

Olefin metathesis over tin-modified non-transition metal oxides

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Abstract

The reaction of tetrabutyltin with an alumina-containing inorganic oxide such as alumina, silica–alumina or boria–alumina, gives active catalysts for olefin metathesis. Infrared results obtained with tin-modified γ -alumina and boria–alumina suggest that the active sites arise from an interaction between $(n\text{-Bu})_4\text{Sn}$ and a coordinatively unsaturated Al site, which is created when bridging OH groups react with the tetraalkyltin compound. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The metathesis of acyclic olefins is catalysed by a great variety of transition metal compounds [1]. In recent years, several publications have also appeared which report olefin metathesis over solid catalysts that do not contain a transition metal. Thus, the system $\text{Me}_4\text{Sn}/\text{Al}_2\text{O}_3$, prepared by deposition of Me_4Sn on alumina which was previously dehydroxylated by heating at $\geq 500^\circ\text{C}$, brings about the metathesis of lower olefins ($\text{C}_3^=$ – $\text{C}_6^=$) at 25°C [2]. Amorphous

as well as mesoporous silica, activated by evacuation at $\geq 525^\circ\text{C}$, catalyse the metathesis of lower olefins under photo-irradiation with a 250 W Hg lamp. It was deduced that the reaction occurs on the silica surface free from water molecules, and that generation of active sites strongly relates to the removal of isolated OH groups, but the nature of the active sites is not known [3–5].

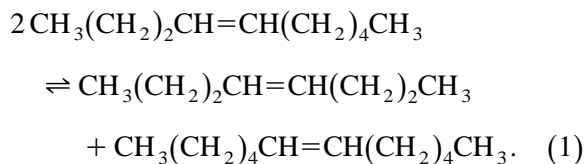
We have recently reported on the metathesis activity of the system $\text{Bu}_4\text{Sn}/\text{SiO}_2\text{--Al}_2\text{O}_3$ [6]. It appeared that this system brings about the metathesis of terminal olefins, such as hex-1-ene, oct-1-ene and dec-1-ene. High conversions into metathesis products were obtained with Bu_4Sn -promoted $\text{SiO}_2\text{--Al}_2\text{O}_3$ containing ca. 24

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wt.% Al₂O₃. The selectivity to primary (i.e., self-) metathesis products of the starting olefin was a function of its chain length. In particular in the case of hex-1-ene, substantial double-bond isomerization took place, followed by cross-metathesis reactions. Tetra-butyltin-modified silica–alumina was more active than alumina while under the same experimental conditions silica showed no catalytic activity at all.

In the present study, we investigated several Bu₄Sn-modified aluminium-containing oxides in order to get some insight into the nature of the active sites. We employed alumina, silica–alumina and boria–alumina, all of which are used as a support in metathesis over supported transition-metal oxide catalysts such as Re₂O₇. The Lewis and Brønsted acidities of these oxides are known to be a function of the alumina content. Besides activity measurements we also applied several spectroscopic techniques to study the interaction of the tetraalkyltin compound with silica–alumina. Moreover, the interaction of (*n*-Bu)₃SnH with silica–alumina was also investigated since this reaction was expected to be more straightforward [7]. All systems were tested in the metathesis of dec-4-ene, as an example of an internal olefin as the substrate (Eq. (1)).



2. Experimental

2.1. Support preparation

γ -Alumina type CK 300 (BET surface area 208 m² g⁻¹) and silica–alumina type HA (24.3 wt.% Al₂O₃, BET surface area 380 m² g⁻¹) were obtained from Akzo Nobel. They were

ground and sieved, and the 125–180 μm fraction was used. An ICP-AES analysis showed the presence of 0.02 wt.% Fe in the alumina, and both 0.05 wt.% Mo and 0.03 wt.% Fe in the silica–alumina. The boria-modified aluminas (BET surface area $\sim 206 \text{ m}^2 \text{ g}^{-1}$) were obtained by multi-step pore-volume impregnation of the γ -Al₂O₃ with an aqueous solution of H₃BO₃. Between two impregnation steps the solids were dried at 120°C for at least 2 h.

