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$MeReO_3/Al_2O_3$ and Me_4Sn–activated Re_2O_7/Al_2O_3 Alkene Metathesis Catalysts Have Similar Active Sites

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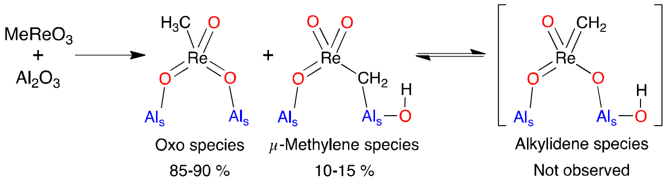
We studied the solid-state NMR signature of Re_2O_7/Al_2O_3 activated with Me_4Sn ($Me_4Sn/Re_2O_7/Al_2O_3$), a heterogeneous alkene metathesis catalyst. These studies showed that the $SnMe_4$ activation step generates μ-methylene $Al\text{-}CH_2ReO_3$ species, similar to the intermediates observed in $MeReO_3/Al_2O_3$. The μ-methylene species probably forms through the *in-situ* generation of $MeReO_3$. These results establish the role of Me_4Sn in this oxide-based heterogeneous catalyst and explain why $Me_4Sn/Re_2O_7/Al_2O_3$ has a reactivity profile more similar to $MeReO_3/Al_2O_3$ than parent Re_2O_7/Al_2O_3.

Introduction

The ethenolysis of 2-butenes to form propene is a central reaction in the Lummus process. This reaction is catalysed by the heterogeneous WO_3/SiO_2 alkene metathesis catalyst at temperatures above 400 °C.[1-4] Related heterogeneous catalysts, such as MoO_3/SiO_2 or $MoO_3/SiO_2\text{-}Al_2O_3$ operate at lower temperatures between 100 and 300 °C,[5-7] while Re_2O_7/Al_2O_3 catalyses this reaction at temperatures as low as 25 °C.[8-10] In general, these heterogeneous metathesis catalysts are incompatible with alkenes containing functional groups unless pre-activated. These catalysts are usually prepared by introducing high-valent metal oxide precursors to the high surface area support by incipient wetness impregnation followed by calcination to form isolated metal sites on the support surface. This preparation technique leads to complicated mixtures of surface sites with a low concentration of catalytically active sites,[11,12] which are difficult to study and to understand at the molecular level.

One approach to studying these heterogeneous catalysts is the synthesis of well-defined supported catalysts by grafting molecular – Mo–, W– or Re–alkylidene – precursors on partially dehydroxylated surfaces.[13-19] For example, $Re(\equiv C\text{-}{}^tBu)(=CH\text{-}{}^tBu)(\text{-}CH_2\text{-}{}^tBu)_2$ grafted on silica forms a heterogeneous catalyst with high concentrations of active sites, fully characterized by spectroscopic techniques and compatible with functionalized alkenes.[18-20] In some cases, these well-defined environments can also lead to the determination of intermediates in the alkene metathesis catalytic cycle,[15,17,21] which is currently not possible for the classical catalysts.

In the context of pure metal oxide heterogeneous catalysts, we showed that $MeReO_3$ supported on alumina has similar reactivity patterns in propene metathesis as the parent Re_2O_7/Al_2O_3 catalyst.[22] Surprisingly, $MeReO_3/Al_2O_3$ and related systems also catalyse the metathesis of ethylene and ethyl oleate, an alkene containing an ester functional group, both of which are unreactive towards the Re_2O_7/Al_2O_3 catalyst.[22-29] Detailed NMR and computational studies of $MeReO_3/Al_2O_3$ revealed that two major surface Re-species are present in this material (Scheme 1).[22,30] The major species (85-90 %) is $MeReO_3$ coordinated to a surface Al by an Re=O group and is inactive (oxo species). The minor species (10-15 %) corresponds to a μ-methylene bridging ligand in which a C-H bond in $MeReO_3$ is activated on an Al–O bond to form a methylene group bound to Re and Al (μ-methylene species). The oxo-bound and μ-methylene species are distinguishable by their characteristic NMR chemical shift. The signal for the oxo-bound complex appears at 30 ppm, while the μ-methylene is at 66 ppm. From titration and selective labelling experiments the minor μ-methylene surface species is active in metathesis.[22,27,30]



Scheme 1: Surface species resulting from the grafting of $MeReO_3$ on Al_2O_3: oxo and μ-methylene species. Al_s corresponds to surface aluminium atoms.

