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Olefin Metathesis

Tuning the Selectivity of Alumina-Supported $(CH_3)ReO_3$ by Modifying the Surface Properties of the Support**

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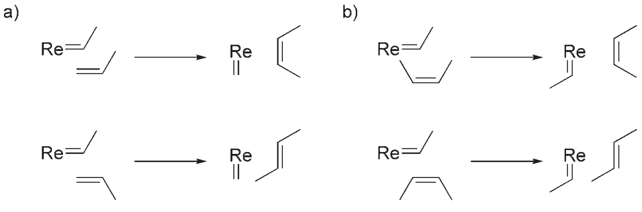
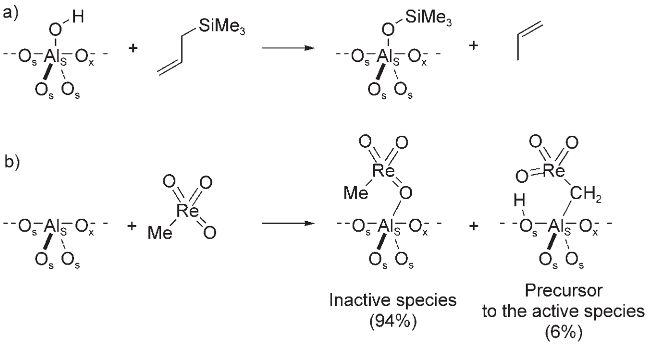
Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

Olefin metathesis has become a key reaction for basic and fine chemical synthesis.[1–3] However, despite years of research and tremendous advances in this field, it is still difficult to control the stereochemical outcome of this reaction, which leads to mixture of (*E*) and (*Z*) isomers.[4–7] In fact, one of the difficulties arises from competing secondary (*Z*)–(*E*) isomerization. This reaction is catalyzed by the same catalyst and involves the same reaction (metathesis) and mechanism (Scheme 1), therefore the products will always eventually equilibrate into a thermodynamic mixture.



Scheme 1. Examples of productive propene metathesis and isomerization in propene metathesis: a) Formation of 2-butenes by productive propene metathesis; b) (*Z*)-2-butene isomerization by degenerate metathesis.

Some homogeneous catalysts, however, are highly stereoselective and can maintain this high stereoselectivity at high conversions.[8] In the case of heterogeneous catalysts, and especially those supported on alumina, the thermodynamic ratio of 2-butenes ($E/Z = 3{:}1$ at 25 °C) is usually observed for the metathesis of propene even under continuous flow conditions. To observe the kinetic product ratio, it is necessary to use very high flow rates and to work at very low conversions[9,10] because the strong adsorption of olefins on alumina favors secondary isomerization (degenerate metathesis).[11] Herein we show that grafting $(CH_3)ReO_3$ onto an alumina[12] whose surface has been previously modified with trimethylsilyl fragments (Scheme 2) leads to an improved activity as well as a (*Z*)-selective catalyst for the metathesis of propene.[10]



Scheme 2. Synthesis of **1**. a) Reaction of AllylTMS with alumina surface hydroxy groups. b) Grafting of $(CH_3)ReO_3$ onto the reactive sites of unmodified or modified alumina supports.

IR spectroscopy: γ-$Al_2O_{3\text{-}(500)}$ was contacted with allyltrimethylsilane (AllylTMS) at room temperature under static vacuum. After 13 h, residual AllylTMS was removed under vacuum for 5 h at 25 °C. The IR spectrum of the product (Figure 1 a–d) shows two bands at 2958 and 2901 cm^{-1} arising from symmetric and asymmetric $\nu(CH_3)$ absorptions along

