Catalysis Communications 108 (2018) 51–54

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

New synthetic approach towards well-defined silica supported tungsten bis-oxo, active catalysts for olefin metathesis

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ARTICLE INFO

Keywords:
Metathesis
Tungsten
Propene
Silica
SOMC

ABSTRACT

A well-defined bis-oxo bisiloxy tungsten surface species has been prepared by a new synthetic non-aqueous approach. The reaction of $[W(=O)(O^tBu)_4]$ with the silica surface dehydroxylated at 200 °C proceeds by W—O cleavage with concomitant ^tBuOH release, leading to bigrafted $[(\equiv SiO)_2W(=O)(O^tBu)_2]$. Upon heating at 300 °C, it converts into the bis-oxo derivative $[(\equiv SiO)_2W(=O)_2]$. Without co-catalyst, this material demonstrated high, sustained activity and selectivity in propene metathesis. This emphasizes the importance of the design of robust bis-oxo catalysts by Surface Organometallic Chemistry and represents a significant step to understand and mimic the active species of the industrial WO_3/SiO_2 system.

1. Introduction

Oxo-molybdenum or tungsten species supported on inorganic oxide carriers constitute a class of highly important catalysts for several reactions [1,2]. In particular, these materials have been successfully employed in the industry for the olefin metathesis reaction. The first commercial process was established by Phillips for propylene metathesis catalysed by WO_3/SiO_2 in order to produce ethylene and 2-butenes [3]. Furthermore, MoO_3/Al_2O_3 and WO_3/SiO_2 are applied in a sequence of the Shell Higher Olefin Process for the production of α-olefins [3,4]. While the aforementioned heterogeneous catalysts have found their applications in petrochemical industries, WO_3/SiO_2 remains the most common industrial olefin metathesis catalyst due to the high resistance to different poisons (oxygen and sulphur) [5], compared to MoO_3/SiO_2 or Re_2O_7/Al_2O_3. Solid experimental evidences by in-operando studies have confirmed that the catalytic performance in propylene metathesis is dependent on the concentration of the isolated bipodal tungsten bis-oxo species $[(\equiv SiO)_2W(=O)_2]$ [6]. Classically, the activation mechanism (carbene formation) was believed to follow a pseudo-Wittig reaction where the metal remains in its highest oxidation state. The expected primary products (aldehydes) have been directly or indirectly observed [7–9]. Recently, this pathway has been challenged by another mechanism involving reduction of the metal centre followed by oxidative addition of propylene [6]. The primary product (acetone) has also been detected. The inconsistency is addressed to the heterogeneity of the materials and the very low concentration of the precursor amenable to the active site upon activation with propylene. In order to resolve the structure-reactivity relationship of the industrial olefin metathesis catalysts and thus ease mechanistic studies, an attractive strategy is to develop single-site bis-oxo tungsten on silica (Scheme 1). Such species should provide a unique entry into the active centre after activation with olefins and thus serve as a representative model of industrial catalyst WO_3/SiO_2 to study the initiation process. In this context, surface organometallic chemistry is a powerful approach to design single metallic sites on solids [10], which has been widely and successfully applied on silica [11]. Nevertheless, preparation of material containing only $[(\equiv SiO)_2W(=O)_2]$ surface fragments is challenging. A series of $[M(=O)(OSi(O^tBu)_3)_4]$ and $[M(=O)_2(OSi(O^tBu)_3)_2]$ (M = Mo, W) complexes have been prepared and grafted onto silica [12,13]. The authors illustrated that the resulting surface species might be a mixture of mono-oxo and bis-oxo moieties, $[(\equiv SiO)_2M(=O)_2]$ and $[(\equiv SiO)_4M(=O)]$, respectively. Note that the latter material corresponds to the same surface species as the industrial catalyst obtained by impregnation of metatungstate salt at lower metal loading, [6,7] which requires high

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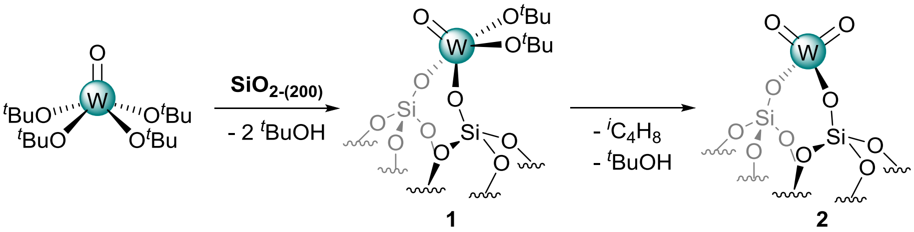
https://doi.org/10.1016/j.catcom.2018.01.031
Received 5 January 2018; Received in revised form 24 January 2018; Accepted 25 January 2018



Scheme 1. Grafting of $[(W(=O)(O^tBu)_4]$ and thermal decomposition of **1** to $[(\equiv SiO)_2W(=O)_2]$, **2**.

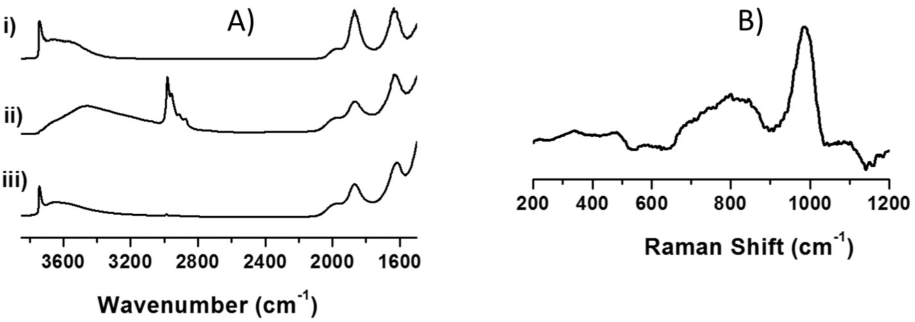


Fig. 1. A) DRIFT spectra of i) SiO_{2-200} ii) after reaction with $[=W(=O)(O^tBu)_4]$, **1** iii) after heating under vacuum at 300 °C, **2**; B) selected region of Raman spectrum of **2**.