Activation of Re_2O_7/Al_2O_3 with Me_4Sn forms $Me_4Sn/Re_2O_7/Al_2O_3$ that displays catalytic properties more similar to $MeReO_3/Al_2O_3$ than Re_2O_7/Al_2O_3. For instance, $Me_4Sn/Re_2O_7/Al_2O_3$ is active in both ethylene and ethyl oleate self-metathesis reactions. Spectroscopic studies of Re_2O_7/Al_2O_3 show that most Re-sites are isolated from one another and adopt a tetrahedral geometry,[11,31-35] and contacting Re_2O_7/Al_2O_3 with Me_4Sn was proposed to result in a surface alkylidene.[36] In view of the similar reactivity patterns between $Me_4Sn/Re_2O_7/Al_2O_3$ and $MeReO_3/Al_2O_3$ we investigated the role of Me_4Sn in the activation step of Re_2O_7/Al_2O_3 by solid-state NMR spectroscopy.

Experimental

General Procedure. Re_2O_7 and Me_4Sn were purchased from STREM chemicals and Aldrich, respectively. Alumina (Alu C) was obtained from Evonik, and agglomerated by slurring the solid in distilled water, following by a drying under air at 100 °C and sieving to obtain compacted alumina with a grain size of 250–400 µm. All gases were purified by passage through activated 4 Å molecular sieves and BASF copper-catalyst prior to use. Carbon tetrachloride and diethyl ether were purchased from Sigma-Aldrich, THF-d_8 was purchased from Cambridge Isotope Laboratories. THF and diethyl ether were distilled over sodium/benzophenone. Gas analyses were performed on an Agilent Technologies 7890A GC systems equipped with a flame ionization detector and a HP-Al/KCl on fused silica column (50 m x 0.32 mm). GC/MS measurements were performed on an Agilent GC 7820 A equipped with a mass Spectrometer (5975). The column used were HP-Al/KCl on fused silica for alkenes type compounds and HP-88 Agilent column for tin based compounds. Solution NMR spectra were recorded on either 250 or 500 MHz Bruker spectrometers. The solid-state NMR spectra were measured on either 400 or 700 MHz Bruker NMR spectrometers equipped with 4 mm triple resonance probe heads. The method used was ^1H-^{13}C cross-polarization magic angle spinning (CP-MAS) using a radio frequency field of 100 kHz on the proton channel.

Preparation of CH_3ReO_3 or $*CH_3ReO_3$ supported on Al_2O_3 (500°C). These compounds were prepared as previously reported.[22, 37] Elemental analysis: Re (5.6 wt%).

Preparation of Re_2O_7/Al_2O_3 by incipient wetness impregnation. Al_2O_3 (5.5 g, Alu C) was impregnated with a solution of 0.78 g of perrhenic acid (99.99% pure) in 4.1 mL of water.[38] The resulting solid was dried at 150 °C (10°C min^{-1} heating ramp) under static air for 16 h, rewetted with 5 mL of water and dried at 300 °C with a ramp of 10 °C min^{-1} for 4 h. This material was calcined under a flow of synthetic air at 500 °C with a ramp of 10 °C min^{-1} for 16 h and evacuated under high vacuum (10^{-5} mBar) line for 60 min. Elemental analysis: Re (8.1 wt%).

