesis catalyst).  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$  similarly prepared was also effective both for the liquid phase metathesis of 1-hexene to 5-decene and ethene and for that of 2-pentene to 3-hexene and 2-butene as Table 2 shows.

Figure 2 shows that the catalytic activity of  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$  for the metathesis of propene increases with increasing the pretreatment temperature of the alumina. This implies that Lewis acid sites( $\text{Al}^{3+}$ )<sub>s</sub> or acid-base sites( $\text{Al}^{3+}\text{-O}^{2-}$ )<sub>s</sub>, rather than the OH groups(OH)<sub>s</sub>, on the alumina surface are essential in the formation of the active sites of the metathesis (see also Table 1). Actually,  $\text{Sn}(\text{CH}_3)_4/\text{SiO}_2$  was inactive for the metathesis even when the support was preheated at high temperatures. Figure 2 also shows that iron is not an essential component because similarly active catalysts were obtained from the completely or almost Fe-free alumina supports.

In order to see the interaction between  $\text{Sn}(\text{CH}_3)_4$  and the preheated alumina supports, we measured the amounts of  $\text{CH}_4$  evolved in the preparation of the catalysts. Table 1 shows that the molar ratio( $R_M$ ) of  $\text{CH}_4$ (evolved)/ $\text{Sn}(\text{CH}_3)_4$ (deposited) is approximately unity for the alumina having excess amounts of (OH)<sub>s</sub>, suggesting that the reaction between  $\text{Sn}(\text{CH}_3)_4$  and (OH)<sub>s</sub> preferentially takes place according to Eq. 1. However, it seems that the



active sites for the metathesis are formed by another reaction, probably by the reaction of  $\text{Sn}(\text{CH}_3)_4$  with ( $\text{Al}^{3+}\text{-O}^{2-}$ )<sub>s</sub>, because a significant amount of  $\text{CH}_4$  was still observed and more active catalysts were obtained when the almost fully dehydroxylated alumina (pretreated at 1223 K) was used as the support. Taking into account these facts in the light of the structure of the active sites (transition metal carbenes, such as  $\text{W}=\text{CH}_2$ ,  $\text{Ti}-\text{CH}_2-\text{Al}$  in Tebbe's reagent, etc.) proposed for the conventional metathesis catalysts,<sup>1)</sup> we currently suggest the following scheme (Eq. 2) as a probable reaction for the formation of active sites of metathesis on the  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$  catalysts.

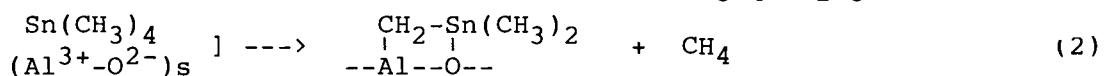


Figure 3 shows that catalytic activity of  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$  remarkably depends not only on the degree of dehydroxylation of the alumina but also on the amount of  $\text{Sn}(\text{CH}_3)_4$  deposited. When the almost fully dehydroxylated alumina was used as the support, the maximum activity was observed around

15  $\mu\text{mol}$   $\text{Sn}(\text{CH}_3)_4/\text{g-Al}_2\text{O}_3$ . While, in the case of the alumina having an excess amount of  $(\text{OH})_s$ , it appeared at a higher loading of  $\text{Sn}(\text{CH}_3)_4$  and was much lower as compared to the above case. The shift of the optimal loading can be attributed to the difference in  $(\text{OH})_s$  content of these supports; it is likely that, in the latter case, larger amounts of  $\text{Sn}(\text{CH}_3)_4$  were consumed by the useless reaction(Eq.1). Figure 3 also shows that the deposition of excess amounts of  $\text{Sn}(\text{CH}_3)_4$  causes a decrease in the catalytic activity. This is probably due to poisoning effects by extra  $\text{Sn}(\text{CH}_3)_4$  molecules.