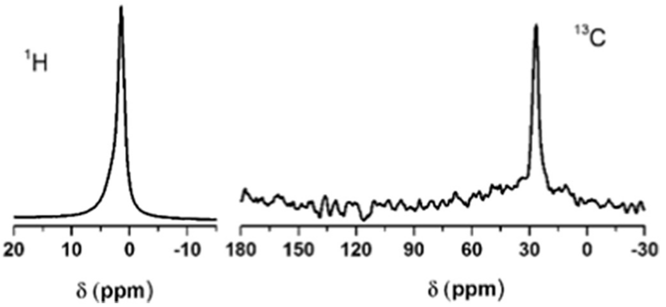


Fig. 2. ^1H MAS NMR spectrum of **1** (left) and ^{13}C CPMAS NMR spectrum of **1** (right) (11.75 T, spinning rate 10 kHz).

Table 1
EXAFS parameters for the supported species in **2**.[a]

Type of neighbour	Number of neighbours	Distance (Å)	σ^2 (Å^2)
$W{=}\underline{\boldsymbol{O}}$	2.1(3)	1.74(1)	0.0022(8)
$W{-}\underline{\boldsymbol{O}}Si{\equiv}$	1.8(5)[b]	1.89(2)	0.0017(9)
$W{-}\underline{\boldsymbol{O}}(Si{\equiv})_2$	2(1)	2.86(6)	0.025(19)
$W{-}O{-}\underline{\boldsymbol{Si}}{\equiv}$	1.8[b]	3.20(5)	0.010(6)

[a] The errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. Δk: [2.0–14.8 Å-1] - ΔR: [0.5–3.7 Å] ([0.5–2.3 Å], when considering only the first coordination sphere); $S_0^2 = 0.85$; $\Delta E_0 = 8.5 \pm 1.5$ eV (same for all shells); Fit residue: ρ = 7.5%; Quality factor: $(\Delta\chi)^2/\nu = 2.26$, with $\nu = 15/28$ ($[(\Delta\chi)^2/\nu]_1 = 4.02$ with $\nu = 10/16$, considering only the first coordination sphere: =O and –O).

[b] Shell constrained to parameters above. Multiple scatterings paths O=W–O (3.65(6) Å) were also included.

temperature to activate the W=O bond. Thus, to date, no single site supported bis-oxo tungsten $[(\equiv SiO)_2W(=O)_2]$ is reported in the literature. The first challenge to resolve the structure-reactivity relationship for the industrial catalysts then lies on the synthetic part, with the ultimate goal to prepare a silica-supported material containing only $[(\equiv SiO)_2M(=O)_2]$ (M = Mo, W) surface fragments. Herein, we report the preparation of well-defined silica supported tungsten bis-oxo species as model of industrial catalyst WO_3/SiO_2. According to our previous studies, the silica support has been dehydroxylated at only 200 °C in order to enforce the bis-grafted nature of the tungsten centre. Furthermore, the easily accessible $[W(=O)(O^tBu)_4]$ was used as the precursor, from which the targeted bipodal tungsten bis-oxo species can be obtained after grafting followed by thermolysis.

2. Experimental section

2.1. Catalyst preparation

Aerosil silica from Degussa (200 m^2·g^{-1}) was hydrated using distilled water and compacted, and partially dehydroxylated at 200 °C under high vacuum (10^{-5} mbar) for 16 h to give a white solid containing 0.83 mmol·g^{-1} of OH. $[W(=O)(O^tBu)_4]$ was synthesised from $(W(=O)Cl_4)$ [14], as reported in the literature.

2.2. Preparation of $[(\equiv SiO)_2W(=O)_2]$

In a double Schlenk, a suspension of 454 mg of $[W(=O)(O^tBu)_4]$ in 20 ml of pentane was added to 2 g of silica (SiO_{2-200}) and stirred for 4 h. The W complex in excess was extracted with three washing and filtration cycles. Drying under high vacuum afforded $[(\equiv SiO)_2W(=O)(O^tBu)_2]$, which was stored in the glove box. $[(\equiv SiO)_2W(=O)(O^tBu)_2]$ (1 g) was then introduced into a glass reactor and heated to 300 °C under high vacuum (10^{-5} mbar) for 2 h. The volatiles were collected in liquid nitrogen trap and analysed by gas chromatography.

2.3. Metathesis catalytic tests

In a continuous-flow stainless steel reactor were introduced 130 mg of catalyst diluted with 500 mg of amorphous silica (calcined at 700 °C). A continuous flow of propene (10 ml.min^{-1}) was sent through the catalyst bed and the samples were heated to 420 °C. Every 30 min, an automatically withdrawn amount was injected by mean of a gas-sampling valve in the GC (Column: Plot Q 50 m × 0.32 mm × 10 µm).

3. Results and discussion

3.1. Catalyst characterisation

The grafting of $[W(=O)(O^tBu)_4]$ [14] on silica dehydroxylated at 200 °C was performed in pentane at room temperature, affording colourless material **1** after repeated washings and evacuation of volatiles (Scheme 1). Infrared studies show consumption of the isolated silanols at 3747 cm^{-1} (Fig. 1). Furthermore, new peaks corresponding to