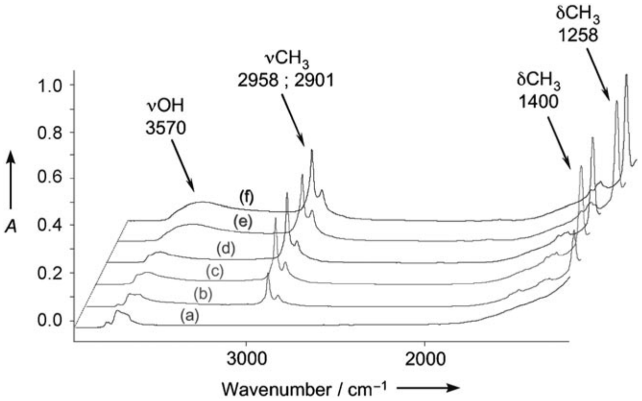


Figure 1. The grafting of both AllylTMS and $(CH_3)ReO_3$ onto γ-$Al_2O_{3\text{-}(500)}$, as monitored by IR spectroscopy: a) γ-$Al_2O_{3\text{-}(500)}$ after calcination and treatment at 500 °C under vacuum (10^{-5} torr); b) +AllylTMS/13 h at 25 °C/5 h at 10^{-5} torr; c) +AllylTMS/13 h at 65 °C/5 h at 10^{-5} torr; d) +AllylTMS/13 h at 150 °C/5 h at 10^{-5} torr; e) after sublimation of $(CH_3)ReO_3$ onto the modified γ-$Al_2O_{3\text{-}(500)}$ and desorption; f) after evacuation at 10^{-5} torr for 2 h.

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with two bands at 1400 and 1258 cm^{-1} assigned to δ(CH_3) absorptions. Almost half of the original Al–OH bands disappear during this step. Further treatment with AllylTMS at 65 °C nearly doubles the number of grafted species, and the residual Al–OH bands are replaced by a weak and broad band centered at 3673 cm^{-1}. This band probably corresponds to OH groups in new environments, such as in interactions with Al-O-Si(CH_3)$_3$ surface species.[13] No major changes are observed upon further treatment of the sample with AllylTMS at 150 °C.

Acidity measurements with pyridine[14–16] showed that most of the stronger Lewis acid sites had been consumed and that the weaker ones had only been partially consumed (see Figure S1 in the Supporting Information). Overall, these experimental data are consistent with a reaction of AllylTMS with the hydroxy groups of alumina to give trimethylsilyl surface species (Scheme 1 a).[17]

In a second step, (CH_3)ReO_3 was sublimed at room temperature onto this modified γ-$Al_2O_{3\text{-}(500)}$ partially covered by surface $OSi(CH_3)_3$ groups. The solid turned deep red. The IR spectrum of this material (Figures 1 e and 1 f) shows two bands at 2958 and 2901 cm^{-1} arising from the symmetric and asymmetric ν(CH_3) absorptions, along with three other bands at 1400, 1258, and 1205 cm^{-1} assigned to δ(CH_3) absorptions. The band at 1205 cm^{-1} corresponds to the methyl group of (CH_3)ReO_3. Moreover, the original Al–OH bands have been replaced by a broad band centered at 3570 cm^{-1} (spanning between 3750 and 3300 cm^{-1}), which probably corresponds to OH groups interacting with (CH_3)ReO_3, as previously observed for (CH_3)ReO_3 grafted onto Al_2O_3.[18] The appearance of these new OH groups could also be due to the formation of new Al_S-OH species resulting from C–H bond activation of the methyl group of (CH_3)ReO_3 on surface defects, in other words reactive Al_S-O-Al_S species (Scheme 1 b; Al_S corresponds to surface Al sites).

Mass balance analysis: γ-$Al_2O_{3\text{-}(500)}$-$Si(CH_3)_3$ contains 1.4 Si atoms per square nanometer (0.7 ± 0.1 wt % according to elemental analysis), which corresponds to the reaction of about 32 % of the surface OH groups of γ-$Al_2O_{3\text{-}(500)}$ (4 OH groups per square nanometer). Partial consumption of the OH groups has already been detected by IR spectroscopy (Figure 1 a–d). This reflects the different reactivity of the various OH groups present on γ-$Al_2O_{3\text{-}(500)}$, as observed previously during the grafting of Zr(CH_2*t*Bu)$_4$ and W(≡C*t*Bu)(CH_2*t*Bu)$_3$.[19] Propene formation was also detected (by GC analysis) during grafting although the amount formed was not quantified, thereby confirming the reaction between AllylTMS and the hydroxyl groups of alumina.[17] The solid obtained after reaction with (CH_3)ReO_3, namely (CH_3)ReO_3/$Al_2O_{3\text{-}(500)}$-$Si(CH_3)_3$ (**1**), contains around 0.9 Re atoms per square nanometer (2.8 ± 0.1 wt % of Re), which is close to the Si surface density reported above. It should be noted, however, that the Re surface coverage in **1** is slightly lower than that obtained for (CH_3)ReO_3/γ-$Al_2O_{3\text{-}(500)}$ (**2**; 1.1 Re atoms per square nanometer), which is in agreement with the consumption of some Al_SOAl_S reactive sites during the reaction with AllylTMS (see above).

