Germanium and silicon compounds as promoters for Re$_2$O$_7$/SiO$_2$-Al$_2$O$_3$ metathesis catalysts

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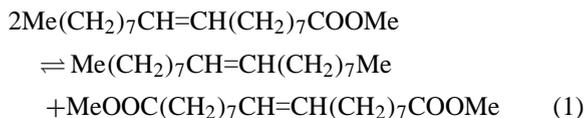[b] *Institute of Molecular Chemistry, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

Abstract

The effect of replacement of R$_4$Sn by germanium and silicon derivatives as the promoter for the catalyst system Re$_2$O$_7$/SiO$_2$-Al$_2$O$_3$ in the metathesis of hex-1-ene, and the system Re$_2$O$_7$/B$_2$O$_3$/SiO$_2$-Al$_2$O$_3$ in the metathesis of methyl oleate, was studied. The new promoters react slowly with the rhenium oxide. An activation time of about 15 min at temperatures varying from 50 to 75 °C is required for obtaining a good catalytic activity. These promoters can replace the toxic tin compounds, although they give rise to lower turnover numbers in the metathesis of methyl oleate.
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1. Introduction

Rhenium oxide supported on alumina or silica-alumina is a well-known catalyst for alkene metathesis [1,2]. The use of silica-alumina as support leads to a higher activity, but the selectivity is lower. An improvement of the catalytic activity is obtained by promotion with R$_4$Sn or R$_4$Pb (R = alkyl) and, moreover, it then becomes active for the metathesis of functionalised olefins such as unsaturated esters, e.g. methyl oleate (methyl *cis*-9-octadecenoate); Eq. (1). The latter reaction has interesting possibilities for the oleochemistry [3].

2Me(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOMe
$$\rightleftharpoons \text{Me(CH}_2)_7\text{CH=CH(CH}_2)_7\text{Me}$$
$$+\text{MeOOC(CH}_2)_7\text{CH=CH(CH}_2)_7\text{COOMe} \qquad (1)$$

In the presence of these catalysts, the reaction takes place already at room temperature. It has been suggested that the promoter is involved in the formation of new initiating metal-alkylidene species via double alkylation of the rhenium, followed by α-H elimination [4]. The active sites generated by R$_4$Sn or R$_4$Pb may be intrinsically different from those present on the unpromoted catalyst [5].

However, the tin- and lead-containing promoters are toxic. Therefore, we studied the possibility to replace these promoters by germanium and silicon compounds, evaluating both their reactivity towards Re$_2$O$_7$-based catalysts and the catalytic performance of the resulting systems in the metathesis reaction.

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Silicon derivatives have been proved to be good co-catalysts for WCl_6 [6] and $WOCl_4$ [7] in the metathesis of functionalised olefins, but there are no reports of a successful application of this kind of compound as a promoter for rhenium oxide based catalysts.

2. Experimental

The Re_2O_7/SiO_2-Al_2O_3 catalyst was prepared by wet impregnation of silica-alumina (Akzo. 24.3 wt.% Al_2O_3, surface area $347\,m^2/g$, porosity $0.88\,cm^3/g$) with an aqueous solution of NH_4ReO_4, followed by drying at $110\,°C$ overnight and calcination under air at $500\,°C$ for 2 h. Silica-alumina supports with 5 wt.% boria were prepared in the same way using an aqueous solution of boric acid for the impregnation step.

For studying the reactivity between neohexene and the system $Re_2O_7/B_2O_3/SiO_2$-Al_2O_3/promoter, the catalyst ($\sim$150 mg) was calcined in flowing air for 2 h at $550\,°C$, followed by a nitrogen purge for 15 min at the same temperature. After cooling to room temperature, calculated volumes of Et_4Ge (Aldrich, 99%), Et_4Si (Aldrich, 97%), Et_4Sn (Aldrich, 97%), Bu_3GeH (Aldrich, 99%), Bu_3SnH (Fluka, 99%) or Et_2SiH_2 (Aldrich, 99%) dissolved in *n*-heptane (Merck, 99%, distilled over Na/benzophenone), were added to the catalyst via a syringe through a rubber septum. The catalytic system was then heated during 15 min for catalyst activation. After cooling to room temperature, 1 ml of 3,3-dimethylbut-1-ene (neohexene, Fluka, 95%) was added to the reaction vessel, via a syringe. After 10 s, the reaction products were trapped in liquid nitrogen. Analyses of the gas phase were performed using an HP 5890 gas chromatograph, equipped with an Al_2O_3/KCl on fused silica capillary column (50 m × 0.32 mm) and a flame ionisation detector.

