Available online at www.sciencedirect.com

ScienceDirect

Journal of Catalysis 253 (2008) 180–190

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

CH_3-ReO_3 on γ-Al_2O_3: Activity, selectivity, active site and deactivation in olefin metathesis

Alain Salameh [a], Anne Baudouin [a], Daravong Soulivong [a], Volker Boehm [b], Michael Roeper [b], Jean-Marie Basset [a,*], Christophe Copéret [a,*]

[a] *Laboratoire de Chimie Organométallique de Surface (UMR 9986 CNRS/ESCPE Lyon), ESCPE Lyon, F-308, 43 Boulevard du 11 Novembre 1918, F-69616 Villeurbanne Cedex, France*

[b] *BASF AG, Forschung Grundprodukte, GCB/K, M 313, D-67056 Ludwigshafen, Germany*

Received 13 June 2007; revised 17 August 2007; accepted 16 October 2007

Abstract

The active sites (15% of total Re) of CH_3ReO_3 supported on alumina arise solely from the reaction of the C–H bond of CH_3ReO_3 with reactive Al_S–O_S sites of a γ-Al_2O_3 surface to yield [$Al_SCH_2ReO_3$], whereas the major species, inactive, corresponds to $MeReO_3$ chemisorbed through its oxo ligand(s) on Lewis acid sites of alumina. Monitoring the active sites of CH_3ReO_3 supported on alumina by solid-state NMR spectroscopy shows that no carbenic signals are observed and that the resting states of the catalyst in the metathesis of propene correspond to μ-methylene and μ-ethylidene species, so that the propagating carbenic species are likely formed only in the presence of olefins. Although this system is highly active in the metathesis of propene, with initial rates similar to some of the best catalysts, it undergoes fast deactivation, which is due to the propene metathesis products, most likely ethene.

Keywords: Heterogeneous catalysis; Olefin metathesis; Methyl trioxorhenium; Alumina; Active site; Flow kinetic; Deactivation

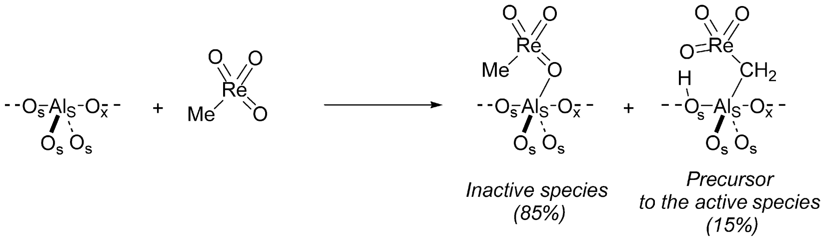
1. Introduction

Olefin metathesis (OM) has been a very important industrial process since the discovery of the first heterogeneous OM catalysts [1], and today it is associated with crackers in petrochemical plants to improve the yield of propene through the cross-metathesis of ethene and 2-butenes [2]. Of the various classical heterogeneous OM catalysts, Re_2O_7/Al_2O_3 is the only one that works efficiently at room temperature [3,4]. Moreover, this heterogeneous catalyst also can be used to convert oleate esters [5] when activated by organotin agents, which are, however, detrimental to the regeneration process [6]. In contrast, in the early 1990s, Herrmann et al. showed that CH_3ReO_3 supported on silica–alumina is a highly active metathesis catalyst for functionalized olefins, without the need for an additional cocatalyst [7]. Activity has been associated with the Lewis acidity of the support [8], and in fact active systems based on CH_3ReO_3 use Lewis acid-containing supports [8–12]. In all these systems, the structure of the active site(s) and the involvement of the methyl as the source of the carbene have long been a matter of debate. Using spectroscopic (IR, NMR and EXAFS) reactivity and molecular modeling studies, we recently showed that the active sites of CH_3ReO_3 supported on γ-$Al_2O_{3\text{-}(500)}$ arise from the methyl and corresponds to only a minor surface species, [$Al_SCH_2ReO_3$], present only as ca. 15% of all Re (Scheme 1) [13]. This species results from the C–H activation of the methyl ligand of CH_3ReO_3 onto reactive Al_S–O sites of alumina (where Al_S denotes surface aluminum sites) [14], thus yielding a μ-methylene bridge species [$Al_SCH_2ReO_3$] that displays a characteristic ^{13}C NMR signal at 66 ppm [13]. Note that no Re alkylidene has been observed at lower fields (180–400 ppm) [15], and that the μ-methylene species is exchanged on contacting ^{13}C-labeled ethene with CH_3ReO_3/γ-$Al_2O_{3\text{-}(500)}$, demonstrating that this μ-methylene species

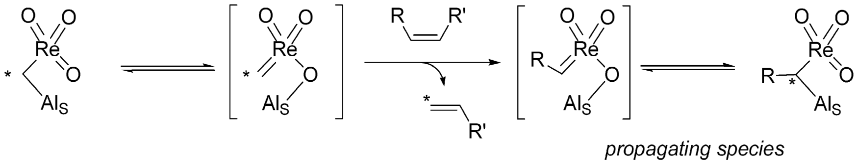
---

[*] Corresponding authors.
E-mail address: coperet@cpe.fr (C. Copéret).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2007.10.007



Scheme 1. Grafting of CH_3ReO_3/Al_2O_3.