2.2. Chemicals

Trans-dec-4-ene (Fluka) was purified by passing through activated alumina. (*n*-Bu)₄Sn (Fluka, 98%) and (*n*-Bu)₃SnH (Fluka, 98%) were used as received. Hexane, the solvent, was distilled over sodium under nitrogen before use.

2.3. Activity measurements

The metathesis reactions were carried out in the liquid phase in a quartz glass batch reactor with a capacity of about 115 ml at room temperature. After drying at 120°C, the oxide was first calcined in situ by heating it to 550°C in an air stream. The catalyst was kept for ≥ 3 h at this temperature and then cooled to room temperature under argon.

In a typical experiment, 200 mg of the calcined oxide was used to which 1 ml of hexane containing 4.6 μl (14 μmol) of (*n*-Bu)₄Sn was added, followed after 5 min by 4 ml of hexane and 1 ml of dec-4-ene.

The reaction was monitored by GC analysis (Carlo Erba 6000 Vega Series 2) of the liquid phase over a capillary column (J&W Scientific, DB-5, 15 m \times 0.32 mm I.D., film thickness 0.25 μm). The GC signals were processed by a Shimadzu C-R5A integrator. For the quantification of the butane released during the reaction between (*n*-Bu)₄Sn and the inorganic oxides, this reaction was carried out without a solvent, and the gas phase was analysed using a Hewlett–Packard 5890 gas chromatograph, with

an $\text{Al}_2\text{O}_3/\text{KCl}$ on fused silica capillary column ($50 \text{ m} \times 0.32 \text{ mm}$).

2.4. Samples preparation for NMR and Mössbauer measurements

A calculated amount of $(n\text{-Bu})_4\text{Sn}$ or $(n\text{-Bu})_3\text{SnH}$, without solvent, was added to ca. 1.0 g of silica–alumina pre-treated as described above, at room temperature. After ca. 15 min, the system was evacuated and the samples were transferred to ampoules (previously connected to the reactor) which were then sealed under vacuum and stored at 0°C .

2.5. MAS NMR measurements

^{119}Sn MAS NMR spectra were recorded on a Bruker AC300 spectrometer operating at 111.9 MHz. The probehead was a commercial 7 mm double-bearing system from Bruker, allowing spinning frequencies up to 4 kHz. The samples were introduced in the zirconia rotor under a dry argon atmosphere in a glove box and tightly closed. The spectra were recorded by using a single pulse and high power decoupling, with a delay between each scan of 2.5 s. Typically, 87 000 scans were accumulated. The chemical shifts are given relative to Me_4Sn , used as external reference and with the IUPAC convention for chemical shifts (higher values for higher frequencies).

2.6. Mössbauer measurements

The samples were transferred to the sample holder under an argon atmosphere. ^{119}Sn Mössbauer spectra were run in standard equipment at liquid nitrogen temperature, using a CaSnO_3 source maintained at room temperature. The isomer shifts are given with respect to this source.

2.7. FT-IR measurements

Before the IR-spectra were recorded the oxides were calcined in air at 550°C for 2 h

(heating rate 10 K/min), and subsequently kept in vacuum ($5 \times 10^{-7} \text{ mbar}$) for 1 h. IR spectra were recorded on a Mattson Cygnus 100 (resolution 2 cm^{-1}), using self-supporting disks of a 25 mg sample (diameter 18 mm). After a sample of the oxide had been measured, tetra-butyltin was added at room temperature. After 3 h this system was evacuated and the spectrum recorded at room temperature.

2.8. Tin determinations

Tin determinations were carried out by inductively coupled plasma-atom emission spectroscopy (ICP-AES).

3. Results

3.1. Activity measurements

Table 1 shows the results of the metathesis of *trans*-dec-4-ene into oct-4-ene and dodec-6-ene (Eq. (1)) on different inorganic oxides treated with $(n\text{-Bu})_4\text{Sn}$. In each case metathesis was observed with high selectivity. The highest conversion was obtained with $\text{SiO}_2\text{-Al}_2\text{O}_3$ as the support: under our reaction conditions equilibrium conversion (50%) was obtained within 0.5 h. $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ gave a lower conversion than silica–alumina or alumina alone, especially at higher B_2O_3 contents. The decrease in activity with increasing boria content correlates to an increase of the coverage of alumina hydroxyls with boria [8]. In all cases, the very high selectivity means that no substantial double-bond isomerization took place.