For the catalytic experiments, the freshly calcined catalyst ($\sim$150 mg) was cooled to room temperature and transferred to a glass batch reactor under argon. The catalyst was then allowed to react with 0.5 ml of an *n*-heptane solution containing the calculated volume of co-catalyst. After stirring at the desired temperature for the selected time, the reactor was cooled to room temperature and the substrate was added via syringe.

In the metathesis of hex-1-ene (Aldrich, 97%), 4.0 ml of *n*-heptane and 0.2 ml of decane (internal standard) were also added to the reaction vessel. Conversions were determined by GC analysis of the liquid phase using an HP 5 capillary column. *Cis/trans* ratios of the diesters were determined using a CP-Sil 88 capillary column.

3. Results and discussion

3.1. Metathesis of hex-1-ene

Metathesis of hex-1-ene was used as test reaction for the catalytic activity (Eq. (2))

$$2CH_2{=}CH(CH_2)_3CH_3$$
$$\rightleftharpoons CH_3(CH_2)_3CH{=}CH(CH_2)_3CH_3 + CH_2{=}CH_2 \quad (2)$$
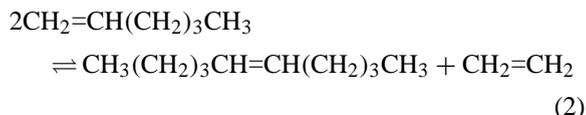
When R_4Ge and R_4Si (R = Me, Et, Bu) were allowed to react with Re_2O_7/SiO_2-Al_2O_3 at room temperature, an instantaneous colour change (from white to brownish) was observed. Because germanium and silicon are less active as alkylating agents than tin and lead, it was anticipated that a higher temperature is required than room temperature as in the case of tin or lead. Heating at 50 or $75\,°C$ for R_4Ge and R_4Si, respectively, for 15 min gave a significant increase in amount of gases evolved during the reaction of the promoter with the catalyst (Fig. 1). For instance, from $<$0.05 (at rt) to 0.12 (at $50\,°C$) mol of butane/mol Re were released in the case of Bu_4Ge. Moreover, the metathesis activity also increased with increasing temperature during the contact between the catalyst and the promoter (Fig. 2).

Table 1 shows that the addition of a promoter improves the performance of the catalyst in the metathesis of hex-1-ene: not only the conversion is increased, but also the selectivity. Clearly, the addition of the promoter decreases side reactions such as double bond shift in the substrate followed by secondary metathesis reactions. In general, germanium compounds are a better promoter than silicon compounds. For R = Me, the activity is the lowest, whereas the release of gas was the highest for Me_4Ge. The addition of Me_4Si even deactivates the catalyst.