Synthesis of $SnMe_2Me*_2$. A 2 neck round bottom flask equipped with a dropping funnel and a condenser was loaded with magnesium (2.6 g, 106 mmol, 2.4 equiv) and 150 mL of diethyl ether. ^{13}C labelled idodomethane (6.2, 44 mmol, 2.2 equiv) was added dropwise to the suspension. The magnesium slowly disappears and a solid was formed in the solution. After one hour the mixture was cooled to 0 °C and a solution of dichlorodimethyltin (20 mmol, 1 equiv) in 40 mL of ether was added dropwise for 30 min. The reaction mixture was warmed to room temperature and maintained at this temperature overnight. 1 M HCl (20 mL) was added to the mixture and the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over anhydrous $MgSO_4$. After 3 successive careful distillations of the azeotrope diethyl ether / Me_4Sn, the desired product was obtained with a yield of 11 % (bp 74 °C at 1 atm). ^1H (250 MHz, C_6D_6) δ: 0.12 (s, Me_4Sn $J_{H\text{-}C}$=120 Hz).

Preparation of $Me_4Sn/Re_2O_7/Al_2O_3$. Representative procedure. To Re_2O_7/Al_2O_3 (500 mg) suspended in 1 mL of CCl_4 in a 50 mL Schlenck under Argon was added Me_4Sn (0.1 mL, 0.56 mmol). The reaction mixture was stirred for 30 min at room temperature, and the colour changed from white to brown. The solid was isolated by filtration, and washed three times with 1 mL of CCl_4. Elemental analysis: Re (6.7 wt%) and Sn (1.1 wt%).Preparation of $SnMe_2Me_2*$ –activated Re_2O_7/Al_2O_3. This compound was prepared as described above using $SnMe_2Me_2*$ in place of Me_4Sn.[39]

Extraction of $Me_4Sn/Re_2O_7/Al_2O_3$ with THF-d_8. To $Me_4Sn/Re_2O_7/Al_2O_3$ (500 mg) was suspended in 1 mL of dry THF d_8 under inert atmosphere. The mixture was stirred 16 h. The resulting liquid was analysed by ^{119}Sn solution NMR and by GC-MS. It revealed the presence of unreacted Me_4Sn, CCl_4 and Me_3SnCl.

Reaction of carbon-13 di-labelled ethene with Me_4Sn–activated Re_2O_7/Al_2O_3. $Me_4Sn/Re_2O_7/Al_2O_3$ (200 mg) was loaded in a 110 mL glass reactor and contacted with carbon-13 di-labelled ethene (0.4 equiv per Re metal centre). After 15 h at room temperature, the gas phase was analysed by GC and GC/MS showing the presence of di-, mono- and non-labelled ethene (di-labelled 81 %, mono-labelled 14 % and non-labelled 5 %). The number of non labelled carbon is therefore 12% in the gas phase, this number is multiplied by the number of equivalent of ethylene added per Re centre. Therefore, the calculated number of active sites is 5%.

Reaction of carbon-13 di-labelled and non-labelled ethene with Me_4Sn–activated Re_2O_7/Al_2O_3. $Me_4Sn/Re_2O_7/Al_2O_3$ (200 mg) was loaded in a 110 mL glass reactor and contacted with 20 equiv. of non-labelled ethene and 10 equivalent of ^{13}C di-labelled ethene and left for 24 hours to react at 25°C. The resulting gas phase was analysed by GC-MS leading a 45/39/16 mixture of non-labelled, mono labelled and di-labelled ethylene (di-labelled 16 %, mono-labelled 39 % and non-labelled 45 %).