Solid-state NMR spectroscopy: The ^{13}C cross-polarization magic-angle spinning (CP-MAS) solid-state NMR spectrum of $Al_2O_{3\text{-}(500)}$-$Si(CH_3)_3$ displays one intense signal at $\delta = 0$ ppm associated with the formation of [Al_S-O-$Si(CH_3)_3$] surface species (Figure 2 a and Scheme 2). The absence of olefinic carbon atoms is consistent with cleavage of the allylic moiety during grafting, as proposed for grafting onto silica.[17] When 100 % ^{13}C-labeled (CH_3)ReO_3 is sublimed onto $Al_2O_{3\text{-}(500)}$-$Si(CH_3)_3$, other signals are also observed for (CH_3)ReO_3/γ-$Al_2O_{3\text{-}(500)}$ along with the signal at $\delta = 0$ ppm associated with [Al_S-O-$Si(CH_3)_3$], (Figure 2 b).[18] For example, a weak signal at $\delta = 67$ ppm can be attributed to [$Al_SCH_2ReO_3$], which results from C–H bond activation of the methyl ligand of (CH_3)ReO_3 on the truncated Al_{O_h} sites of the alumina surface, along with three other signals at $\delta = 32$, 22, and 11 ppm, which correspond to (CH_3)ReO_3 coordinated to various surface Lewis acid sites of alumina through its oxo ligands (Scheme 2 b).[18]

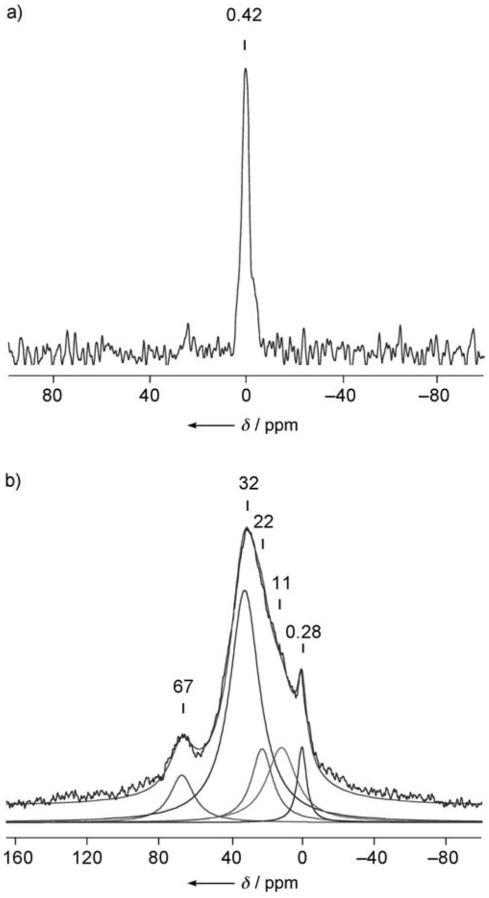
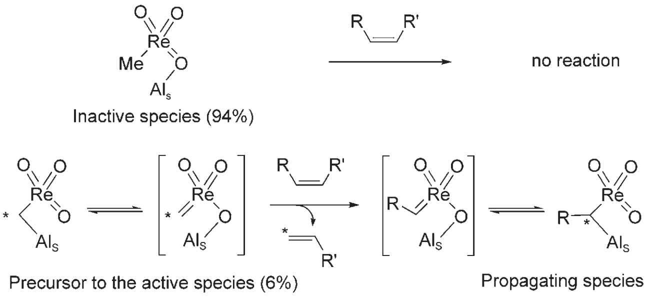


Figure 2. a) ^{13}C CP-MAS solid-state NMR spectrum of $Al_2O_{3\text{-}(500)}$-$Si(CH_3)_3$ (spinning frequency: 10 kHz). The number of scans was 10000 and the recycle delay was set to 2 s. A CP step of 2 ms was used. b) ^{13}C CP-MAS solid-state NMR spectrum of ^{13}C-labeled (CH_3)ReO_3 on γ-$Al_2O_{3\text{-}(500)}$-$Si(CH_3)_3$ (spinning frequency: 10 kHz). The number of scans was 5146 and the recycle delay was set to 2 s. A CP step of 2 ms was used.