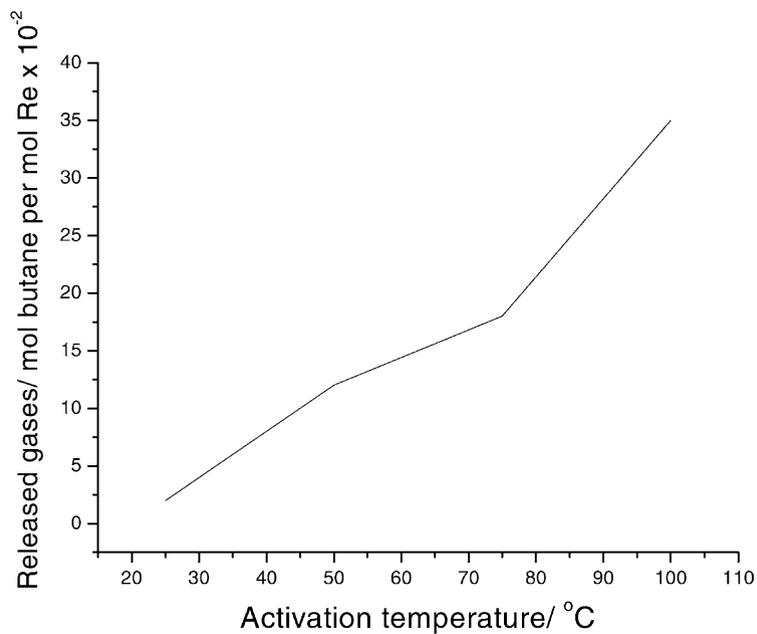Fig. 1. Amount of butane evolved upon interaction between Bu$_4$Ge and 3 wt.% Re$_2$O$_7$/SiO$_2$-Al$_2$O$_3$ as a function of the activation temperature.
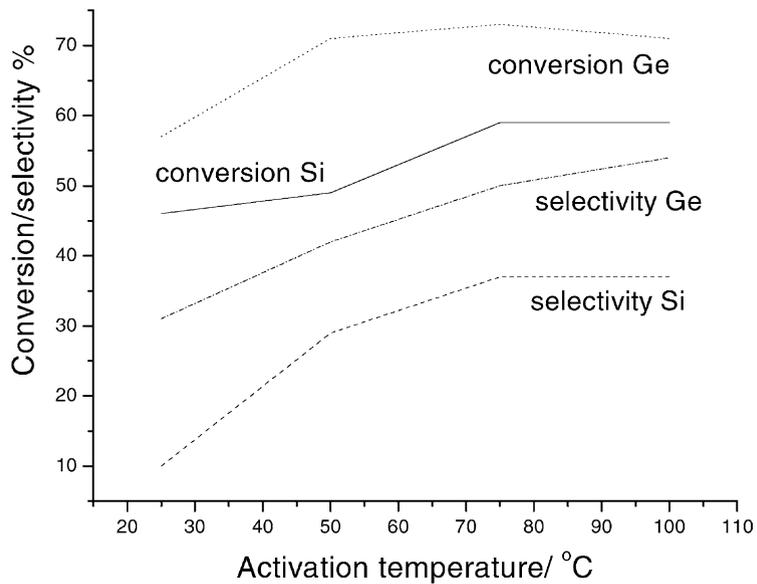

Fig. 2. Conversion and selectivity for the metathesis of hex-1-ene of the systems Re$_2$O$_7$/SiO$_2$-Al$_2$O$_3$/Bu$_4$Ge and Re$_2$O$_7$/SiO$_2$-Al$_2$O$_3$/Et$_4$Si as a function of the activation temperature.

Table 1

Effect of the promoter on the catalytic activity of 3 wt.% Re_2O_7/SiO_2-Al_2O_3 in the metathesis of hex-1-ene[a]

Promoter	Conversion (%)	Selectivity (%)[b]	[RH]:[Re][c]
No promoter	38	9	–
Me_4Ge	54	30	0.53
Et_4Ge	72	41	0.23
Bu_4Ge	71	42	0.12
Bu_3GeH	66	36	<0.01
Me_4Si	31	17	n.d.
Et_4Si	59	37	0.27
Bu_3SiH	57	32	n.d.
Et_2SiH_2	59	31	0.12

[a] [olefin]:[Re]:[promoter] = 250:1:0.55; reaction temperature: $23.5 \pm 0.5\,°C$; reaction time: 5 min; activation time: 15 min at $50\,°C$ (for Ge-containing promoters) or $75\,°C$ (for Si-containing promoters).

[b] Other products, resulting from cross-metathesis reactions between hex-1-ene and its internal isomers, detected in the liquid phase: heptenes, octenes (mainly oct-3-ene) and nonenes (mainly non-4-ene, the major by-product in all cases).

[c] Mol of liberated alkane per mol of Re after 15 min reaction between promoter and catalyst at $50\,°C$ (for Ge-containing promoters), or at $75\,°C$ (for Si-containing promoters).

For Si-containing promoters the highest activity was obtained when the reaction temperature between promoter and catalyst was $75\,°C$. In the case of Bu_4Ge, a further increase in activation temperature led to a higher amount of released butane, but the catalytic activity did not improve. This suggests that heating above $50\,°C$ promotes a reaction between unreacted Bu_4Ge and remaining surface OH groups. An increase of the ratio Ge/Re gave an increase in conversion as well as in selectivity up to a value of 0.55 for the selectivity.