Under the same experimental conditions, $(n\text{-Bu})_3\text{SnH}$ -modified silica–alumina showed almost no activity for the metathesis of dec-4-ene (ca. 2% conversion in 3 h).

With silica–alumina alone (no tin compound), we got 19% conversion of dec-4-ene after 2 h of reaction time, with a selectivity of 48% for primary metathesis products of dec-4-ene. Other products observed were C_{6-7} , C_9 , C_{11} , and C_{13-14} olefins. Thus, it is possible that also in

Table 1
Metathesis of *trans*-dec-4-ene over (*n*-Bu)₄Sn-promoted Al-containing oxides^a

Support	After 1-h reaction time		After 2-h reaction time	
	Conversion (%)	Selectivity to C ₈ and C ₁₂ (%)	Conversion (%)	Selectivity to C ₈ and C ₁₂ (%)
γ-Al ₂ O ₃	42	100	47	100
3 wt.% B ₂ O ₃ -Al ₂ O ₃	35	100	42	100
5 wt.% B ₂ O ₃ -Al ₂ O ₃	20	97	20	96
10 wt.% B ₂ O ₃ -Al ₂ O ₃	5.5	98	8.3	96
SiO ₂ -Al ₂ O ₃	50 ^{b,c}	96 ^b		

^aConditions: *trans*-dec-4-ene/(*n*-Bu)₄Sn/catalyst = 5.3 mmol/14.4 μmol/200 mg; room temperature.

^bAfter 0.5-h reaction time.

^cEquilibrium conversion.

this case, besides double-bond isomerization, metathesis took place. Apparently, double-bond isomerization is suppressed by the addition of (*n*-Bu)₄Sn to the silica–alumina. Under our experimental conditions, neither (*n*-Bu)₄Sn nor (*n*-Bu)₃SnH in solution show any catalytic activity.

3.2. NMR measurements

¹¹⁹Sn NMR spectra of both (*n*-Bu)₄Sn/SiO₂-Al₂O₃ and (*n*-Bu)₃SnH/SiO₂-Al₂O₃ (Fig. 1) reveal the presence of only one resonance assignable to a surface tin species, at δ ca. 101. This resonance has been ascribed to a ≡SiOSn(*n*-Bu)₃ species [7,9]. In the case of (*n*-Bu)₄Sn/SiO₂-Al₂O₃, the presence of physisorbed Bu₄Sn is clear (peak at δ = -11.9). In the latter case, when the sample was prepared under the catalytic reaction conditions, after the catalytic experiment only the ≡SiOSn(*n*-Bu)₃ species was detected, (*n*-Bu)₄Sn being washed away.

3.3. Mössbauer measurements

For both (*n*-Bu)₄Sn- and (*n*-Bu)₃SnH-modified SiO₂-Al₂O₃, Mössbauer spectra (Fig. 2) show two asymmetric absorption peaks. These peaks were best fitted through two doublets characterised by isomer shifts (IS) in the range 1.33–1.36 mm s⁻¹ (site I) and 1.51–1.53 mm s⁻¹ (site II), and one singlet in the range

-0.26–0.07 mm s⁻¹ (site III). According to the literature, site I can be ascribed to a ≡SiOSn(*n*-Bu)₃ species [11], in agreement with our NMR results. By comparison with molecular analogues (see Table 2) site II might reasonably be assigned to a tin atom linked to the surface by two Sn–O bonds, as both IS and QS (quadrupolar splitting) values increase when a butyl ligand is replaced by an X ligand (X = Cl or aryloxy). Such a site, possibly (≡SiO)(≡AlO)Sn(*n*-Bu)₂, could not be detected by