Results and discussion

Re_2O_7/Al_2O_3 (8 wt % Re) was synthesized by incipient wetness impregnation of perrhenic acid on alumina followed by calcination at 500 °C for 16 h.[40] Contacting Re_2O_7/Al_2O_3 with a solution of Me_4Sn in CCl_4 generates $Me_4Sn/Re_2O_7/Al_2O_3$.[41] This activated material catalyses the self-metathesis of propene. For instance, $Me_4Sn/Re_2O_7/Al_2O_3$ converts 450 equivalent of propene into the equilibrium mixture of ethene (*ca.* 15%), propene (*ca.* 65%) and 2-butenes (*ca.* 20% in *E/Z* isomers of

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3:1 ratio) in 90 min at 25 °C.[38] Contacting non-labelled and carbon-13 di-labelled ethylene with $Me_4Sn/Re_2O_7/Al_2O_3$ results in a statistical mixture of isotopomers, indicating that the activated material catalyses ethylene self-metathesis, in contrast to Re_2O_7/Al_2O_3.[25]

The number of active sites in $Me_4Sn/Re_2O_7/Al_2O_3$ was evaluated by contacting the catalysts with 0.4 equiv of carbon-13 di-labelled ethylene, with respect to Re, for 15 h at 25 °C. A mixture of di-labelled, mono-labelled and non-labelled ethylene isotopomers was obtained in 81/14/5 ratio. The quantity of unlabelled carbons in the gas phase is directly related to the number of exchangeable active sites because the $Me_4Sn/Re_2O_7/Al_2O_3$ was activated with natural abundance $SnMe_4$. Considering that only 0.4 equiv of labelled ethylene was added (per Re centre) to the catalyst, the number of active sites is ca. 5% in $Me_4Sn/Re_2O_7/Al_2O_3$, which is slightly lower than in $MeReO_3/Al_2O_3$ (ca. 10-15 %).[22,27]

The ^{13}C CPMAS NMR of $Me_4Sn/Re_2O_7/Al_2O_3$ contains a signal at 0 ppm (Figure 1a), consistent with the presence of a surface methyltin group.[42] We also found that small amounts of Me_3SnCl were formed during the activation process from ^{119}Sn NMR and GC-MS analyses. After reacting $Me_4Sn/Re_2O_7/Al_2O_3$ with carbon-13 di-labelled ethylene (0.4 equiv./Re), the ^{13}C CPMAS NMR contains signals at 66, 30, 18, 10 along with the surface methyltin peak at 0 ppm (Figure 1b). The signals at 10 and 18 ppm were previously attributed to the formation of ethylene oligomers on the Al_2O_3 surface.[22,27,28] The signals at 30 and 66 ppm are similar to those obtained in carbon-13 labelled $*MeReO_3/Al_2O_3$ shown in Figure 1d.[22] These peaks were previously assigned to the oxo-, and the μ-methylene surface species shown in Scheme 1.[22,27,28] The observation of both μ-methylene and oxo species after exposure to ^{13}C-labelled ethene indicates that these species probably interconvert; possibly through H-transfer or tautomerization processes (see Scheme S1).[43]

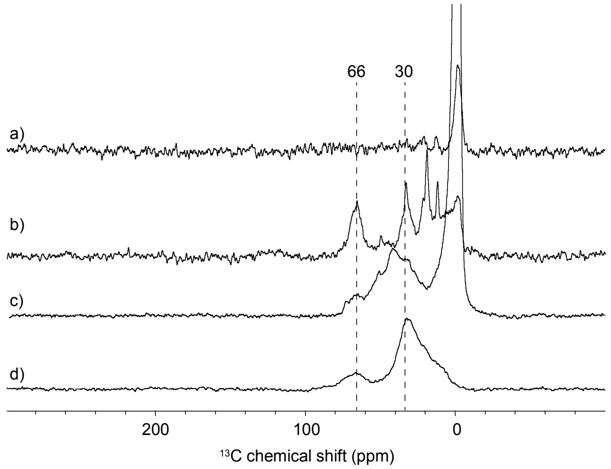
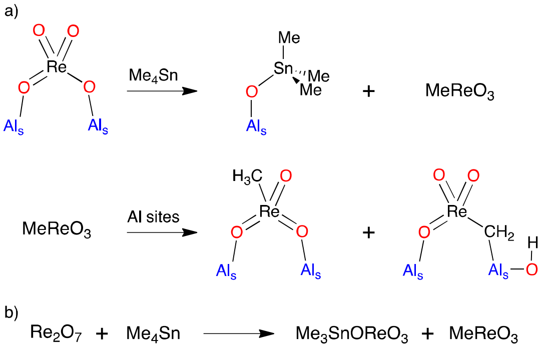