Kawai et al. [8] tested some of these promoters in the metathesis of 4-bromobut-1-ene in the presence of a Re_2O_7/Al_2O_3 catalyst. Me_4Ge gave some enhancement in activity, whereas Me_4Si showed no enhancement in activity at all.

3.2. Metathesis of methyl oleate

Next, the activity for the metathesis of methyl oleate was studied. For this study we choose B_2O_3/SiO_2-Al_2O_3 as the support, because it leads to a higher activity, at least in the metathesis of methyl undecenoate [3,9]. Table 2 shows the activities of the catalyst system $Re_2O_7/B_2O_3/SiO_2$-Al_2O_3 after treatment with different promoters. We choose a loading of 2 wt.% Re_2O_7 because that loading gives the highest specific activity [11]. It should be kept in mind that without a promoter the catalyst is not active in this reaction. For comparison, data obtained with a Bu_4Sn promoter are also given in the Table. Table 2 shows that the catalytic activity is not only promoted by R_4M (M = Ge, Si or Sn), but also by mono-hydride derivatives ($HMBu_3$) (M = Ge, Si, Sn), although to a lower extent. H_2SiEt_2 does not induce activity. The Table also shows that with a tetraalkyl-metal promoter the obtained *cis/trans* ratio of the diester is ~0.22, which is the thermodynamic equilibrium value. With the hydrides we got a higher *cis/trans* ratio, viz. 0.83, which

Table 2

Catalytic activity of promoted 2 wt.% Re_2O_7 supported on SiO_2-Al_2O_3 or B_2O_3/SiO_2-Al_2O_3 in the metathesis of methyl oleate[a]

Support	Promoter	TON[b]	Selectivity (%)[c]	*Cis/trans* ratio of diester
SiO_2-Al_2O_3	Bu_4Ge	30	73	n.d.
SiO_2-Al_2O_3	Bu_4Sn	118	81	0.22
B_2O_3/SiO_2-Al_2O_3	Bu_4Ge	46	70	0.22
B_2O_3/SiO_2-Al_2O_3	Et_4Si	30	80	n.d.
B_2O_3/SiO_2-Al_2O_3	$HGeBu_3$	17	70	0.83
B_2O_3/SiO_2-Al_2O_3	$HSiBu_3$	7.4	94	0.83
B_2O_3/SiO_2-Al_2O_3	$HSnBu_3$	34	92	n.d.
B_2O_3/SiO_2-Al_2O_3	H_2SiEt_2	0	–	–
B_2O_3/SiO_2-Al_2O_3	Bu_4Sn[d]	198	90	0.22

[a] [olefin]:[Re]:[promoter] = 120:1:0.55; reaction temperature: $41 \pm 1\,°C$; reaction time: 3.5 h.

[b] Turnover number = mol of products formed per mol of Re.

[c] Other products obtained in the metathesis of methyl oleate: alkenes higher than C_{18} and diesters shorter than C_{18}.

[d] [olefin]:[Re] = 360:1.
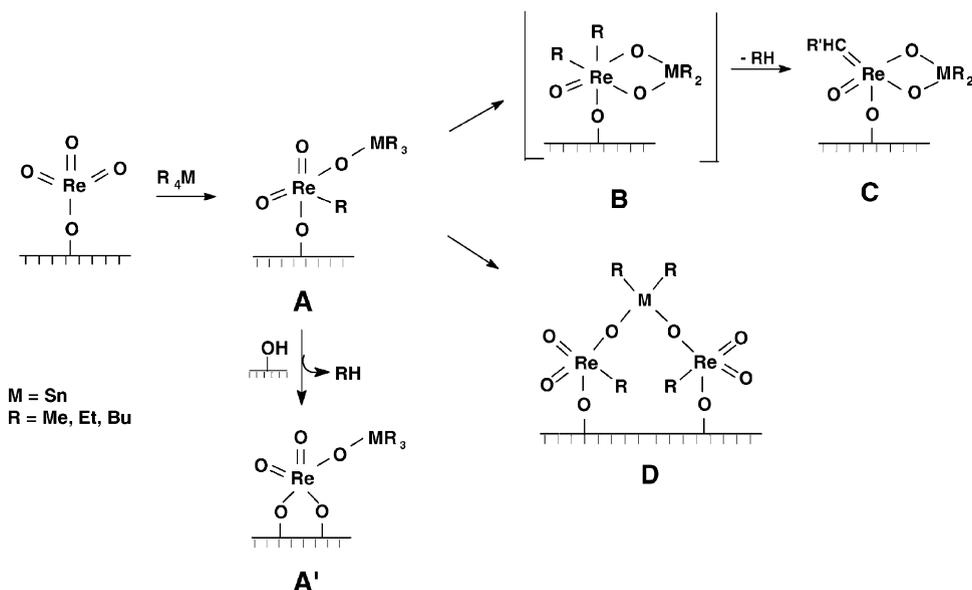
Scheme 1.