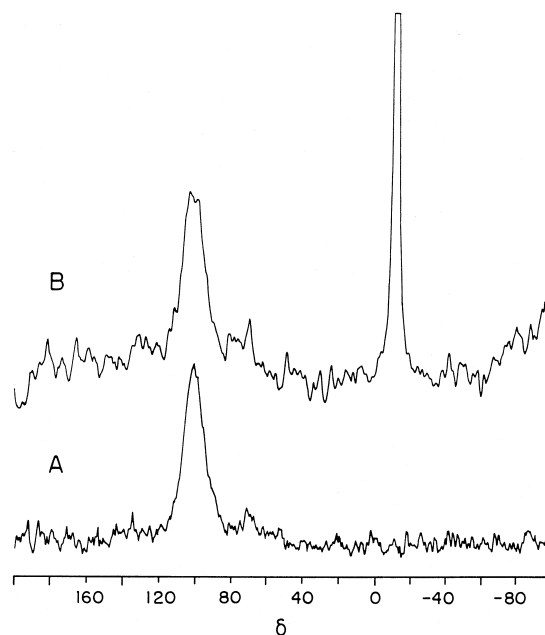


Fig. 1. ¹¹⁹Sn MAS NMR spectra of silica–alumina modified with (*n*-Bu)₃SnH (A) and (*n*-Bu)₄Sn (B).

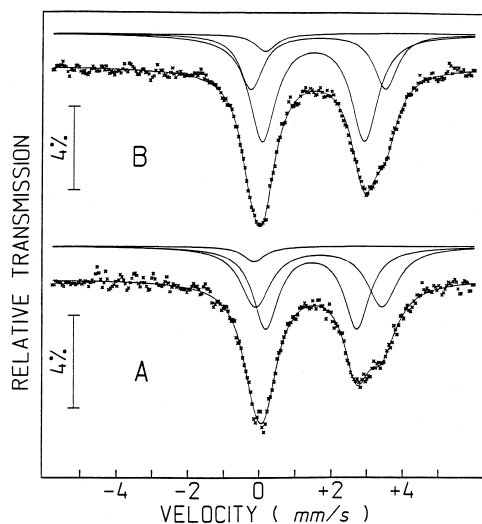


Fig. 2. ^{119}Sn Mössbauer spectra of silica-alumina modified with $(n\text{-Bu})_3\text{SnH}$ (A) and $(n\text{-Bu})_4\text{Sn}$ (B).

^{119}Sn NMR spectroscopy due to its rigidity and, thus, high relaxation time [11,14]. Although site III has Mössbauer parameters characteristic of tin (IV) ionic species, its presence in very minor amounts (allowing for a low accuracy in the measurement) hampers any further interpretation.

3.4. FT-IR measurements

Fig. 3 shows the OH stretch region of the IR spectrum of alumina before (curve A) and after

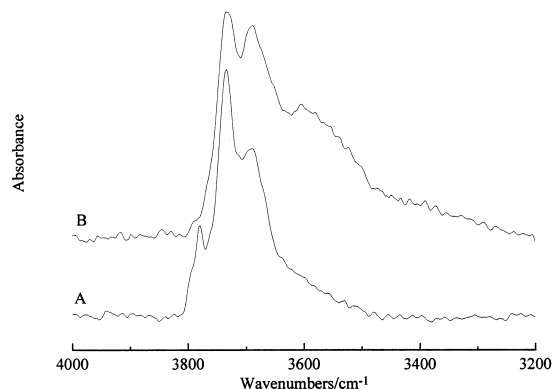


Fig. 3. FTIR spectra in the OH region of alumina before (curve A) and after (curve B) addition of $(n\text{-Bu})_4\text{Sn}$.

(curve B) the addition of tetrabutyltin. The spectrum of alumina shows three main bands which can be ascribed to basic OH groups (3779 cm^{-1}), neutral OH groups (3732 cm^{-1}) and acidic OH groups (3688 cm^{-1}), respectively [15]. When γ -alumina was allowed to react with $(n\text{-Bu})_4\text{Sn}$ the following changes in the OH region were observed: (i) disappearance of the band at 3779 cm^{-1} ; (ii) a decrease in the ratio of the relative intensities between the bands at 3732 and 3688 cm^{-1} ; (iii) appearance of a band at ca. 3600 cm^{-1} ; (iv) a broadening of the whole spectrum. The broadening of the spectrum and the band at 3600 cm^{-1} are assigned to