Figure 1: ^{13}C CPMAS spectra of supported Re-based catalysts on alumina. For all the spectra the contact time was set to 0.6 ms and the recycling delay was 1 sec. a) $Me_4Sn/Re_2O_7/Al_2O_3$, 400 MHz, 60k scans, b) Spectrum of $Me_4Sn/Re_2O_7/Al_2O_3$ contacted with 2-^{13}C $*C_2H_4$ 100k scans, c) $*Me_2Me_2Sn/Re_2O_7/Al_2O_3$, 80k scans, 400 MHz and d) ^{13}C labeled $*MeReO_3/$ Al_2O_3, 5k scans, 700 MHz.

The surface Re-species generated, after contacting $Me_4Sn/Re_2O_7/Al_2O_3$ with carbon-13 labelled ethylene, are in low concentration. To determine the spectroscopic signature of $Me_4Sn/Re_2O_7/Al_2O_3$ we synthesized the carbon-13 enriched material by treating Re_2O_7/Al_2O_3 with $*Me_2Me_2Sn$. The ^{13}C CPMAS spectrum of $*Me_2Me_2Sn/Re_2O_7/Al_2O_3$ contains an intense signal at 0 ppm associated with carbon-13 enriched methyltin compounds as well as the two signals at 66 and 30 ppm, as already observed in Figure 1b. The close chemical shift agreement between $*Me_2Me_2Sn/Re_2O_7/Al_2O_3$ (Figure 1c) and $MeReO_3/Al_2O_3$ (Figure 1d) also supports the assignment of these peaks as the μ□methylene and oxo species, respectively.[22,27,28] The peak assigned to oxo species at 40 and 51 ppm in Figure 1c are shifted to higher frequency in comparison to $MeReO_3/Al_2O_3$. This may be due to Re=O units binding to different alumina sites on the surface. However, these species are inactive in ethylene metathesis since they are not observed in Figure 1b. Contacting $*Me_2Me_2Sn/Re_2O_7/Al_2O_3$ with an excess of non-labelled propylene induces a significant decrease in the resonance intensity for the signals at 66 and 40-30 ppm (Figure S1).

The reaction of Me_4Sn with Re_2O_7/Al_2O_3 forms a catalyst that has similar reactivity trends and solid-state NMR spectral features as $MeReO_3/Al_2O_3$. The carbon-containing surface species include surface methyltin species, physisorbed Me_3SnCl, μ□methylene and oxo species. Grafting alkyltin species on oxide surfaces[42,44] and reaction of Me_4Sn with $XReO_3$ (X = $OReO_3$, $OCOCF_3$, etc.)[37,45] are well known. In this case, these reactions would form Me_3SnO-Al and $MeReO_3$ (Scheme 2). Me_3SnCl formation may arise from the reaction of CCl_4 and Me_3SnO-Al. The μ□methylene and oxo species would arise from the reaction of aluminium bound perrhenate and Me_4Sn to form $MeReO_3$, which further reacts with Al,O sites to provide the active μ□methylene sites along with some adsorbed oxo (Scheme 2).[45]



Scheme 2: a) Generation of $MeReO_3$ from surface perrhenate and Me_4Sn, and subsequent reaction of $MeReO_3$ with surface Al sites. b) Formation of $MeReO_3$ by reaction of Re_2O_7 and $SnMe_4$.