Active site of (CH_3)ReO_3 supported on γ-$Al_2O_{3\text{-}(500)}$-$Si(CH_3)_3$ (**1**): When (CH_3)ReO_3/γ-$Al_2O_{3\text{-}(500)}$-$Si(CH_3)_3$ (**1**) is treated with 0.61 equivalents of doubly ^{13}C labeled ethene, 11 % of singly labeled ethene is detected, in other words

0.06 equivalents per Re (6 % of active sites). This result shows that some active sites originate from the methyl group of $(CH_3)ReO_3$ as in the original $(CH_3)ReO_3/\gamma\text{-}Al_2O_{3\text{-}(500)}$ (**2**),[18] but that there are less of them (6 % versus 15 % for **1** and **2**, respectively). This is probably due to the presence of fewer defect sites on $\gamma\text{-}Al_2O_{3\text{-}(500)}$ after grafting the silylating agents. Furthermore, the solid-state ^{13}C CP-MAS NMR spectrum of **1** after treatment with 0.61 equivalents of 100 % doubly ^{13}C labeled ethene displays a large and intense signal at $\delta = 66$ ppm, a weaker signal at $\delta = 31$ ppm, and three sharp signals at $\delta = 30$, 20, and 0.6 ppm (see Figure S2 in the Supporting Information). No carbenic signal is detected between $\delta = 150$ and 400 ppm. The two signals at $\delta = 30$ and 20 ppm can be assigned to ethene oligomers formed on alumina acid sites.[18,20] It should be noted, however, that those oligomers are present in a lesser amount and that no physisorbed olefin is observed, in contrast to what has been observed for $\gamma\text{-}Al_2O_{3\text{-}(500)}$ alone or **2**. This observation is in agreement with the weaker acidity of **1**. Similarly, the signal at $\delta = 66$ ppm in **1**, which has been assigned to $[Al_SCH_2ReO_3]$ species,[18] is weaker than the signal observed for **2** (Scheme 3).



Scheme 3. Metathetical exchange at the active site of $(CH_3)ReO_3/\gamma\text{-}Al_2O_{3\text{-}(500)}\text{-}Si(CH_3)_3$ (**1**).

Activity, selectivity, and stability as a function of time on stream: At 30 °C and a flow rate of 34.5 mL min^{-1} (142 mol (mol Re)$^{-1}$ min^{-1}), propene is transformed into a mixture of ethene and 2-butenes with an initial rate after 6 min of 21 mol of propene transformed per mol of Re per minute (see Figure S3 in the Supporting Information). Over 7800 min, the turnover number (TON) reaches 23 500, while the conversion decreases from 14.5 % to 0.5 %, thereby showing that catalyst **1** is rapidly deactivated. The initial rate and the cumulative number of turnovers (at 7800 min) per active site can be estimated from the initial number of active sites (approx. 6 %)—a rare possibility in heterogeneous catalysis—to be 350 mol of propene transformed per mol of active sites per minute and 330 000, respectively (see Figure S4 in the Supporting Information), which is far better than all currently known rhenium-based catalysts, including the well-defined silica-supported Re system (approx. 6000).[21] Moreover, catalyst **1** displays a very high selectivity for 2-butenes, particularly for (*Z*)-2-butene (1-butene: $<1\times10^{-4}$ %; isobutene: approx. 0.003 %), and does not give a thermodynamic ratio of 2-butenes even at rather high conversions (approx. 10 %), in contrast to most alumina-supported catalysts (including **2**; Figure 3). The *E*/*Z* ratio increases nearly linearly with conversion and thereby with respect to the partial pressure of (*Z*)-2-butene (P_{C4Z} is proportional to conversion) for **1**, while catalyst **2** displays a hyperbolic-like dependence of the *E*/*Z* ratio as a function of conversion or (*Z*)-2-butene partial pressure.