Table 2

^{119}Sn Mössbauer data for $(n\text{-Bu})_4\text{Sn}/\text{SiO}_2\text{-Al}_2\text{O}_3$ and $(n\text{-Bu})_3\text{SnH}/\text{SiO}_2\text{-Al}_2\text{O}_3$ systems and some related compounds

Compound		IS (mm s^{-1}) ^a	QS (mm s^{-1}) ^b	Reference
$\text{Bu}_4\text{Sn}/\text{SiO}_2\text{-Al}_2\text{O}_3$	site I	1.36	2.88	this work
	site II	1.51	3.74	this work
	site III	0.07	0	this work
$\text{Bu}_3\text{SnH}/\text{SiO}_2\text{-Al}_2\text{O}_3$	site I	1.33	2.51	this work
	site II	1.53	3.51	this work
	site III	-0.26	0	this work
$\text{Bu}_4\text{Sn}/\text{Al}_2\text{O}_3$		1.39	3.01	[10]
$\equiv\text{SiOSnBu}_3$		1.31	2.50	[11]
$(\equiv\text{SiO})_2\text{SnBu}_2$		1.23	2.77	[11]
Bu_3SnCl		1.36–1.65	2.78–3.40	[12]
Bu_2SnCl_2		1.50–1.75	3.25–3.50	[12]
$\text{Bu}_3\text{SnOC}_6\text{H}_5$		1.42	2.85	[13]
$\text{Bu}_2\text{Sn}(\text{O})_2\text{C}_6\text{H}_4$		1.52	3.62	[13]

^aAccuracy for sites I/II: $\pm 0.01\text{ mm s}^{-1}$.

^bAccuracy for sites I/II: $\pm 0.03\text{ mm s}^{-1}$.

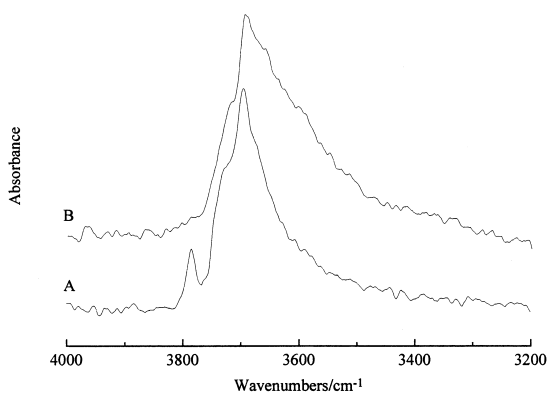


Fig. 4. FTIR spectra in the OH region of boria–alumina before (curve A) and after (curve B) addition of $(n\text{-Bu})_4\text{Sn}$.

H-bridged OH groups due to an interaction between Al–OH and $(n\text{-Bu})_4\text{Sn}$.

Fig. 4 shows the spectra for boria–alumina (5 wt.% B_2O_3) before and after $(n\text{-Bu})_4\text{Sn}$ addition. The spectrum of $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ differs from that of alumina in the sense that the band assigned to neutral OH groups appears as only a shoulder on the band assigned to acidic hydroxyls. New surface hydroxyls bonded to boron are formed when alumina is modified with B_2O_3 , for which the IR absorption is at 3695 cm^{-1} [8]. After $(n\text{-Bu})_4\text{Sn}$ addition, similar features are observed as for alumina; the band assigned to basic hydroxyls (at 3784 cm^{-1}) has disappeared. These results suggest that for both alumina and boria–alumina only basic and neutral OH groups are involved in the surface reaction with $(n\text{-Bu})_4\text{Sn}$.

Hardly any change was observed in the OH region of the infrared spectrum of silica–alumina after reaction with $(n\text{-Bu})_4\text{Sn}$. The only difference was a tailing on the stretching band at 3748 cm^{-1} (assigned to isolated $\equiv\text{Si-OH}$). Since no other OH bands, i.e., Al–OH or Si(OH)–Al, can be observed in the spectrum of silica–alumina [9,16], and a reaction indeed took place (appearance of ν_{CH} bands as well as release of butane), the only information given by IR spectroscopy is that $\equiv\text{Si-OH}$ groups are not involved in the surface reaction.

For all the oxides studied, after heating up to 200°C a small decrease in the intensities of ν_{CH}

bands was observed, suggesting that some $(n\text{-Bu})_4\text{Sn}$ was physically adsorbed to the surface.

