Metathesis of terminal olefins over tin-modified silica–alumina: A letter

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The metathesis of acyclic olefins is catalysed by a great variety of transition metal compounds [1]. Recently, a few publications have also appeared which report a non-transition metal compound as catalyst for this reaction. Thus, silica, photo-irradiated with a 250 W Hg lamp, catalyses the metathesis of lower olefins [2,3], while metathesis of linear alkenes also takes place with the system Me_4Sn/Al_2O_3 (Al_2O_3 pretreated at 900°C) [4]. Here, we report on the metathesis of linear α-alkenes in the presence of $SiO_2–Al_2O_3$ promoted with tetrabutyltin (Eq. (1)).

$$2Me(CH_2)_nCH=CH_2$$
$$\rightarrow Me(CH_2)_nCH=CH(CH_2)_nMe$$
$$+ CH_2=CH_2 \tag{1}$$
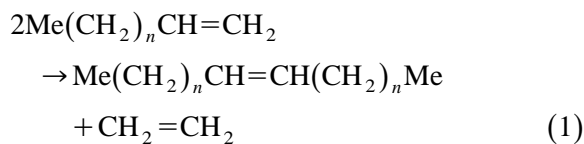
The metathesis reactions were carried out in the liquid phase in a glass batch reactor at room temperature. Silica–alumina (Akzo, type HA [2]) was first calcined at 550°C in an air stream, followed by a nitrogen purge at the same temperature. The catalyst was then cooled to room temperature. Subsequently tetrabutyltin was added, followed by the substrate. The reaction was monitored by GC analysis.

1-Hexene, 1-octene and 1-decene underwent metathesis to give the expected products, i.e., 5-decene, 7-tetradecene and 9-octadecene, respectively. Typical results are presented in Table 1.

Although the selectivity to metathesis products was high in all cases, 1-hexene readily underwent isomerization to 2- and 3-hexene, followed by cross-metathesis between terminal and internal hexene molecules leading to a low selectivity for primary (i.e., self-) metathesis

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[2] Chemical composition (balance being SiO_2): Al_2O_3 24.3 wt.%; Na_2O 0.010 wt.%; SO_4 0.9 wt.%; Fe 0.04 wt.%. With SEM–EDX no transition metals could be detected. A Rutherford backscattering spectrometry (RBS) analysis indicated the presence of molybdenum in an atomic ratio relative to iron of ca. 0.5.

Table 1
Metathesis of terminal olefins over $Bu_4Sn/SiO_2-Al_2O_3^a$

	1-Hexene[b]	1-Octene[c]	1-Decene[c]
Conversion to primary metathesis products[d] (%)	7(4)	66	61
Total conversion to metathesis products (%)	75(44)	80	84

[a]Reaction conditions: olefin/Bu_4Sn/$SiO_2-Al_2O_3$ = 6.5 mmol/42–50 μmol/500 mg; heptane as the solvent; room temperature; reaction time 3–4 h.
[b]Conversion based on analysis of the gas phase; between brackets data for 16 μmol Bu_4Sn.
[c]Conversion based on analysis of the liquid phase.
[d]According to Eq. (1).

Table 2
Metathesis of 1-decene over $Bu_4Sn/SiO_2-Al_2O_3$ with different silica–aluminas[a]

Oxide	wt.% Al_2O_3	Surface area (m^2/g)	Conversion[b] (%)	Selectivity[c] (%)
γ-Al_2O_3, Akzo	99.9	208	3.4	73
$SiO_2-Al_2O_3$-Siral 40, Condea[d]	58.5	498	21	8
$SiO_2-Al_2O_3$-HA, Akzo	24.3	380	84	73
$SiO_2-Al_2O_3$-LA, Akzo	13.0	464	8	9
SiO_2, Akzo	0	344	0	

[a]Reaction conditions as in Table 1.
[b]Conversion to metathesis products in 2.5 h.
[c]Selectivity to primary metathesis products.
[d]With 1-hexene, 5.3% conversion to metathesis products, 19% conversion to dimers.