means a preference for the *cis* isomer compared to the thermodynamic value. This result suggests a different environment for the rhenium centre in the active site.

3.3. Reactivity between promoted Re$_2$O$_7$/B$_2$O$_3$/SiO$_2$-Al$_2$O$_3$ and neohexene

Based on volumetric and spectroscopic studies of the interaction between R$_4$Sn and Re$_2$O$_7$ supported on silica-alumina or alumina, Buffon et al. proposed

Table 3
Products observed after interaction between Re$_2$O$_7$/SiO$_2$-Al$_2$O$_3$/ promoter and neohexene

Promoter	Ethene	Propene	Butene	Butene/propene (area/area)[a]
Et$_4$Si	x[b]	x	x	9.7
Et$_4$Ge	x	x	x	13
Et$_4$Sn	x	x	x	20
Bu$_3$SnH	Traces	Traces[c]	Traces	–
Bu$_3$GeH	Traces	Traces[c]	Traces	–
Et$_2$SiH$_2$	–	–	Traces	–

[a] Integrated areas of the related peaks in the chromatogram.
[b] x means that the alkene was observed in significant amounts.
[c] Pent-1-ene was expected as the first formed product, but was not observed.

the formation of surface species as depicted in Scheme 1 [4,10]. A double alkylation, followed by an α-H-abstraction would lead to a rhenium-alkylidene species **C**, a minor surface species. They also observed that there was no direct correlation between the amounts of gas released during the interaction catalyst—R$_4$Sn and the catalytic activity of the resulting system. We observed the same feature with Ge and Si derivatives. In order to verify if an alkylidene ligand could be identified via a metathetical exchange reaction, the catalysts were allowed to react with neohexene in a flow reactor. Neohexene is a very bulky alkene and its self-metathesis has never been reported [1]. If the reaction of Re$_2$O$_7$/support with Et$_4$Si or Et$_4$Ge led to the formation of a rhenium-alkylidene ligand, propene (as well as 4,4-dimethylpent-2-ene) should be detected as a first formed product; Eq. (3).

$$\tag{3}$$
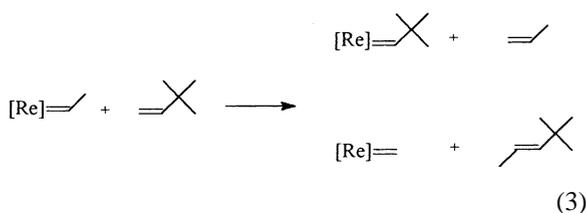
Self-metathesis of the propene formed would lead to ethene and but-2-ene. Qualitative results obtained using Et$_4$Si, Et$_4$Ge and Et$_4$Sn indeed showed the formation of such products (Table 3). Moreover, the ratios butene/propene are in good agreement with the increasing catalytic activity induced by these promoters (Et$_4$Si < Et$_4$Ge < Et$_4$Sn). Et$_2$SiH$_2$ did not lead to a Re-ethylidene species. With Bu$_3$GeH and Bu$_3$SnH, pent-1-ene would be the first formed alkene. Its presence was not detected, nor the formation of ethene, its self-metathesis product. These results suggest that no Re-alkylidene species are formed with promoters bearing hydride ligands. The initial carbene species necessary for metathesis would arise from a reaction between surface hydride species and the olefin.

4. Conclusions

After appropriate treatment, germanium and silicon alkyl compounds are active promoters for supported rhenium catalysts in the metathesis reaction. They can replace the toxic alkyltin- and -lead analogues, although they induce a lower activity.

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