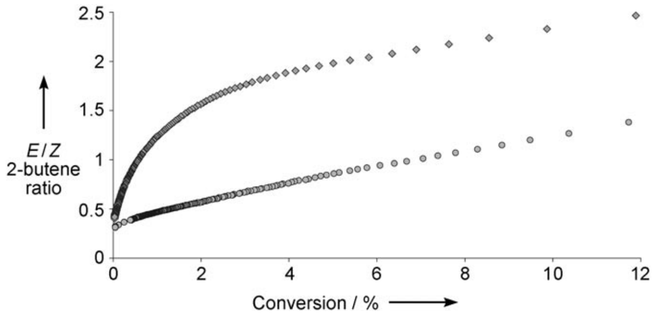


Figure 3. *E*/*Z* ratio of 2-butene as a function of conversion for **2** ($(CH_3)ReO_3/\gamma\text{-}Al_2O_{3\text{-}(500)}$; ◆) and **1** ($(CH_3)ReO_3/\gamma\text{-}Al_2O_{3\text{-}(500)}\text{-}Si(CH_3)_3$; ●).

The above observation is consistent with the two solids having different adsorption properties. While describing the exact analytical expression for the rates would be complex and beyond the scope of this discussion (competition between the adsorption of gases, equilibrium), it is possible to express the rate of *Z* to *E* isomerization of 2-butenes when far from equilibrium as $r_{\mathrm{isom}} = k_{\mathrm{isom}}\,\theta_{\mathrm{C4Z}}$, where the surface coverage is expressed according to Langmuir and Hinshelwood as $\theta_n = \lambda_n P_n/(1+\Sigma\lambda_i P_i)$ (for a gas *n* in a mixture of *i* gases, where P_i is the partial pressure of the gas *i* and λ_i the equilibrium constant of adsorption for *i*). Combining these two equations gives $r_{\mathrm{isom}} = k_{\mathrm{isom}}\theta_{\mathrm{C4Z}} = k_{\mathrm{isom}}\lambda_{\mathrm{C4Z}}P_{\mathrm{C4Z}}/(1+\Sigma\lambda_i P_i)$. For a catalyst with low adsorption properties ($\lambda_i P_i \ll 1$), $r_{\mathrm{isom}} = k_{\mathrm{isom}}\theta_{\mathrm{C4Z}} = k_{\mathrm{isom}}\lambda_{\mathrm{C4Z}}P_{\mathrm{C4Z}}$ (linear dependence, as observed for **1**), while for a catalyst with stronger adsorption properties $r_{\mathrm{isom}} = k_{\mathrm{isom}}\theta_{\mathrm{C4Z}} = k_{\mathrm{isom}}\lambda_{\mathrm{C4Z}}P_{\mathrm{C4Z}}/(1+\Sigma\lambda_i P_i)$ (hyperbolic dependence, as observed for **2**). These two equations indicate that the adsorption properties of the solid can indeed dramatically alter the overall performance of a catalyst (e.g. activity, stereoselectivity). For the alumina-supported system **2**, it is therefore necessary to use a very high inverse space velocity (flow rates and low conversion) to reach high *Z* selectivity and obtain the kinetic ratio because of the high adsorption of the support.[11,14,15] A direct consequence of this is the lower (*Z*)-2-butene selectivity for **2** than for **1**. Another less obvious consequence, however, is the higher initial activity of **1** (TOF = 350 versus 185 mol of propene transformed per mol of active sites per minute for **1** and **2**, respectively). This activity is not due to **1** having more efficient active sites per se (they are the same, as shown by NMR spectroscopy), but to a difference of adsorption properties between the two catalysts: catalyst **1** converts propene more rapidly because the products can desorb, while catalyst **2** isomerizes the products strongly adsorbed on the surface in a metathesis reaction that competes with the productive propene metathesis (Scheme 1).

In conclusion, modifying an alumina surface with trimethylsilyl groups has a drastic effect on the selectivity and activity of the catalytic system.[22] The trimethylsilyl groups change the adsorption properties of alumina by favoring desorption and thereby disfavoring secondary reactions. This system appears to be very promising, and we are currently investigating ways to obtain a single-site system based on $(CH_3)ReO_3$ and modified oxide surfaces which could, in principle, allow highly efficient catalysts to be obtained.

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