3.5. Reaction between $(n\text{-Bu})_4\text{Sn}$ and the inorganic oxides

The surface reaction between $(n\text{-Bu})_4\text{Sn}$ and the inorganic oxides was monitored by analysis of the gas (i.e., butane) released as a function of time (Fig. 5). Starting with $70\text{ }\mu\text{mol}$ of $(n\text{-Bu})_4\text{Sn}$ per gram of silica–alumina, the amount of evolved butane reached a maximum of 0.3 mol of butane per mol of tin after ca. 3-h reaction time. Assuming that for each mol of grafted tin one mol of butane is released, this result implies that a maximum of 30% of the added tin compound is covalently bonded to the surface ($\sim 0.25\text{ wt.}\%$ or $21\text{ }\mu\text{mol g}^{-1}$). However, ICP-AES analysis carried out after washing two different samples three times with hexane revealed tin loadings as high as 0.69 wt.%, suggesting that, in this case, some $(n\text{-Bu})_4\text{Sn}$ might be strongly physisorbed on the surface. On the other hand, when $32\text{ }\mu\text{mol}$ of $(n\text{-Bu})_4\text{Sn}$ per gram of silica–alumina was employed, the amount of released butane was ca. 1 mol per mol. of tin, indicating that now all grafted tin

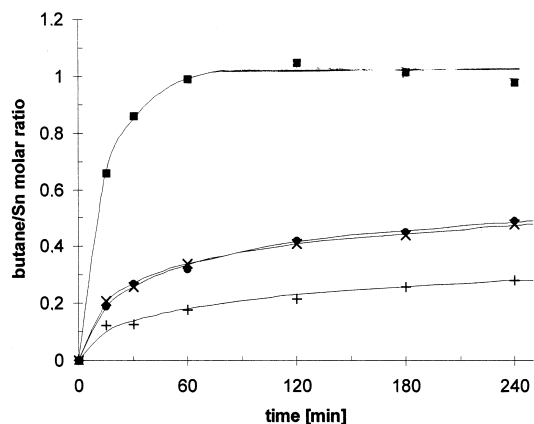


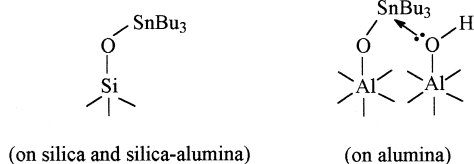
Fig. 5. Gas evolution (mol. of butane per mol. of tin) as a function of time during the reaction between $(n\text{-Bu})_4\text{Sn}$ and the various inorganic oxides starting with $70\text{ }\mu\text{mol}$ of $(n\text{-Bu})_4\text{Sn}$ per gram of support. (+) silica–alumina; (●) alumina; (×) 5 wt.% boria–alumina; (■) silica–alumina starting with $32\text{ }\mu\text{mol}$ of $(n\text{-Bu})_4\text{Sn}$ per gram of support.

was covalently bonded to the surface. For alumina and 5 wt.% boria–alumina a maximum of 32 μmol of Sn per gram of oxide was reached (~ 0.38 wt.%), in agreement with ICP-AES analyses.

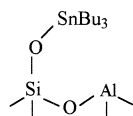
4. Discussion

Our results clearly indicate that metathesis of linear alkenes can take place over $(n\text{-Bu})_4\text{Sn}$ -promoted alumina, silica–alumina and boria–alumina. Earlier we established that silica is inactive [6]. Thus, it seems that in this case, the presence of alumina is a necessary condition for metathesis to take place. Although silica–alumina gives the highest activity, there seems to be no correlation between the catalytic activity of these oxides and their Brønsted acidity, because for boria–alumina systems the activity decreases when the boria loading increases (i.e., when the Brønsted acidity increases [17]).