It is interesting that the metathesis of alkenes is also catalysed by such a non-transition metal catalyst system as  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$ . This implies that studies for developing metathesis catalysts should no longer be restricted to those on particular transition metal catalysts.

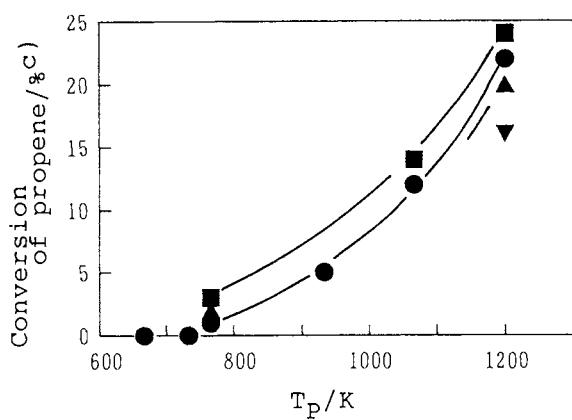


Fig. 2. Effects of the pretreatment temperature( $T_p$ ) of alumina and alumina source on the catalytic activity of  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$ .<sup>a,b)</sup>

a) Starting alumina:● JRC-ALO-4 [see text and Table 1], ■ JRC-ALO-4 [washed with  $\text{HNO}_3$  : see text], ▲  $\gamma\text{-Al}_2\text{O}_3$  [ $190 \text{ m}^2 \text{ g}^{-1}$ , Fe-free, prepared by the hydrolysis of  $\text{Al}(\text{NO}_3)_3$ ], ▽  $\gamma\text{-Al}_2\text{O}_3$  [ $160 \text{ m}^2 \text{ g}^{-1}$ , Fe ca.100 ppm, prepared from an alumina sol]; b)  $\text{Sn}(\text{CH}_3)_4$  7.3  $\mu\text{mol}/0.5 \text{ g-Al}_2\text{O}_3$ ; Reaction conditions: see Fig.1 ; c) Yield of  $\text{C}_2\text{H}_4+\text{C}_4\text{H}_8$  for the first pulse in each run

#### Reference

1) R.H. Crabtree, "Organometallic Chemistry of the Transition Metals," John Wiley & Sons(1987); K.J. Ivin, "Olefin Metathesis," Academic Press (1983).

Table 2. Metathesis<sup>a)</sup> of 1-hexene or 2-pentene over  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$ <sup>b)</sup>

	Reaction time/min		
	20	60	100
Conv. of 1-hexene/%	5.5	10	14
Conv. of 2-pentene/%	7.2	12	17

a)At 298 K in benzene( $5 \text{ cm}^3$ ), alkene:  $0.5 \text{ cm}^3$ . b) 7.3  $\mu\text{mol}/0.5 \text{ g-Al}_2\text{O}_3$  preheated at 1223 K.

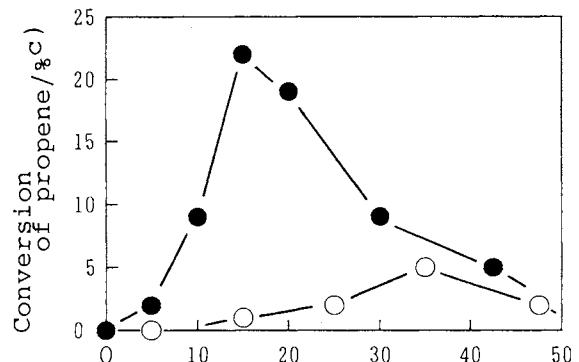


Fig. 3. Variations in the catalytic activity of  $\text{Sn}(\text{CH}_3)_4/\text{Al}_2\text{O}_3$  prepared from the alumina<sup>a)</sup> preheated at 1223 K (●) or at 773 K (○) for the metathesis of propene<sup>b)</sup> as a function of the loading of  $\text{Sn}(\text{CH}_3)_4$ .  
a)JRC-ALO-4;0.5 g, b)Reaction conditions : See Fig. 1; c) See Fig. 2.

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