Scheme 2. Proposed active and inactive sites for the CH_3ReO_3/Al_2O_3.

corresponds to the resting state of the catalyst and that the alkylidene species is probably formed in situ in the presence of olefins (Scheme 2).

Here we present a detailed kinetic study of the propene metathesis in a flow reactor (effect of time on stream and space time velocities) and an investigation of the active sites and their life cycle by titration studies and by solid-state NMR spectroscopy.

2. Experimental

2.1. General procedure

All gases were purified on R-3/11 provided by BASF and MS 4 Å before use. Gas-phase analysis was performed on a Hewlett–Packard 5890 series II gas chromatograph equipped with a flame ionization detector and a KCl/Al_2O_3 on fused silica column (50 m × 0.32 mm).

2.1.1. Solid-state NMR spectroscopy

All solid-state NMR spectra were recorded under MAS ($\nu_R = 10$ kHz) on a Brüker Avance 500 spectrometer equipped with a standard 4-mm double-bearing probe head (125.73 MHz for ^{13}C). The freshly prepared samples were introduced in the 4-mm zirconia rotor in a glove box and tightly closed. Compressed air was used for both bearing and driving the rotors. Chemical shifts are reported in ppm downfield from $Si(CH_3)_4$ (±0.1 and 1 ppm for ^1H and ^{13}C NMR spectra, respectively). The typical cross-polarization sequence was used for the ^{13}C CP MAS NMR spectra: 90° proton pulse, cross-polarization step to carbon spins, and detection of the carbon magnetization under proton decoupling TPPM-15 [16]. For the CP step, a ramp radio frequency (rf) field centered at $\nu^{CP} = 60$ kHz was applied on protons, whereas the carbon rf field was matched to obtain the optimal signal. The contact time for CP was set to 2 ms. An exponential line broadening of 80 Hz was applied before Fourier transform. All other details are given in the figure captions.

2.2. Preparation of γ-$Al_2O_{3\text{-}(500)}$

γ-Al_2O_3 from Degussa was calcined at 500 °C in dry air for 18 h and then treated at 500 °C under vacuum (0.13 mPa) for 18 h to give γ-$Al_2O_{3\text{-}(500)}$ (105 m^2/g).

2.3. Reaction of γ-$Al_2O_{3\text{-}(500)}$ with CH_3ReO_3

γ-$Al_2O_{3\text{-}(500)}$ (1 g) was contacted, while stirring, with 100 mg of CH_3ReO_3 at 25 °C. After 3 h, removal of the excess of molecular complex was performed by reverse sublimation, and the resulting solid was then treated under vacuum (0.13 mPa) for 3 h. Elemental analysis: Re 3.8 wt%.

2.4. Metathesis of propene catalyzed by $CH_3ReO_3/Al_2O_{3\text{-}(500)}$

$CH_3ReO_3/Al_2O_{3\text{-}(500)}$ (50 mg, 10.2 µmol of Re) was introduced under Ar in a 195-mL batch reactor. After evacuation of Ar, 533 Torr of propene (547 equiv) was added. During the reaction at 25 °C, aliquots were expended in a small volume, brought to atmospheric pressure, and analyzed by gas chromatography (GC).

2.5. Metathesis of ethyl oleate catalyzed by $CH_3ReO_3/Al_2O_{3\text{-}(500)}$

Into a 22-mL batch reactor was introduced 104 mg of $CH_3ReO_3/Al_2O_{3\text{-}(500)}$ (21.4 µmol of Re) and 2.8 mL of a 0.8 M solution of ethyl oleate in pentane (2.24 mmol). During the reaction at 25 °C, aliquots (1 to 2 drops) were taken, diluted in pure solvent (0.2 mL), and analyzed by GC.

2.6. Reaction of $CH_3ReO_3/Al_2O_{3\text{-}(500)}$ with *Z* 2-butene followed by contact with ^{13}C di-labeled ethene (titration of active sites)

$CH_3ReO_3/Al_2O_{3\text{-}(500)}$ (98 mg, 20 µmol of Re) was introduced under Ar in a 22-mL batch reactor. After evacuation of the gas phase, *Z* 2-butene (44 Torr, 2.6 equiv) was added. After