In several papers aimed to study the reactivity of $(n\text{-Bu})_3\text{SnH}$ towards silica, alumina and silica–alumina, Basset et al. [7,9,11,18] proposed the formation of the following species:

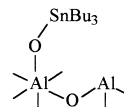


On silica–alumina the reaction would take place on the acidic bridging OH groups ($\text{Al}-(\text{OH})-\text{Si}$). Such a reaction would lead to a coordinatively unsaturated Al site:



The same kind of reaction is to be expected for $(n\text{-Bu})_4\text{Sn}$ [9]. On the other hand, our results

show that basic and neutral OH groups are involved in the interaction of $(n\text{-Bu})_4\text{Sn}$ with alumina. If the bridging, neutral OH groups were directly involved in the formation of $\equiv\text{AlOSn}(n\text{-Bu})_3$ species, a coordinatively unsaturated Al site would also become available:



Basic OH groups might be responsible for hydrogen bonding with CH_3 groups of the butyl ligands and also in pentacoordination to the tin atom. Therefore, the band due to basic OH groups would shift to lower wavenumbers and could lie under the bands corresponding to neutral or acidic OH groups.

If such coordinatively unsaturated Al sites were related to the catalytic active species, the decrease in the catalytic activity observed for the boria–alumina systems could be accounted for: upon addition of boria most neutral OH groups are consumed, and thus being less available for reaction with $(n\text{-Bu})_4\text{Sn}$. Another point to be taken into account is the fact that silica–alumina modified with $(n\text{-Bu})_3\text{SnH}$ was found to be almost inactive in the metathesis of dec-4-ene. According to our Mössbauer and NMR results, $(n\text{-Bu})_3\text{SnH}$ and $(n\text{-Bu})_4\text{Sn}$ lead to the same surface species.² However, we observed that $(n\text{-Bu})_3\text{SnH}$ reacts completely with the surface (through the Sn–H bond) for amounts of Sn between 32 and 80 μmol Sn/g $\text{SiO}_2-\text{Al}_2\text{O}_3$. The same was not observed for $(n\text{-Bu})_4\text{Sn}$: when starting with 70 μmol Sn/g $\text{SiO}_2-\text{Al}_2\text{O}_3$ a maximum of 21 μmol of Sn was grafted on the surface. Moreover, the catalytic activity was improved when the ratio $(n\text{-Bu})_4\text{Sn}/\text{SiO}_2-$

² Mössbauer analysis took several days to be accomplished, and could not be carried out with fresh samples. Therefore, it is possible that the second species detected by Mössbauer spectroscopy (bonded to the surface through two Sn–O bonds) was not present during the metathesis reaction (always carried out with a fresh sample).

Al_2O_3 was raised from 32 to 85 $\mu\text{mol Sn/g SiO}_2\text{-Al}_2\text{O}_3$ [6]. Therefore, some $(n\text{-Bu})_4\text{Sn}$ not involved in the formation of the surface species detected by Mössbauer and ^{119}Sn NMR spectroscopy seems to be responsible for the catalytic activity. Since $(n\text{-Bu})_4\text{Sn}$ alone is not active in metathesis, the active site might arise from some kind of interaction between $(n\text{-Bu})_4\text{Sn}$ and a coordinately unsaturated Al site. This interaction would be favoured under the catalytic reaction conditions.

However, it is not clear whether the active site bears a carbene ligand. A few stannene species ($[\text{Sn}] = \text{CR}_2$) have been reported, for which R must be bulky to prevent association [19]. Their association would be less likely, however, if a stannene species were formed from a grafted tin species. If such a species were indeed formed in very minor amounts, its detection by spectroscopic techniques would be almost impossible.

5. Conclusions

Alumina-containing inorganic oxides show activity as catalysts for the metathesis of *trans*-dec-4-ene when promoted with tetrabutyltin. ^{119}Sn NMR and Mössbauer spectroscopic studies suggest the presence of $\equiv\text{SiOSn}(n\text{-Bu})_3$ and, possibly, $(\equiv\text{SiO})(\equiv\text{AlO})\text{Sn}(n\text{-Bu})_2$ on the surface of silica–alumina. However, it seems that such species are not directly related to the catalytic activity. Infrared results obtained with tin-modified γ -alumina and boria–alumina suggest that the active sites arise from an interaction between $(n\text{-Bu})_4\text{Sn}$ and a coordinately-unsaturated Al site (a Lewis acid site). This Al site is created when bridging OH groups react with the tetraalkyltin compound.

Acknowledgements

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