products. In a kinetic study, it was indeed observed that the secondary (i.e., cross-) metathesis products propene, 1-butene and 1-pentene were the first formed lower alkenes. 1-Butene and 1-pentene subsequently isomerized to their internal analogues. The first formed higher alkenes ($> C_6$) were already internal. These results suggest that cross-metathesis is favoured over self-metathesis of the internal alkenes. For the metathesis of 1-hexene there seems to be a correlation between the amount of tin compound and the conversion to metathesis products: for a lower $Bu_4Sn/SiO_2-Al_2O_3$ ratio the conversion was lower (see Table 1).
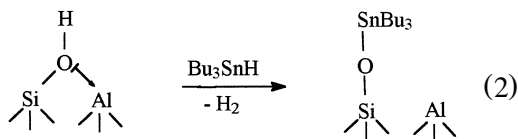
1-Octene and 1-decene underwent isomerization to a far lower extent than 1-hexene. Moreover, for 1-hexene dimerization, a reaction to be expected in the presence of carbocations (although these are known to promote dimerization of 2-methyl-1-alkenes only [5,6]), was also ob-

served.[3] Thus, with $Bu_4Sn/SiO_2-Al_2O_3$ as the catalyst the selectivity for metathesis seems to be a function of the chain length of the alkene.

In order to gain some insight into the nature of the active sites, other silica-aluminas with different Al_2O_3 contents were also tested (Table 2). It seems that the presence of alumina is a necessary condition for metathesis to take place. Moreover, the highest catalytic activity was observed for a 25 wt.% Al_2O_3 sample, which is known to have the highest Brönsted/Lewis acid sites ratio [7]. Concerning the role of the tin compound it should be noted that its presence not only affects the catalytic activity for

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[3] When silica–alumina was doped with CsOH (1 wt.%), isomerization was almost suppressed. Selectivity to metathesis, however, was not improved, since the metathesis/dimerization ratio was not affected.

metathesis, but also the rate of isomerization (experiments with pure silica-alumina showed isomerization of 1-hexene to a thermodynamic equilibrium mixture of hexenes within 1 h, i.e., $[1 - C_6]/\Sigma[C6] = 0.04$; in the presence of Bu_4Sn this ratio was 0.51). The latter was indeed expected as it has been shown that Bu_3SnH reacts with the surface of silica-alumina through the highly acidic bridging OH groups (Eq. (2)) [8,9]. The same kind of reaction is to be expected for Bu_4Sn [8]. ^{119}Sn NMR experiments confirmed this hypothesis, although in our case the presence of physisorbed Bu_4Sn was also observed.

$$\begin{array}{ccc}
\text{H} & & \text{SnBu}_3 \\
| & & | \\
\text{O} & \xrightarrow[-\,H_2]{Bu_3SnH} & \text{O} \\
\diagdown & & | \\
\text{Si}\quad\text{Al} & & \text{Si}\quad\text{Al}
\end{array} \qquad (2)$$

Whether the catalytic site is located on a tin or on an aluminium site remains to be determined. Although stannene ($R_2Sn{=}CR_2$) species are known, it is necessary for the R groups to be bulky to prevent association [10]. Moreover, they cannot be prepared via a simple α-H-abstraction on an alkyltin compound. On the other hand, a pure aluminium compound, $EtAlCl_2$, has been described as being active for ring-opening metathesis polymerization (ROMP) of norbornene [11]. A mechanism which could account for both metathesis and oligomerization of olefins on the same Al centre has been proposed by Ivin [12]. We observed dimerization of 1-hexene but not the dimerization of higher alkenes: it is known that the activity of cationic oligomerization catalysts decreases with increasing chain length of the alkene [13]. How-

ever, the active site could also arise from a reaction between an $[Al]^{3+}$–$[O]^{2-}$ site and Bu_4Sn [4]. Such site would be more available after reaction between silica–alumina and Bu_4Sn (see Eq. (2)). Studies aiming to verify these hypotheses are currently underway.

Acknowledgements

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