Conclusions

The activation of Re_2O_7/Al_2O_3 with Me_4Sn results in the formation of μ-methylene (Al-CH_2ReO_3) and oxo species, similar to that found in CH_3ReO_3/Al_2O_3. This explains the similar reactivity of $Me_4Sn/Re_2O_7/Al_2O_3$ and CH_3ReO_3/Al_2O_3

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towards functionalized alkenes and ethylene, and distinguishes these catalysts from the pure oxide based Re_2O_7/Al_2O_3.

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Notes and references

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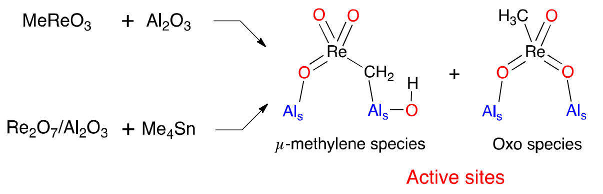
TOC FIGURE



$MeReO_3/Al_2O_3$ and Re_2O_7/Al_2O_3 activated with Me_4Sn, which have the same reactivity toward functionalized alkenes and ethylene, share similar active sites.

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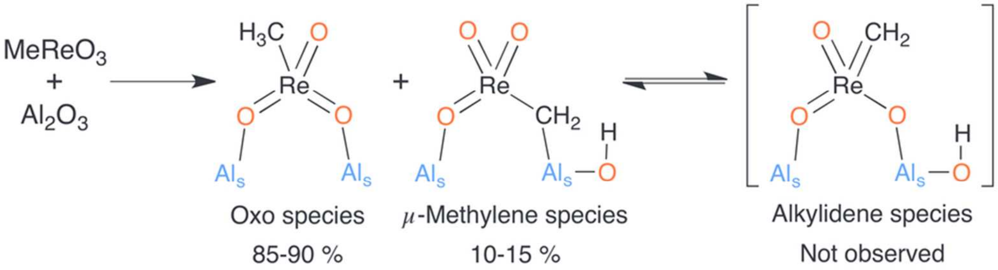

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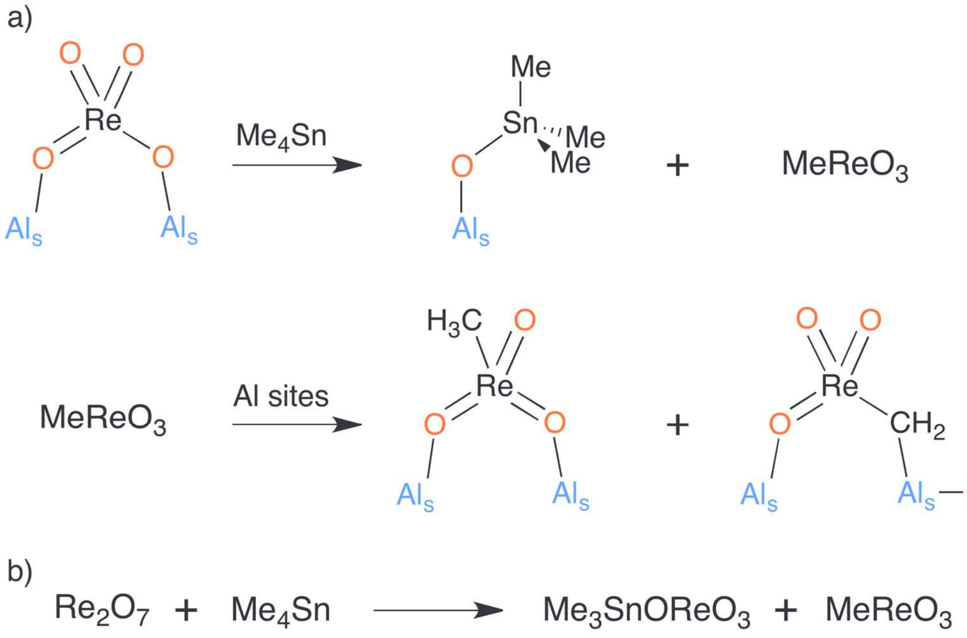

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